Desulphurisation of Fine Coal Waste Tailings Using Algal Lipids

In fulfilment of the requirements for the degree of
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Disclaimer

The outcomes, conclusions and/recommendations expressed in this work are of the authors and Water Research Commission (WRC), Council for Scientific Industrial Research (CSIR) and the Department of Science and Technology (DST) will not be accountable for any financial loss arising from application, in part or in full, of the results presented herein.

Abstract

The South African economy is an energy-driven economy which relies on coal to meet most of its energy demands. Coal mining has resulted in the generation of coal waste over 60 million tonnes, annually. Apart from the huge footprint of this waste, the sulphide minerals contained in the waste have resulted in the generation of acid rock drainage (ARD). A lot of techniques have been developed to prevent and mitigate ARD, however most of these techniques have fallen short in terms of meeting their desired objectives due to the long-term nature of ARD generation which can persist for hundreds of years after mine closure. This has resulted in emphasis being put on long-term prevention techniques that remove ARD risk over treatment techniques. One prevention technique which has shown good technical potential is the two-stage flotation method developed for desulphurisation of hard rock tailings and coal fines, developed at the University of Cape Town. On desulphurising coal, the first stage produces an upgraded coal product that may be sold, with the second stage used to separate the tailings from the first stage into targeted high-sulphide and low-sulphide fractions which may then be appropriately used or disposed of. An economic assessment of the process showed across a wide range of coal wastes the high cost of oleic acid used in the first stage of the process as a collector was a major contributor to the operating costs.

The investigation undertaken in this thesis looked at the potential of algal lipids and their derivatives as biocollectors to replace the oleic acid collector in the desulphurisation process at the laboratory scale. A review of cost was carried out for a process that used raw algal lipids (RALs) or fatty acid methyl esters (FAMEs), which are derived from RALs through transesterification. Batch flotation experiments were used to assess the performance of the two bioflotation reagents in comparison to oleic acid and dodecane, an alternative but less successful chemical collector. The algal lipids cost review was a desktop study which was done by adapting literature data from Davis et al. (2014) which focused on economic evaluation of algal lipid biofuels production pathways.

Results from laboratory experiments for two different coal waste feed samples showed that the performance of RALs and FAMEs was similar to that of oleic acid for the sample that was high in ash and sulphur, and better than oleic acid for the sample that was low in ash and sulphur. For example, the product from Site 1 discards from Waterberg had 24.37% ash and 2.76% sulphur using FAMEs, 26.13% ash and 2.56% sulphur with RALs, and 23.48% ash and 2.41% using oleic acid, at a reagent dose of 2.8 kg/t for all reagents. For Site 2 waste tailings from the Witbank area, the product had 23.17% ash and 0.72% sulphur when FAMEs were used as collector, 22.75% ash and 0.75% sulphur with RALs, and 20.18% ash and 0.74% sulphur using oleic acid, at the same reagent dose. Discards from Site 1 had an initial ash and sulphur content of 47.61% and 5.71%, respectively. Site 2 waste tailings had 25.56% ash and 0.91% sulphur before flotation. Increasing biocollector dosage resulted in higher yields with a compromise on the upgraded coal quality. The pH tests showed that the performance of the two bioflotation reagents was best at pH 4 in terms of yield. However, increasing the pH of the process from the natural pH of the sample (pH 2.7) to 7 resulted in collection of more ash and sulphur, thus reducing the product quality. The algal lipids cost review showed that RALs and FAMEs were potentially 20 to 21% cheaper than oleic acid, with more room for improvement. Both the laboratory experiments and the technical evaluation showed that algal lipids and their derivatives have the potential to replace oleic acid in the two-stage desulphurisation process for coal waste to obtain a saleable quality coal product while simultaneously decreasing the impact of ARD from coal waste.

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Glossary of Terms

Acid Rock Drainage (ARD)	The generation of acid water from mine waste as a result of oxidation of sulphide upon exposure to air, water and bacteria
Activator	A reagent that facilitates the attachment of a collector to a mineral's surface
Autotrophic	A metabolic pathway in which organisms use an inorganic carbon source to make complex organic chemicals for growth, maintenance, storage and reproduction
Biocollector	A biological chemical that selectively attaches to a mineral surface resulting in an increase in hydrophobicity of the overall mineral surface
Bioflotation	A flotation process that uses biological reagents to selectively separate minerals based on their difference in surface properties
Collector	A reagent that increases surface hydrophobicity of a mineral, resulting in its selective separation from other minerals
Combustibles recovery	The percentage of combustibles material originally in the feed which reports to the concentrate
Depressant	A reagent that suppress the collection of gangue material by increasing surface hydrophilicity
Flocculation	The coming together of particles, forming flocs (woolly cloudlike aggregations)
Flotation	The selective separation of one mineral from a mixture of minerals based on differences in surface properties. Hydrophobic particles float by attaching to rising air bubbles while hydrophilic particles remain in the pulp
Flotation Efficiency Index (FEI)	The difference between combustibles and ash recovery. This gives an indication of how well a collector separates combustibles material from ash material
Frother	A reagent used to stabilise the froth formed when air is bubbled through the pulp in a flotation process.
Gangue	Material that has no economic value. It is found mixed with the desired mineral
Heterotrophic	Relating to organisms that use organic carbon for growth and respiration
Hydrophilic	Strong affinity for water

Hydrophobic	Lacking affinity for water
Point of zero charge (PZC)	The pH at which the surface charge of a particle in suspension in an electrolyte is zero
Sulphur recovery	The percentage of sulphur originally in the feed that reports to the concentrate
Zeta potential	The difference in charge between a solid particle's surface and the bulk liquid (electrolyte) in which it is suspended

Acronyms and Abbreviations

AD	Anaerobic digestion
ARD	Acid rock drainage
BBM	Bold's basal medium
DAF	Direct air flotation
FAMEs	Fatty acid methyl esters
FEI	Flotation efficiency index
IRR	Internal rate of return
MIBC	Methyl isobutyl carbinol
MSP	Minimum selling price
NPV	Net present value
PAX	Potassium amyl xanthate
PBR	Photobioreactor
PZC	Point of zero charge
RALs	Raw algal lipids
ROI	Return on investment
TAG	Triacylglyceride

1 Introduction

1.1 Background

1.1.1 Fine Coal waste in South Africa

Coal mining is a well-developed industry in South Africa. According to the Chamber of Mines of South Africa (2018), over 260 million tonnes of coal per year is extracted. This yearly output is coupled with generation of coal waste at a rate of about 60 million tonnes, which has already accumulated to around a billion tonnes of coal waste (Department of Energy South Africa, 2018). This coal waste contains many different components, but one in particular, namely pyrite (FeS_2), is a major environmental concern as microbially-aided oxidation of the pyrite can lead to the production of acid rock drainage (ARD).

Many ARD prevention and treatment measures have been proposed and developed. One such technique is the two-stage coal flotation desulphurisation method, developed at the University of Cape Town. This method aims to recover valuable coal from fine waste while mitigating the risk associated with any remaining materials (Kazadi Mbamba et al., 2013). The first flotation stage recovers clean saleable coal from the fine coal waste feed through the agency of oleic acid collector and methyl isobutyl carbinol (MIBC) frother. The second flotation stage separates pyrite from the remaining gangue material in the tails from the first stage using a potassium amyl xanthate collector, dextrin depressant and MIBC frother. Results from Kazadi Mbamba et al. (2013) showed that it was feasible to recover fine coal from waste. The shortcoming of the two-stage desulphurisation technique was that an economic evaluation carried out by Jera (2013) found the process to be profitable only under favourable coal price conditions with best case coal recoveries. The economic evaluation showed that the first stage flotation reagents contributed the most to the operating cost. This motivated a search for alternative reagents in order to render the process more economically viable.

Mycobacterium phlei was investigated as a potential coal biocollector (Fagan-Endres et al., 2017). Lab-scale flotation experiments showed that its performance was similar to that of a dodecane collector under the same conditions. However, unpublished preliminary economic evaluation using the preliminary experimental data showed that the application of *M. phlei* in coal flotation was not economically feasible owing to the high cost of the *M. phlei* biomass production.

The aim of this research is to test algal lipids as potential bioflotation reagents that will be cost effective when applied to the two-stage desulphurisation flotation of coal.

1.2 Research approach

1.2.1 Hypotheses

Hypothesis 1

Raw algal lipids and their derivatives (fatty acid methyl esters) have the necessary functional groups (–OH, $–COO^-$, $–(C_nH_{2n-1})$, $–(C_nH_{2n+1})$) to qualify them as polar collectors and contain an ester head which is polar and hydrocarbon tails with varying carbon chain lengths in the range from 12 to 22. They therefore have the necessary characteristics to replace currently used coal chemical flotation reagents, such as oleic acid and dodecane, in the two-stage coal flotation desulphurisation method.

Hypothesis 2

Algal lipids have the potential to produce a stable froth without the addition of MIBC because they contain low molecular weight fatty acids with surface active properties. This will either result in no or little frother dosage being required for the flotation process.

Hypothesis 3

Using previous economic studies on algal lipid production as a basis, raw algal lipids and their derivatives present an economically cheaper and environmentally friendly alternative to oleic acid and other currently used chemical collectors in the prevention and remediation of acid rock drainage from fine coal waste tailings using froth flotation.

1.2.2 Objectives and key question

Based on the hypotheses presented in Section 1.2.1, the goals of this study were:

- To culture algae for lipid production.
- To extract lipids from algae and convert some to fatty acid methyl esters.
- To carry out a technical evaluation of the bioflotation process using the extracted lipids and their derivatives.
- To review the algal lipids cost

The following key questions were posed in order to test the hypotheses and meet the set objectives.

- Which algae species are characterised as high lipid producers?
- What growth conditions foster high lipid productivity?
- Are the chemical properties of the extracted algal lipids similar to chemical flotation reagents?
- Will the extracted lipids aid in coal collection in a flotation process?
- Will chemical modification affect the performance of algal lipids in the flotation process?
- What is the quality to be attained for the product?
- What are the cost/benefit implications of the bioflotation process?
- What are the key economic performance indicators to be evaluated?
- Which process variables are going to have a greater impact on the economics of the process?
- What is the current cost of algal lipids?
- Will algal lipids be cheaper than oleic acid or dodecane?

1.2.3 Scope and limitations

The focus of this investigation is on the first stage of the two-stage coal desulphurisation process. This stage recovers valuable coal in the concentrate from a fine coal waste feed, with the tails becoming the feed for the second flotation stage.

The lipids extracted from the algae were used in their raw form. No attempt was made to purify them. The algal lipids cost review was a desktop study using data published in literature. The errors that may have risen due to the underlying assumptions in the economic evaluation literature data adopted were not accounted for in this study

1.3 Thesis layout

The foundation of the study, which highlights the problem aimed to be solved by this study, has been presented in the preceding sub-sections. The hypotheses upon which the whole investigation lies have been presented together with the key questions and objectives that are going to guide the researcher in testing the stated hypotheses. The following chapter is an in-depth review of the relevant literature, aimed at understanding the current practices in bioflotation of coal. Chapter 3 presents the experimental methods used to in this study. Chapter 4 presents the results and discussion of the flotation experiments. Bioreagent performance was assessed in terms of yield, recovery (combustibles, ash and sulphur) as well as product quality (ash and sulphur content). Chapter 5 presents the second half of the project – the evaluation of algal lipids production cost. A literature review of the current lipid production pathways and economic evaluations of the process was carried out to get a full understanding of the status quo. The method used to determine the minimum selling price of raw algal lipids and fatty acid methyl ester in the context of this investigation was also presented in Chapter 5. The results of the algal lipids cost review are presented and discussed in this Chapter. Conclusions and recommendations for the technical evaluation and the outcomes of the algal lipids cost review are presented in Chapter 6.

2 Literature Review

2.1 Introduction

Previous research at the University of Cape Town by Kazadi Mbamba (2011) and Iroala (2014a) has presented an in-depth review and discussion of the coal types in South Africa and their floatability, as well as a justification for the use of froth flotation to desulphurise coal waste while at the same time producing valuable coal. This chapter therefore provides an in-depth look at coal flotation and flotation parameters. Thereafter, the potential for algal lipids as coal collectors, their source, chemistry and properties which makes them suitable as collectors, are discussed.

2.2 Coal desulphurisation by froth flotation

2.2.1 Froth flotation mechanism and background

Froth flotation is used to separate particles that have relatively similar densities but different physico-chemical surface properties (wettability in this case). In the presence of water, hydrophobic material will repel the water, hence their surfaces are not wetted, while hydrophilic minerals attract water and their surfaces are wetted. When air bubbles are introduced to a mixture of hydrophobic and hydrophilic material in water, the hydrophobic material rises with the buoyant air bubbles while the hydrophilic particles remain in water. Chemical reagents (collectors or depressants) may be used to enhance the hydrophobicity or hydrophilicity of particle surfaces. Frothers can be used to stabilise the froth that is formed by the air bubbles that have risen to the surface of the water.

A representation of a typical coal flotation setup is shown in Figure 2.1. Air is sparged from the bottom of the flotation cell while mechanical agitation is used to keep the particles in suspension. Due to their hydrophobicity, coal particles attach to the rising bubbles and end up in the froth where they are collected as coal concentrate, while pyrite and other gangue materials sink to the bottom of the flotation cell where they are collected as tails. The separation process is often enhanced through the addition of chemical reagents, primarily a collector to improve the hydrophobicity of coal and a frother, typically methyl isobutyl carbinol (MIBC), to stabilise the froth formed.

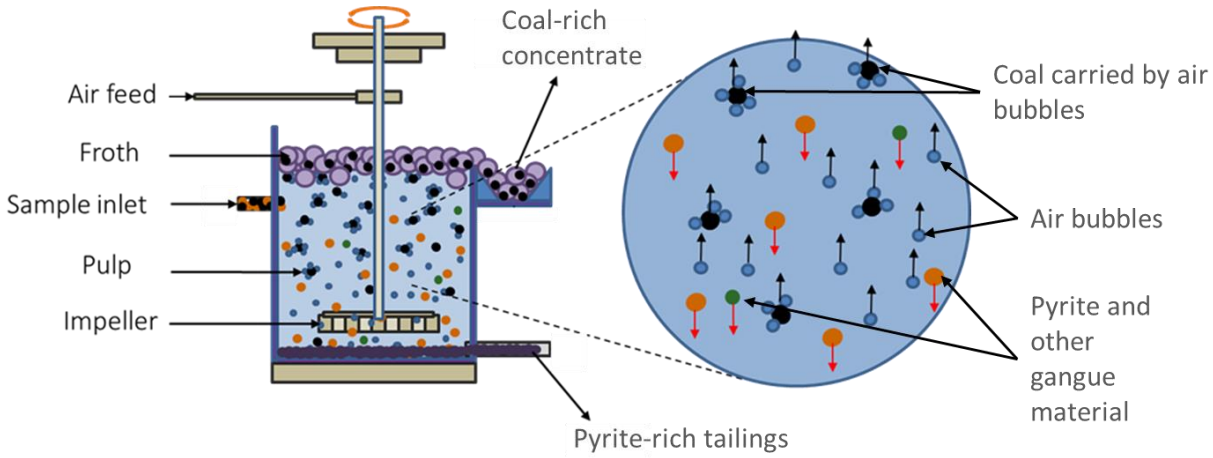

Figure 2.1: Flotation cell for coal cleaning. Modified from Fagan-Endres et al. (2017)

Most industrial flotation processes are operated as continuous processes. The froth formed is mechanically scraped off as it is formed (Kawatra, 2009).

Froth flotation is mainly used for fine coal particles (-150 µm). Fine grinding results in the formation of pyrite particles that have the same surface properties as coal particles (Han, 1983). Because of this, pyrite ends up floating together with coal unless it is oxidised. Han (1983) suggested the pre-treatment of freshly ground coal with a hot basic (high pH) solution rich in dissolved oxygen to render the pyrite

surface hydrophilic. Demirbas and Balat (2004) also commented on flotation of fine coal by stating that mechanical entrainment of hydrophilic particles occurs because of their small particle size. The hydrophilic particles are transported up the flotation cell trapped in the water between air bubbles. This results in high yields but low grades of concentrates. Han (1983) and Demirbas and Balat (2004) proposed the application of column flotation over conventional flotation to avert the effects mechanical entrainment.

Research has shown that coal floatability is affected by the type of coal. Gray et al. (1979) showed that coals that are high in inertinite were difficult to float than those with lower inertinite. They carried out carried out a float/sink experiment on a sample from Kriel (Mpumalanga province - Table 2.1) and observed that the floats had a relative density of 1.4, inertinite composition of 6.5% and an ash content of 6.7% while the sink fractions had a relative density of 1.65, 15.9% inertinite and about 45% ash.

Table 2.1: Maceral composition of coals from dominantly exploited coal mines in South Africa. Extracted from Gray et al. (1979).

Coal mine	Vitrinite (%)	Inertinite (%)	Exinite (%)
Grootegeluk (Waterberg)	83.2	5.7	4.2
Kriel	50.8	21.5	12.1
Sigma	27.9	58.9	3.1
Landau	57.2	28.4	6.0
Matla	75.9	15.6	6.2

Flotation as a mineral beneficiation process became popular in the 1860s (Lynch et al., 2008). Early commercial developments were aimed at concentrating sulphide minerals (zinc and lead). It was not until 1920 that attention was shifted to coal cleaning by flotation. The technology became available for cleaning of the fine fraction (<0.5 mm) of coking coal. However, there was little incentive to use the process in the US because coal was mined on thick coal seams and relatively few fines were made in the mining exploits. High adoption rates of the flotation technology in coal cleaning happened in Europe where most of coal mining was done on thin, underground coal seams using mechanical methods. The mechanised mining methods and the transportation produced a high proportion of fines, which made flotation an attractive technology (Floatworks, 2016). To handle fine coal generated during the mining process, new technologies were developed, and one of the outstanding ones is the Jameson cell for the flotation of fine coal (Clayton et al., 1991).

2.2.2 Flotation conditions

2.2.2.1 Reagent type

Since flotation exploits the surface properties of the components to be separated by flotation, there are cases where these surface properties need to be enhanced to achieve the desired separation of the different minerals. This is the role that is played by flotation reagents, which may be used to either enhance or depress the floatability of a mineral.

The reagents used for flotation processes are classified into four types: collectors, depressants, frothers and modifiers (which shall not be discussed in this report because of their lack of relevance). Their properties and functions are discussed in the following sections. Nagaraj and Ravishankar (2005) gives a detailed review of the development and specific types of the reagents in flotation processes.

2.2.2.1.1 Collectors

Collectors are mostly organic chemicals which causes mineral particles to become more hydrophobic. They are generally used in small quantities, enough to just form a monolayer on the particle's surface (Han (1983). Higher concentrations, apart from the cost, result in the flotation of the unwanted material

due to reduced selectivity. To increase yields without loss of selectivity, collectors with longer hydrocarbon chains (non-polar groups) are used. Longer hydrocarbon tails provide greater water-repellence to the particle they are attached to. Hydrocarbons with branched chains are more preferable than straight-chain hydrocarbon tails due to the increased solubility of the collector without compromising its ability to induce hydrophobicity.

Classification of ionising collectors is based on the type of the active ion attached to the hydrocarbon tail (Glembotskii et al., 1972). These types are anionic collectors and cationic collectors, and are expanded on below.

Anionic Collectors

Anionic collectors ionise into a negatively charged polar group (the negative ion does not participate in the collector-particle interaction). They are grouped into two based on the chemical composition of the functional polar head: 1) Oxyhydryl collectors, and 2) Sulphydryl collectors.

Oxyhydryl collectors contain an anionic acid (organic or sulpho) in their polar group. The acids are typically naturally occurring fatty acids from vegetable oils and animal fat (Han, 1983). Soaps (salts of fatty acids) are also popular as collectors, due to their high solubility regardless of the long hydrocarbon tails. The carboxylates are strong collectors but fall short on their selectivity. The commonly used Oxyhydryl collector is oleic acid, and its derivatives (sodium oleate and linoleic acid).

Figure 2.2 shows an example of an anionic collector, sodium oleate, and how it attaches to a coal particle with its negatively charged polar end. The hydrocarbon tail sticks outwards and results in the particle repelling water, thus rendering it more hydrophobic. This mechanism has been found useful in flotation of heavily oxidised coals because they have a lot of positively charged groups on their surface (Dube, 2012). Gangue material does not have surface charge, and therefore do not attract the collector molecules.

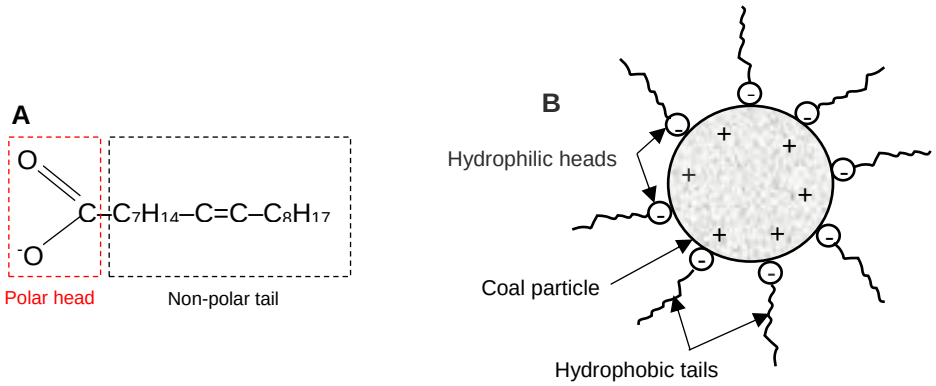

Figure 2.2: The mechanism of operation of anionic collectors. A is an oleate molecule, produced by the ionisation of sodium oleate or oleic acid. B: the polar head (negatively charged) attaches to the positively charged mineral surface while the non-polar tail sticks out, rendering the mineral hydrophobic.

The sulphates and sulphonates, which possess similar properties to fatty acids, are rarely used because of their weak polarity resulting in low collecting power (Kawatra, 2009). Sodium dodecylsulphate is an example of a sulphate collector used for coal flotation. It is mainly used as a modifier since it does not cause sufficient surface change for flotation to take place. A modifier is a chemical that affects the surface properties of a mineral in such a way that it becomes more susceptible to interaction with a collector or a depressants.

The sulphydryl collectors have in their polar groups bivalent sulphur. They are popular in sulphide mineral flotation due to their very powerful and selective nature. The common forms of these are the xanthates and dithiophosphates, with the xanthates being the most important ones. Xanthates chemically attach to the sulphide mineral resulting in the formation of an insoluble metal xanthate which is strongly hydrophobic.

Cationic Collectors

Cationic collectors have a positively charged polar group and a hydrophobic tail. The polar head has pentavalent nitrogen, with the amines being the commonly used (Tai et al., 1977; Glembotskii et al., 1972). Amines interact with the mineral particles electrical double layer via electrostatic attractions (a mechanism similar to that of anionic collectors shown in Figure 2.2). Due to the reversible nature of this type of attachment, cationic collectors tend to be weak collectors. For the same reason, they are sensitive to pH in their action of surface modification. Their activity has been found to be best around neutral to slightly acidic conditions and inactive under extreme pH conditions (Wills and Napier-Munn, 2006). Effective cationic collectors for oxidised coal have been found to be laurylamine, resin amine-D acetate, and isoamyl amine (Sun, 1954).

Non-ionising Collectors

Non-ionising collectors lack the ability to ionize in water because they do not have any polar groups (Wills and Napier-Munn, 2006). Therefore, their solubility in water is very low compared to ionising collectors. They are mostly hydrocarbon liquids obtained from petroleum or coal. Since non-ionising collectors do not have solidophil groups (polar heads), the attachment to the mineral surface is purely by adhesion. They attach easily to minerals surfaces that are not hydrated. They therefore work best on minerals with greater natural hydrophobicity (with little or no surface oxidation).

Non-ionising collectors are used in combination with emulsifiers because they are less soluble in water. The emulsifier ensures the required degree of dispersion of collector upon introduction into the pulp by keeping the collector droplets from coalescing into large droplets. The most prevalent non-ionising collectors are paraffin and various hydrocarbon oils (typically gas oil), fractional distillation products of coal tar or wood (Fazaelipoor et al., 2010; Han, 1983).

2.2.2.1.2 Depressants

Although not extensively used in coal flotation, depressants help improve recoveries by suppressing unwanted material from floating. Their function is exactly the opposite of collectors; they render the surface they attach to more hydrophilic. Klassen and Vlasova (1967) and Han (1983) mentioned the use of starch, tannin and glue as depressants in coal flotation. There are other depressants such as lime for pyrite and water glass for clay minerals.

2.2.2.1.3 Frothers

Bulatovic (2007) stated that the purpose of frothers is to strengthen the rising bubbles and to stabilise the froth once formed. An ideal frother is one that acts entirely in the liquid phase without affecting the state of the particle surface (Nagaraj and Ravishankar, 2005; Khoshdast and Sam, 2011). A good frother is one that has negligible collecting power, and results in the formation of a stable froth that is able to keep the floated coal particles in the froth phase during concentrate collection (Han, 1983).

A frother's surface-active properties gives it the ability to concentrate at the air-water interface (Han, 1983). This occurs because the dipole moments on water readily interact with the polar ends of the frother, while no reaction takes place between the water molecules and the non-polar hydrocarbon tail. This causes the polar head to be oriented towards the water and the non-polar group to be oriented towards the air. This reduces the surface tension of the water, thus enhancing the stability of the bubble. Good frothers must have some degree of solubility to ensure even distribution in the pulp, and this has been found to be in the ranges from 0.2 to 0.5 g/L H_2O (Nagaraj and Ravishankar, 2005; Khoshdast and Sam, 2011; Bulatovic, 2007).

Han (1983) gave a list of functional groups expected on effective frothers, summarised in Table 2.2.

Table 2.2: Functional groups found on frothers used in flotation processes.

Functional group	Symbol
Hydroxyl	-OH
Carboxyl	-COOH
Carbonyl	=CO
Amine	$-NH_2$
Sulpho	$-OSO_2OH$ or $-SO_2OH$

The most commonly used frothers are organic acids, amines and alcohols. Alcohols have preferential use over other frothers because they do not possess any collecting property. The existence of both frothing and collecting properties in a single reagent may result in selective flotation being difficult (Han, 1983). A low molecular weight alcohol frother is used when selectivity is important for feed containing a higher than normal percentage of fines (Kawatra, 2009).

Methyl isobutyl carbinol (MIBC) is a widely used alcohol in flotation processes that involve complex ores. It has been reported as the best and most efficient frother in coal flotation processes (Laskowski, 2001).

Other frothers used in coal flotation are pine oil and cresylic acid. Pine oil, made up of a combination of aromatic alcohols, has both collecting and frothing properties. It adsorbs on the surface of coal; thus, a higher amount of pine oil is required for the equivalent flotation yield with MIBC frother. Cresylic acid is also adsorbed on the surface of coal, but to a greater extent compared to pine oil.

'Salt flotation', which is a rapid and selective method, has also been demonstrated in Russia where inorganic salts or seawater are used as frothing agents (Glembotskii et al., 1972). The salts commonly used are chlorides of sodium, calcium and potassium, and calcium sulphate at concentrations of 2 wt. % in the pulp (Han, 1983). The performance of these frothers is affected by the extent of oxidation of the coal and the pH of the pulp. At higher degrees of surface oxidation of coal and increased pH, the degree of flotation decreases.

2.2.2.2 pH

In the early years of flotation for mineral beneficiation, researchers generalised the effect of pH on coal flotation to a statement which says that the optimum pH for this process is neutral (Han, 1983; Bulatovic, 2007). The explanation given for this was that the net charge on the surface of coal is close to zero, thus it is more hydrophobic and has higher chances of floating. However, this is a sweeping statement which only applies to specific types of coal.

More recent studies have shown an interesting role that pH plays in coal desulphurisation flotation. An investigation by Liu et al. (1993) revealed that increasing pH, from 4 to 8, increased pyrite rejection in coal flotation. This was shown to be caused by the decrease in hydrophobicity of pyrite as pH increases. However, this increase in rejection was not coupled with an increase in the rejection of non-pyritic material from coal. Liu et al. (1993) explained that non-pyritic material selectivity decreased with increase in pH is caused by the precipitation and adsorption of ions in the system. Another noteworthy observation made in the same study was that increasing pH resulted in the precipitation of iron ions which considerably depressed the flotation of coal, without affecting selectivity.

A study by Humeres and Debacher (2001) explained the effect of pH as resulting from *"the adsorption of protons (or hydroxide ions) by the particles and bubbles through multiple equilibria, assuming that there is no interaction between the binding sites."* This protonation or deprotonation results in the surface of coal being either positive (in the case of protonation) or being negatively charged (when deprotonation occurs). Thus, there exist a point at which the surface charge is neither positive nor negative. This is the point where flotation is optimum with respect to pH. Humeres and Debacher (2001)

showed that, for the coal type they were working with, this optimum pH was 5. It was observed that the relative rate constant increases as pH is increased from 2 to 4 due to the protonation of surface sites with pK^+ and reaches a plateau, beyond which it starts to decrease until a succeeding surface site with pK^- is deprotonated, causing an increase in the rate constants as shown in Figure 2.3.

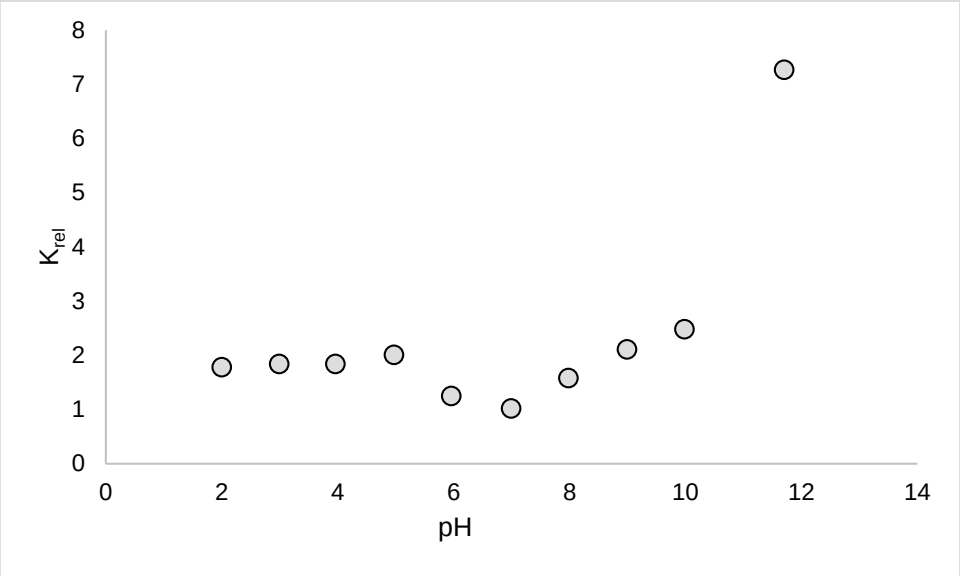

Figure 2.3: Relative rate constant of coal flotation as a function of pH at 25°C. K_{rel} is the rate constant standardised against a rate constant at pH 7. Data from Humeres and Debacher (2001)

Dube (2012) showed that the optimum pH depends on coal type as summarised by the relationship between zeta potential and pH in Figure 2.4. Therefore, the optimum pH for coal flotation is not fixed to a single value for all coals. It varies from coal to coal, and as shown by Dube (2012), Liu et al. (1993) and Humeres and Debacher (2001) on the degree of oxidation and protonation/deprotonation of the coal. Asghar et al. (2015) showed that the optimum pH for the coal they studied was 10.

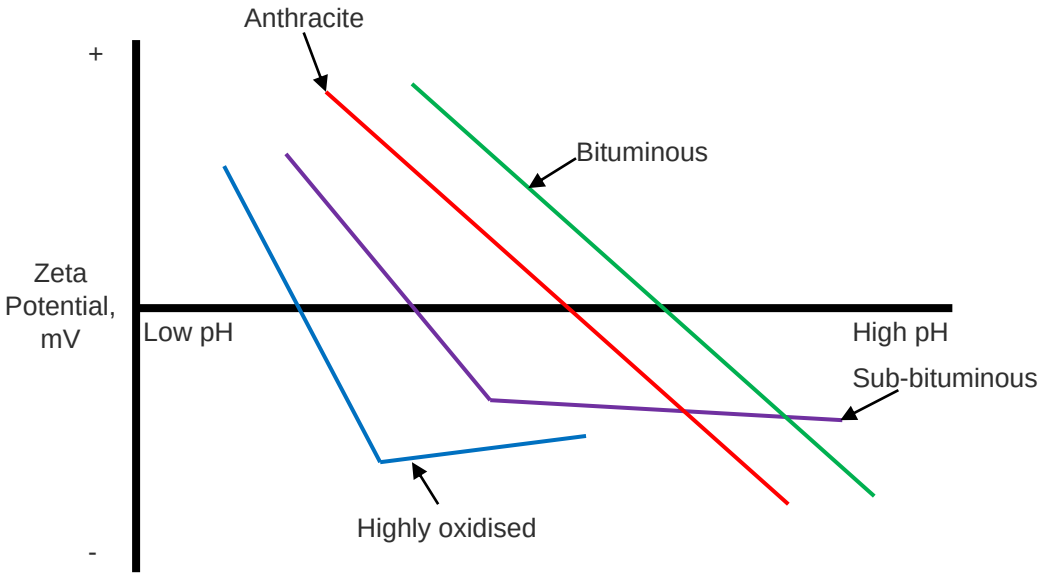

Figure 2.4: A generalisation of zeta potentials for different coal types. A zeta potential value of zero means the net charge on the surface is zero

2.2.2.3 Pulp density

The efficiency of a flotation process is inversely linked to the amount of solids in the flotation cell. It has been found that pulp density varies from 6 to 25% and is a function of coal characteristics (type, grade and rank) (Han, 1983). Zhang (1989) tested the effect of solids loading at 6.25% and at 9.1% and found that the yield of combustible material was higher at the pulp density of 6.25%. Han (1983) reported that other researchers have obtained better results at pulp densities of 20%, which is contradictory to what Zhang (1989) found. Lower pulp densities give cleaner products because there is little mechanical entrainment, while higher pulp densities result in higher feed recovery. However, there is one researcher who found that the entrainment factor (the ratio of entrained particles to particles in suspension) decreased with increasing pulp density (Paryad et al., 2017). The justifications made for this observation were that the relationship was affected by the distribution of ash in different size fractions. For samples with the majority of the ash distributed mainly to the lower size fractions, coarser particles accumulate in the upper zone of the flotation cell due to their higher flotation rate and lower settling rates and in so doing prevent the finer particles from entraining in the froth zone. This effect is increased as the pulp density increase because the mass of coarse particles to occupy the upper zone of the pulp increases. This study used a fixed pulp density for all experiments based on experimental work by Kazadi Mbamba et al. (2012).

2.2.3 Two-stage coal desulphurisation flotation

Two-stage desulphurisation of coal is a technique that was developed and has been extensively used at the University of Cape Town to deal with issues of ARD associated with pyritic sulphur in coal waste (Kazadi Mbamba, 2011). This method was developed and described in a Water Research Commission (WRC) project by Harrison et al. (2010) to separate valuable material from sulphur in two stages from both hard rock tailings and fine coal wastes. Two technical pathways were considered for the coal case. Route 1 removed sulphur by pyrite flotation followed by coal flotation to remove the remaining pyrite and the Route 2 considered the removal of coal first, leaving a pyrite rich tails product which is further concentrated by sulphide flotation.

Due to the natural hydrophobicity of coal, Route 2 was chosen as the logical choice. Kazadi Mbamba (2011) investigated this process route (Figure 2.5) using fine coal waste from the Witbank coalfield. Collectors investigated for the first stage were oleic acid, dodecane and kerosene, and the second stage used potassium amyl xanthate (PAX). Methyl isobutyl carbinol was used in both stages as the frothing agent and dextrin was used to as a coal depressant in the second stage (Kazadi Mbamba et al., 2012; Kazadi Mbamba et al., 2013).

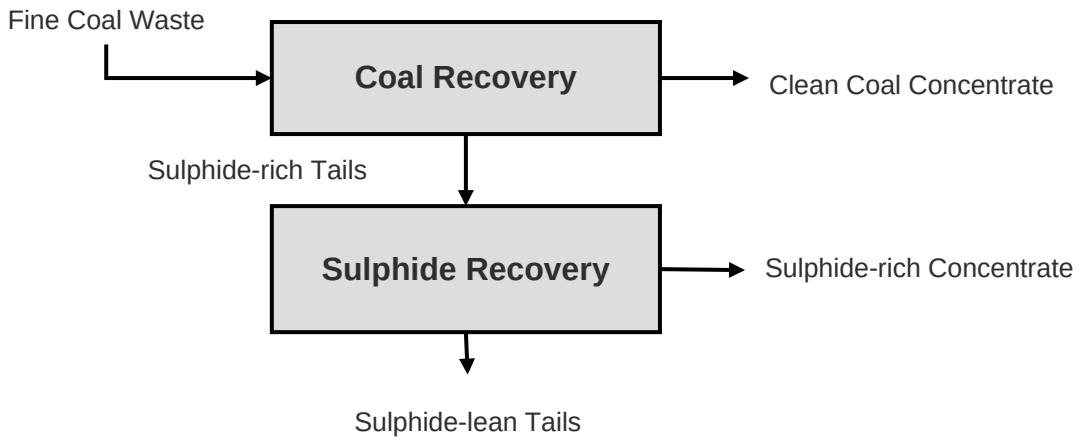

Figure 2.5: Two-stage desulphurisation process for coal cleaning. Adapted from Kazadi Mbamba (2011).

Table 2.3 shows the results for the collectors independently tested in the first stage desulphurisation flotation by Kazadi Mbamba (2011) and Iroala (2014b). As seen in Table 2.3, the polar collector (oleic

acid) performed better than the non-polar collectors (dodecane and kerosene), however with a compromise on ash and sulphur recovery. This could be explained by mechanical entrainment of fine hydrophilic particles in the water between air bubbles (Demirbas and Balat, 2004) which is enhanced by the frothing ability of oleic acid. The trend shown in the results from the two investigations was that sulphur recovery increased with yield. This is because of the organic sulphur which is part of the organic material that was recovered in the floats. This data proved that clean coal can be recovered in the 1st stage of the desulphurisation process.

Table 2.3: Results from coal flotation experiments on a coal sample from the Witbank coalfield, South Africa. Collector dosed at 2.8 kg/t, with the exception of dodecane marked with an asterisk (*) which was dosed at 27.9 kg/t, and MIBC at 0.28 kg/t.

Collector	Yield (%)	Quality (%)		Recovery (%)		
		Ash	Sulphur	Combustibles	Ash	Sulphur
Witbank waste coal sample (Kazadi Mbamba, 2011)						
Dodecane	27.37	15.5	0.47	33.79	16.89	13.47
Kerosene	31.44	15.4	0.47	38.74	15.43	22.11
Oleic acid	55.98	18.1	0.5	68.72	32.68	42.11
Witbank waste coal sample (Iroala, 2014b)						
Dodecane*	6.7	22.9	3.4	-	-	-
Oleic acid	43.5	22.1	4.1	-	-	-
Nalflote 9858	34.6	25.7	3.3	-	-	-
Waterberg waste coal sample (Iroala, 2014b)						
Dodecane*	6.6	31.8	1.1	-	-	-
Oleic acid	27.5	42.6	1.4	-	-	-
Nalflote 9858	54.6	35.1	2.0	-	-	-

Iroala (2014b) used the same desulphurisation process with an added reflux classification step to remove ash and sulphur from fine coal waste. The samples used in that work were from Witbank and Waterberg. The Witbank coal waste sample was a high ash (48.1%), high sulphur (4.2%) waste while the Site 1 discards was a high ash (49.2%), low sulphur (2.0%) sample. For the coal flotation process, dodecane performed poorly, with product yields as low as 6%, despite the use of high collector dosages (27.9 kg/t). This was justified as being caused by the high ash content of the samples used (48% for the Witbank sample, compared to 34% in Kazadi Mbamba (2011)'s work). Oleic acid showed poor selectivity for Waterberg coal as the ash content of the product remained high (42.6%); Product from the Witbank coal waste floats had 22.1% ash. There was relatively greater ash rejection (22.1% ash in product) for the Witbank coal waste, but the sulphur content remained high at 4.1%.

Jera (2013) performed an economic evaluation on the two-stage coal desulphurisation process treating coal waste at a rate of 100 t/hr, with a clean coal yield of 80% in the first stage of the process and a sulphide-lean tailings yield of 40% in the second stage. This sulphide-lean tailings stream was classified as non-acid forming (NAF) in terms of ARD. The evaluation used technical data on the two stage froth flotation process from Kazadi Mbamba (2011), with additional assumptions of plant availability of 82% and plant life of 15 years.

The results obtained from Jera (2013)'s economic analysis included a net present value (NPV) of $5.2 million (2013 – $). This NPV gave an internal rate of return (IRR) of 19%. NPV is the difference between the present value of benefits and cost while IRR is the interest rate that results in a net present value

of zero (Luernberger, 1998). This analysis excluded taxes, interest on borrowed capital and depreciation. These economic indicators showed that the project was viable.

A sensitivity analysis showed that the economics of the process were sensitive to capital and operating costs, capacity utilisation, coal yield and price, and reagent costs. In particular, reducing the reagent cost by a factor of 10 increased the NPV to $60.1 million (2013 – $) and IRR to 59%. All reagents contributed 72% to the annual operating cost and oleic acid contributed about 82% of the reagent cost. This was based on an oleic acid cost of $10.29/gal in 2013 - $. Halving the cost of oleic acid reduced the annual operating cost by 22%.

Reducing the expected product yield from 80% to 69% resulted in a NPV of $20 790 (2013 - $) and an IRR of 14%. Jera (2013) showed that yields below 69% would result in an economically unfeasible process at the prevailing coal prices of that time in that particular case study. Further analysis across additional coal plants shows similar trends (Kotsiopoulos and Harrison, unpublished data). Economic feasibility in the presence of today's lower coal prices requires improved efficiency and reduced costs. One starting point is the reduction of operating expenses by reducing reagent cost. Therefore, it is this project's objective to investigate alternative reagents that are cheaper and offer similar or better yields as oleic acid

2.3 Bioflotation reagents for coal desulphurisation

In bioflotation, microorganisms or their products are applied to change the surface properties of the mineral to be floated or depressed. The attachment and surface modification generally takes the same amount of time as chemical reagents (Rao and Somasundaran, 1995).

Acidthiobacillus ferrooxidans (previously known as *Thiobacillus ferrooxidans*) is one of the microorganisms that has found great application in mineral processing and beneficiation. In coal flotation, it has been used as a depressant for pyrite (Blazquez et al., 1993; Nagaoka et al., 1999; Amini et al., 2009). The depressant effect is achieved by the oxidation of pyrite, thus making it more hydrophilic. In an investigation by Nagaoka et al. (1999), *At. ferrooxidans* reduced the floatability of pyrite from 90% to less than 20%.

Another microorganism that has been studied as a coal biocollector is *Mycobacterium phlei*. Its use was first reported by Misra et al. (1995). Fagan-Endres et al. (2017) reported obtaining overall coal yield as high as 39% using *M. phlei* in the absence of a frother. This was comparable to the yield obtained using dodecane under the same flotation conditions (about 37% overall yield). However, unpublished data of a preliminary economic evaluation showed that it was not economically feasible to use *M. phlei* for coal flotation due to the high biomass production cost.

The use of *Staphylococcus carnosus* in recovering coal from fine coal waste tailings was investigated by Ramos-Escobedo et al. (2014). They reported increasing coal recovery from about 50% to close to 75% after 5 minutes and 90% after 12 hours at pH 9. The surface modification of coal was achieved through biofilm formation. Infrared spectroscopy showed that extracellular polymeric substances were secreted to form a biofilm on the surface of the coal (Ramos-Escobedo et al., 2016).

El-Midany and Abdel-Khalek (2014b) investigated the use of *Bacillus subtilis* and *Paenibacillus polymyxa* for desulphurising coal. For a feed sample with 6.7% ash and 3.3% total sulphur, a coal concentrate with 1.95 % ash and 0.92% total sulphur was obtained using *B. subtilis,* in comparison to 2.65 % ash and 1.12% total sulphur using *P. polymyxa.* The overall yield was reported to be above 72% for both bioreagents. In a different study, El-Midany and Abdel-Khalek (2014a) found that higher yields are obtained when the difference in point of zero charge (PZC) between the coal particles and the bacteria is large. PZC refers to the pH at which the overall surface charge of a particle is zero (Figure 2.4 in Section 2.2.2.2). The better performance obtained using *B. subtilis* was attributed to a larger PZC difference between coal and the bacteria.

Biological products from microorganisms have also been used in coal cleaning by froth flotation. Khoshdast et al. (2011a) reported on the use of rhamnolipids, produced by *Pseudomonas aeruginosa* MA01, as a biofrother. The study compared surface tension and frothability of rhamnolipids to

conventional frothers such as MIBC, Aerofroth-65 (A-65), Dowfroth-250 (DF-250), and pine oil. Rhamnolipids showed better surface activity compared to the other frothers. Its performance in coal flotation was compared to pine oil and it was observed that higher dosages (50g/t) were required to achieve higher yields (about 77%) above those obtained using pine oil (71%) at a dosage of 20 g/t (Khoshdast et al., 2011b; Khoshdast and Shojaei, 2012). when the dosage was matched to that of pine oil, the overall yield of coal reduced to about 63%.

Tall oil, which is a mixture of plant-based fatty acids obtained as by-product from the pulp and paper industry, has also been used as a collector in froth flotation. It has been shown to float quite a variety of minerals including phosphates and haematite (Kou et al., 2010). Coal flotation using tall oil showed improved recovery of combustibles (Hines et al., 2011). This was because the major component of the oil is oleic acid, which has been demonstrated to be a good collector in its pure form (Kazadi Mbamba, 2011).

Fatty acid methyl esters (FAMEs) were used in coal flotation by Vasumathi et al. (2013) and Yi et al. (2015), separately. These FAMEs were derived from vegetable oil by transesterification. Flotation results showed that lower dosages of FAMEs were required to clean coal compared to other collectors such as diesel and NALCO products. Table 2.4 gives a summary of flotation results where FAMEs were used as collector.

Table 2.4: Comparison of collector performance in coal flotation.

Collector	Dosage (g/t)	Yield (%)	Ash (%)	Combustibles recovery (%)	Reference
FAMEs	96.9	67.35	16.25	77.35	Vasumathi et al. (2013)
Diesel	545.0	67.86	16.60	76.40	
FAMEs	70.0	75.03 – 77.50	9.22 – 10.44		Yi et al. (2015)
Diesel	900.0	-	11.00 – 13.00		
Nalco	70.0	76.00	10.40		

Although microorganisms have been demonstrated to be good coal collectors at lab-scale, their large scale application is constrained by the cost of biomass production. Goede and Hein (2016) reported that the cost of production was heavily driven by feedstock materials for growing the bacteria (74% of the operating cost was due to media components). Despite the successful use of FAMEs in coal cleaning by froth flotation, the food versus fuel debate stands as a limitation to further development of the conversion of food crops to FAMEs. Therefore, microalgae are an alternative source of oil which can be converted to FAMEs.

2.4 Algae for lipid production

Microalgae have been shown to be more productive that terrestrial crops on an oil per unit cultivation area basis. This is summarised in Table 2.5. Because of the high oil yields from microalgae, much attention and research has been put in identifying high lipid producers and optimising the cultivation process for economic extraction. Identified species of microalgae are discussed in Section 2.4.1.

Table 2.5: Comparison of oil sources. Adapted from Chisti (2007).

Crop	Oil yield (gal/acre)	Land usage (acres)
Microalgae	6283–14641	4.94 – 11.12
Palm oil	636	111.20
Coconut	287	244.63
Jatropha	202	345.95
Canola	127	551.05
Soya beans	48	1 467.81
Corn	18	3 805.42

2.4.1 High lipid-producing algae

A lot of research has gone into finding microorganisms with high lipid contents for the purposes of biofuel production, and different methods have been developed to maximise lipid productivity in the identified organisms. Microalgae have been found to be a good biofuel feedstock as they displayed high growth rates and an ability to store large quantities of lipids (up to 80% of their dry weight) compared to other microorganisms (Schlagermann et al., 2012).

Griffiths and Harrison (2009) and the Aquatic Species Program (Lohrey, 2012) evaluated microalgal species on a basis of biomass growth rate, lipid content and lipid productivity. Lohrey (2012) identified around 300 algae species with the potential for oil production at industrial scale. Table 2.6 shows some of the microalgae species that have been investigated for their potential in oil production. Griffiths et al. (2012) investigated the lipid productivity of 11 microalgal species from freshwater and saltwater environments, identified for high lipid productivity potential in their 2009 study. Of the 11 species that were tested, freshwater *Scenedesmus* sp. and *Chlorella vulgaris*, and saltwater species *C. fusiformis* and *Nannochloropsis* sp. were found to be the top lipid producers. Other researchers found *Parachlorella kessleri* to be a high lipid producer, with overall lipid productivity ranging from 0.48 – 0.58 g/L/day and lipid content of about 50%DW (Přibyl et al., 2012; Ota et al., 2016; Li et al., 2012). This was in the same range as data for *C. vulgaris*.

Table 2.6: Lipid productivity and lipid content of some microalgal species that have been investigated for their potential in algal-derived oil production.

Microalgae	**Productivity (mg/L/day)**	**Lipid content (%dry wt)**	**Source**
Ankistrodesmus falcatus	230 – 250	12 – 30	Griffiths et al. (2012)
Botryococcus braunii	–	25 – 75	Chisti (2007)
Chaetoceros calcitrans	18	40	Naghdi et al. (2016)
Chaetoceros muelleri	22	34	Naghdi et al. (2016)
Chlorella sp.	45 – 1840	21 – 55	Chisti (2007), Naghdi et al. (2016), Griffiths et al. (2012)
Crypthecodinium cohnii	–	20	Chisti (2007)
Cylindrotheca sp.	290 – 350	16 – 37	Chisti (2007), Griffiths et al. (2012)
Dunaliella sp.	120	17 – 23	Chisti (2007)
Isochrysis sp.	38 - 340	15–33	Chisti (2007), Naghdi et al. (2016), Griffiths et al. (2012)
Monallanthus salina	–	>20	Chisti (2007)
Nannochloris sp.	–	20–35	Chisti (2007)
Nannochloropsis sp.	84 – 413	23–68	Chisti (2007), Naghdi et al. (2016)
Neochloris oleoabundans	290	13 – 54	Chisti (2007)
Nitzschia sp.	–	45–47	Chisti (2007)
Parachlorella kessleri	480 – 580	50	(Přibyl et al., 2012; Ota et al., 2016; Li et al., 2012)
Phaeodactylum tricornutum	–	20–30	Chisti (2007)
Scenedesmus sp.	36 – 150	18 – 36	Naghdi et al. (2016), Griffiths et al. (2012)
Schizochytrium sp.	–	50–77	Chisti (2007)
Spirulina sp.	210 – 290	2 – 4	Naghdi et al. (2016), Griffiths et al. (2012)
Tetraselmis sueica	–	15–23	Chisti (2007)

Techniques such as nutrient limitation (e.g., nitrogen and/or phosphorus starvation), heavy metals and other chemicals, pH, osmotic stress, radiation, temperature, as well as genetic engineering have been shown to improve lipid productivity (Sharma et al., 2012). Nitrogen limitation was adopted for this research as it was easy to implement and there was kinetics data already available on it (Griffiths, 2011; Griffiths et al., 2014). The suitability of other techniques at industrial scale is discussed by Sharma et al. (2012) and Zhu et al. (2016), separately.

2.4.2 Algal lipid chemistry

The majority of lipids found in algal oil are triacylglycerides (TAGs). These are three fatty acids chemically bonded to a glycerol molecule by an ester bond. Transesterification (replacement of one alcohol molecule with another different alcohol attached to the ester bond) of TAGs using methanol over a basic or acidic catalyst produces FAMEs. For one mole of TAGs, 3 moles of methanol are required to produce one mole of glycerol and three FAMEs (Figure 2.6). Since the reaction is a reversible reaction, industrial processes use twice the amount of methanol in order to favour the forward reaction (Chisti, 2007). Basic catalysts are preferred over acidic catalyst because they catalyse the reaction faster.

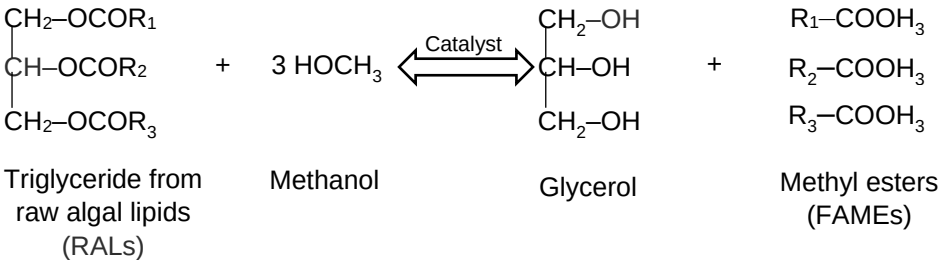

Figure 2.6: Transesterification reaction for converting RALs to FAMEs. R_1, R_2 and R_3 and hydrocarbon tails with chain lengths ranging from 12 to 20

The ester bond in both raw algal lipids (RALs) and FAMEs is polar. This results in them falling in the category of polar collectors. The $R_{1\text{-}3}$ groups are the parts of the molecule that offer hydrophobicity. It is hypothesised in this investigation that the –C=O group attaches to coal surfaces through polar interactions (negatively charged heads attracted to positively charged functional groups on coal surfaces) and the hydrocarbon tails renders the coal particles hydrophobic.

Due to the repulsion between the polar ester bonds in RALs, the hydrocarbon tails are branched out in such a way that reduces the force of repulsion (Figure 2.7). According to Han (1983), this orientation of hydrocarbon groups increases solubility. However, the same author highlighted that collectors with large molecular weights are less soluble, which is the case with RALs.

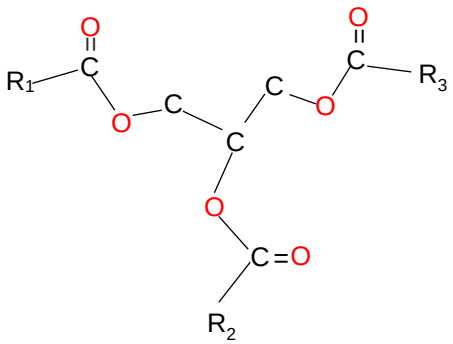

Figure 2.7: Orientation of the hydrocarbon groups in RALs to minimise the force of repulsion between the polar ester bonds

2.5 Chapter summary

Relevant literature has been presented in this section. It was seen that floatability of coal depends on its composition and other chemical physical properties such as particle size, for example.

Microorganisms and their products have been successfully used in coal flotation lab scale, but some of the limitations of their practical application in the industry have been cited. This has led to the selection of algal lipids as coal biocollectors. No researcher has investigated their use as bioflotation reagents before. The following chapter presents the experimental methods used to evaluate the performance of raw algal lipids and their derivatives in coal desulphurisation by froth flotation.

3 Methodology

3.1 Introduction

The aim of this research study was to investigate the selective recovery of valuable coal from fine coal waste by desulphurisation flotation using biologically derived lipids. A series of tests were performed to evaluate the performance of algal lipids and their product of esterification, fatty acid methyl esters in the coal flotation process under different operating conditions.

This chapter lays out the experimental procedures used in attaining the set goals. This includes a description of the algal culture conditions and lipid extraction, coal characterisation, flotation procedures and evaluation of flotation performance.

3.2 Algae culture and lipid extraction

3.2.1 Algae culture

Scenedesmus sp. and *Parachlorella* sp. were chosen for their relatively high lipid production (lipid content and productivity) and availability. These two microalgal species were grown under the same conditions of temperature, media, air supply, light and batch time as described by Griffiths et al. (2012).

The microalgal species chosen for this study were cultured under limited nitrogen (150 mg/L) using Bold's basal medium (recipe in Appendix B.1). The limited nitrogen growth condition was motivated by a study by Griffiths et al. (2012) who showed that lipid productivity is enhanced at limited nitrogen concentrations with a compromise, however, on biomass productivity.

Starter cultures of *Scenedesmus* sp. and *Parachlorella* sp. were cultured in 500 mL flasks, under normal air, for 10 to 15 days before inoculating the airlift photobioreactors. Full description of airlift photobioreactors in Langley et al. (2012). Inoculation of the bioreactors achieved a starting concentration for all cultures was equivalent to an optical density of 0.1 (at a wavelength of 750 nm, using the Helios α Spectrophotometer (Thermo Scientific)). The reactors were operated for at least 25 days to maximise lipid production (Mandal and Mallick, 2009). Algal growth was monitored by absorbance at 750 nm with time (Griffiths et al., 2011). The optical density data measured spectrophotometrically was converted into cell dry weight estimations using a standard curve which was generated using the first batch of each algae species.

3.2.2 Lipid extraction and characterisation

Algae was harvested on day 30 and dewatered by centrifuging at 10 000 × g for 15 minutes. Raw algal lipid extraction was done on the dewatered algae using the Axelsson and Gentili (2014) method outlined in Appendix B.2. FAMEs were produced by the direct transesterification of the dewatered algae using a protocol developed by Griffiths et al. (2010) as outlined in Appendix B.3.

The extracted lipids and FAMEs were recovered from the solvent using a rotary evaporator (Heidolph Hei-VAP Value) with a fixed vacuum pressure of 890 mbar from a Chemker 400 vacuum pump. The hexane phase containing the lipids was heated in a water batch set at 85°C based on the rule of 20 (Sigma-Aldrich, 2007). The rule of 20 says that the heating bath temperature should be at least 20°C above the boiling point of the liquid being evaporated for sufficient distillation. Likewise, the cooling medium temperature was set below 40°C for sufficient condensation of the vapour. The algal lipids which remained in the evaporating flask after solvent recovery were dissolved in a small amount of hexane and then transferred into a 200 mL storage container. The hexane was left to evaporate overnight in a fume hood. After all the hexane was evaporated, absolute ethanol was added to the lipids to make a 10 wt% lipid solution in ethanol, and the container sealed. Ethanol was chosen as the carrier solvent because it was shown that it does not interfere with the flotation process (Klassen and Vlasova, 1967). Characterisation of the lipids was done using gas chromatography (Varian GC 3900) using the procedure outlined in Griffiths et al. (2010).

3.3 Fine coal waste characterisation

3.3.1 Coal samples used

Two coal samples were used in this study. The sample from Site 1 was a coal discards sample from the Waterberg while the sample from Site 2 was a fine coal waste sample collected in the Witbank region.

The as-received samples were thoroughly mixed and blended using a riffle sample splitter. The sample was subsequently split in two stages into 500 g units; the sample was first split by using a 1 kg capacity rotary splitter. The 1 kg splits were combined into 5 kg units and further split into 500 g units. The splits were then sieved using a +212 µm sieve and the oversize fraction milled for 7 minutes in a lab scale rod mill containing ten steel rods (Φ25 × 288 mm). The milled fractions were recombined with the -212 µm fraction and then blended and split into 200 g sample units which were used for the flotation experiments.

3.3.2 Solubility tests

Solubility tests were performed to quantify the amount of soluble fractions in the coal samples. 30 g coal sample was put in the flotation cell with 500 mL tap water and the agitation speed set to 170 rpm. No air was sparged through the pulp and no reagents were used for this analysis. The pulp was agitated for 12 minutes (accounting for the reagent conditioning time and the flotation time). After 12 min, the pulp was drained and filtered using Whatman™ 1001-320 Grade 1 Qualitative Filter Paper with pore size of 11 µm. The filter cake was washed and dried and then weighed to determine the loss in mass and was analysed for ash and sulphur according to the procedures in Section 3.3.4.

The filtrate was analysed for dissolved sulphur. A 100 µL filtrate aliquot was diluted with 4 900 µL deionised water. A dilution series was performed by taking 100 µL from the diluted sample and adding 4 900 µL deionised water. A 250 µL aliquot of conditioning reagent (75 g NaCl, 30 mL HCl (32%), 50 mL glycerol and 100 mL ethanol in 300 mL deionised water) was added to each of the serial dilutions, followed by a micro scoop of barium chloride salt. The test tubes were then vortexed for 1 min. The optical density of the resulting precipitate in solution was read at a wavelength of 420 nm using the Helios α Spectrophotometer (Thermo Scientific). The absorbance data was translated to sulphate concentration using a standard curve generated using a standard sulphate solution made by dissolving 0.1479 g Na_2SO_4 in 1 L deionised water.

3.3.3 Particle size distribution

Particle size analysis was done using a Malvern Mastersizer 2000 housed in the Analytical Lab at the University of Cape Town (Department of Chemical Engineering, UCT). The samples for ash- and sulphur-by-size fractions were obtained by sieving 200 g samples using screen sizes 25, 75, 106, 150, and 212 µm supplied by the Centre for Mineral Research at UCT. The final particle size distribution results are presented in Section 4.3.1.

3.3.4 Ash and sulphur analysis

Ash analysis was performed gravimetrically on size fractions based on the sieve sizes in Section 3.3.3 using a Carbolite Furnace at 850°C. A sample of coal of mass around 1g was weighed and put into a crucible and placed in the furnace for 3 hours. After the 3 hours had lapsed, the crucible with the residual ash was cooled and weighed. Total sulphur analysis was done using LECO S 632 Analyser in the Analytical Laboratory in the Department of Chemical Engineering at UCT. A detailed procedure of this analysis is available at www.leco.co.za (2012).

3.4 Flotation experiments

Bioflotation reagent performance was assessed using a 500 mL mini flotation cell shown in Figure 3.1. The cell is a batch flotation cell that is sub-aerated with analogue impeller speed and air flow rate

regulators. The flotation cell was cleaned with tap water for ten minutes between each set of experiments.

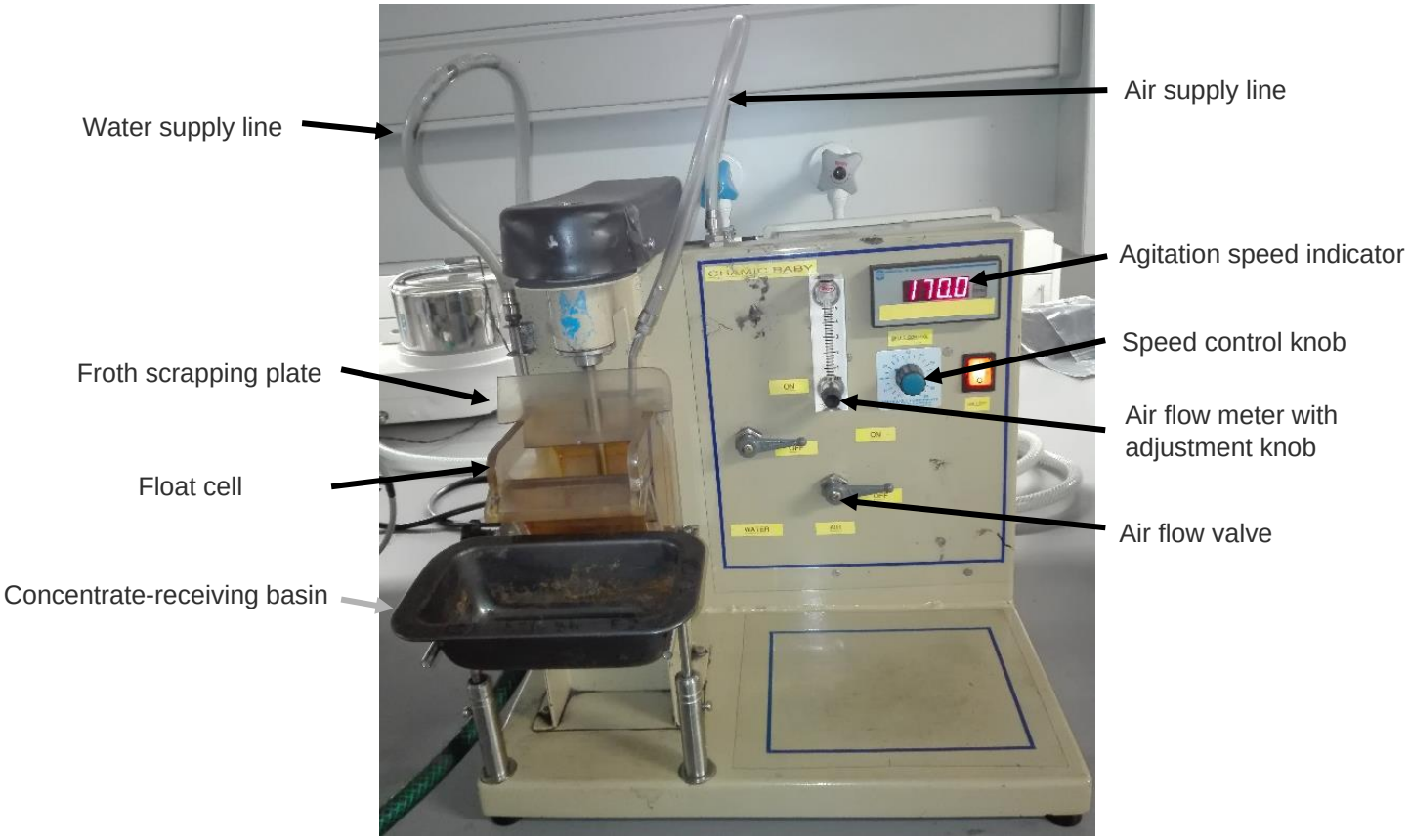

Figure 3.1: Charmic Baby Flotation Cell with a 500 mL capacity. Impeller speed and aeration rate are adjusted before flotation starts to avoid premature froth formation which hinders effective collector and frother distribution in the pulp.

3.4.1 Flotation reagents

The flotation reagents used in this study are shown in Table 3.1. Oleic acid and dodecane were used as control reagents dosed at 2.8 kg/t, the optimum found by Kazadi Mbamba et al. (2013). All reagents were kept refrigerated when they were not in use to reduce the risk of biodegradation.

Table 3.1: Reagents used in the flotation experiments.

Reagent	Function	Dosage	Supplier
Oleic acid	Collector	2.8 kg/t	May & Baker LTD Dagenham England
Dodecane	Collector	2.8 kg/t	Sigma-Aldrich
Raw algal lipids (RALs)	Collector	1.2 – 3.7 kg/t	UCT
Fatty acid methyl esters (FAMEs)	Collector	1.2 – 3.7 kg/t	UCT
Methyl isobutyl carbinol (MIBC)	Frother	0.28 kg/t	Sigma-Aldrich

3.4.2 Flotation procedure

Flotation tests were done in batches at room temperature using tap water. The mass of coal required to achieve a 6% solids loading was calculated based on the bulk density of the coal and the amount of water required was based on the mass of coal used.

At the start of the experiment, the cell was filled with about 20 mL of water. The impeller was switched on, running at 170 rpm, followed by addition of the coal sample. The rest of the water was then added, followed by the appropriate amount of collector. The pulp was conditioned for 5 min to allow for even distribution throughout the pulp, at the end of which MIBC was added and left to condition for a further 1 min. After the conditioning period was over, a feed sample was collected and then 5 L/min of air was supplied to the cell to induce froth formation. The froth produced was collected at regular intervals in concentrate basins. Four concentrates were collected: initial concentrate was collected in the first 30 s, Concentrate 2 collected in the next 30 s, Concentrate 3 collected over the subsequent 1 minute, and Concentrate 4 collected over the last 3 minutes. This gave a total flotation time of 5 min. The cell was drained to collect the tails at the end of each batch.

The feed sample, concentrates and tails were filtered on filter papers of a known mass and dried in an oven set at 80°C for 24 hours (Memmert, Laboratory and Scientific Equipment Co. (LASEC)). The dried feed samples, concentrates and tails were weighed for yield determination. The samples were then removed from the filter papers and stored in zip-lock plastic bags.

All experiments were done in triplicate for each set of flotation conditions. For reagent dosage, the appropriate amount of collector was calculated on a volume basis. Pipettes were then used to add the reagents to the pulp. For pH test, concentrated hydrochloric acid and sodium hydroxide were used for pH adjustment. Concentrated solutions were used to avoid diluting the pulp since the working volume was small.

3.5 Experimental approach

The performance of the bioflotation reagents extracted from microalgae was assessed based on overall coal yield, recoveries, and flotation efficiency index and product quality. The equations for calculating these performance indicators are found in Appendix A:. The data input to these equations was obtained from the weights of the collected samples (feed, concentrates and tails), ash and sulphur analysis results.

Control experiments were done using oleic acid and dodecane which were dosed at 2.8 kg/t. The first set of flotation experiments evaluated the effect of bioreagent dosage on coal flotation. The dosage of both RALs and FAMEs was varied from 1.2 to 3.7 kg/t. The pH of the system was measured but not adjusted. The second parameter evaluated was the effect of pH on bioreagent performance. In these sets of experiments, pH was adjusted using concentrated hydrochloric acid and sodium hydroxide.

Frothability studies of the bioreagent were done in two ways. The first was visual observation where the sample was put in the flotation cell with everything except MIBC. The impeller and air were then switched on. A video of the formation of froth as air bubbled through the flotation cell was taken. Still images were then taken from the videos at time equals 2 s, 7 s and 15 s. The images were then compared for bubble size and persistence. The second evaluation was flotation experiments with bioreagent dosage at 2.8 kg/t and frother dosage of 0.28 kg/t in the positive test and no frother in the negative test. The results were collected and analysed as was done for other flotation tests mentioned earlier. The data reported in this work is in the form mean ± standard error. Analysis of variance (ANOVA), two-tailed t-test and Fisher pairwise least significant difference (LSD), all at the 95% confidence interval, were used to interpret the data in order to determine whether there was statistical difference between RALs and FAMEs in terms of performance at different dosages. A detailed description of the statistical models is given in Appendix D.

3.6 Chapter summary

The methods used for algae cultivation and lipid extraction have been presented in this chapter. Flotation experiments evaluating the performance of RALs and FAMEs were done in a 500 mL flotation cell. The effect of reagent dosage and the effect of pH were assessed. The results for these flotation experiments are presented and discussed in Chapter 4.

4 Results and discussion – Experimental Study

4.1 Introduction

The results of algae growth and lipid extraction to provide flotation chemicals, coal characterisation and coal flotation experiments for the separation of coal values and sulphide bearing ash are presented in this chapter. The flotation results for the Waterberg discards from Site 1 are presented first followed by those of the coal waste tailings from Site 2 in the Witbank region. The flotation experiments tested the effect of varying collector type, concentration and flotation pH, while holding all other factors constant. The pH tests were not performed on the sample from Site 2 since its natural pH was already at the recommended pH for a two-stage desulphurisation process by froth flotation.

4.2 Algal lipid characterisation

4.2.1 Algae growth

Of the two algal species chosen for lipid production, *Parachlorella* sp. was eliminated based on the challenges that were faced in dewatering it by centrifugation. This resulted from the extracellular polysaccharides produced by this strain in response to the stress of low nitrogen concentration. However, the difficulty to dewater this microalgae does not disqualify it from a list of potential sources of algal lipids at industrial scale since there are many dewatering techniques that may be able to achieve this goal. Therefore, the algal lipids used in all flotation experiments were extracted from *Scenedesmus* sp. which was supplied from the stock cultures maintained by the Centre for Bioprocess Engineering Research (University of Cape Town).

The biomass concentration reached at the end of the batch cultures (at the end of day 30) in the airlift reactors was 1.20 g/L. This is comparable to the maximum biomass concentration of 1.73 g/L reported by Griffiths et al. (2012). Kinetic data were not generated on this algae for this work since this was already extensively covered by Griffiths (2011) under the same operating conditions in her PhD thesis.

4.2.2 Lipid characterisation

Figure 4.1 shows the lipid profile for *Scenedesmus* sp. in terms of fatty acid composition. The results showed that the majority of lipids produced by this microalgae are poly-unsaturated fatty acids, which agrees well with the findings from an investigation by Griffiths et al. (2012). Fatty acids with 18 carbon atoms and two double bonds in the chain were the most abundant in the mixture, followed by fatty acids with 16 carbon atoms. When analysed by GC, the peak for dodecane would appear where C12 peaks appear and oleic acid would appear at C18:1.

The volumetric lipid content achieved for *Scenedesmus* sp. in this research was about 373 mg/L. This accounted for approximately 31% of the dry weight of the final biomass obtained.

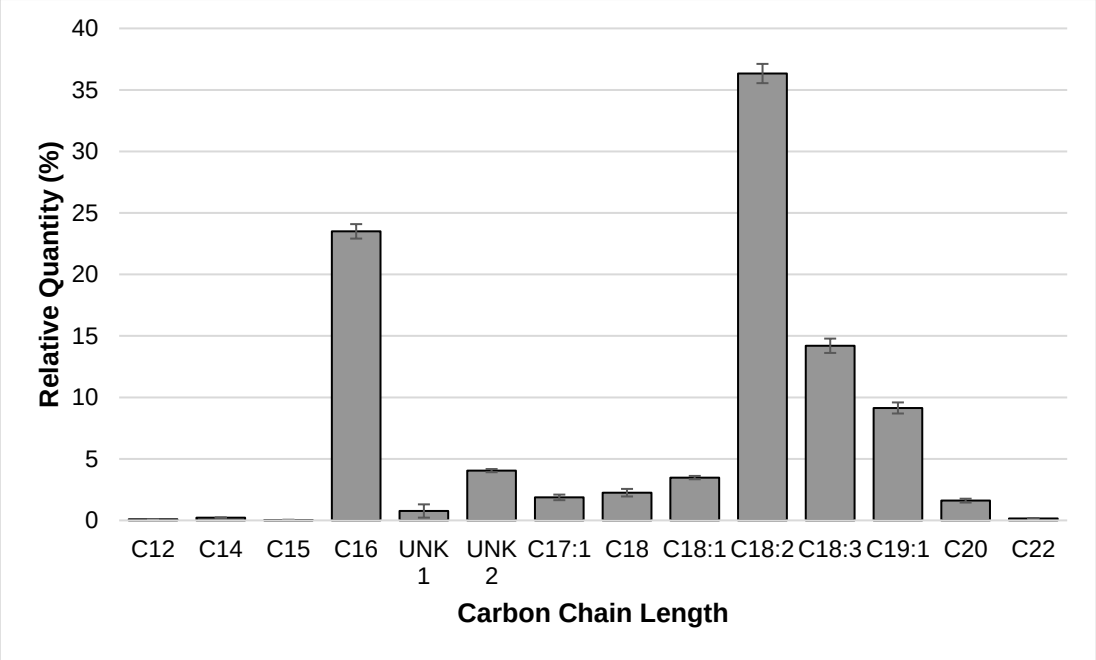

Figure 4.1: Gas chromatography results for lipids extracted from Scenedesmus sp. Results shown here are the average of four batches. 'UNK' means the fatty acid was not identified by the reference standards used. The lipids are abbreviated based on the carbon chain length; C12 means a lipid with 12 carbon atoms and C18:1 means a lipid with 18 carbon atoms and 1 double bond

4.3 Coal characterisation

4.3.1 Size analysis

The as received samples were rod-milled to reduce their particle size as they were most coarse. This was performed not to achieve a specific size distribution but to get the particles in the 100 – 150 µm range which is the recommended range for fine coal flotation (Kawatra, 2009).

The particle size distribution analysis for the milled samples is presented in Figure 4.2 for Site 1 discards and in Figure 4.3 for Site 2 waste tailings. For Site 1 discards, 75% of the particles passed 100 µm and 90% passed 273 µm while more than 90% of the particles in the sample from Site 2 passed 100 µm.

Size fractions from sieve analysis showed that Site 2 waste tailings had a significant amount of fine particles (42.50% between 25 and 75 µm - Table 4.2).

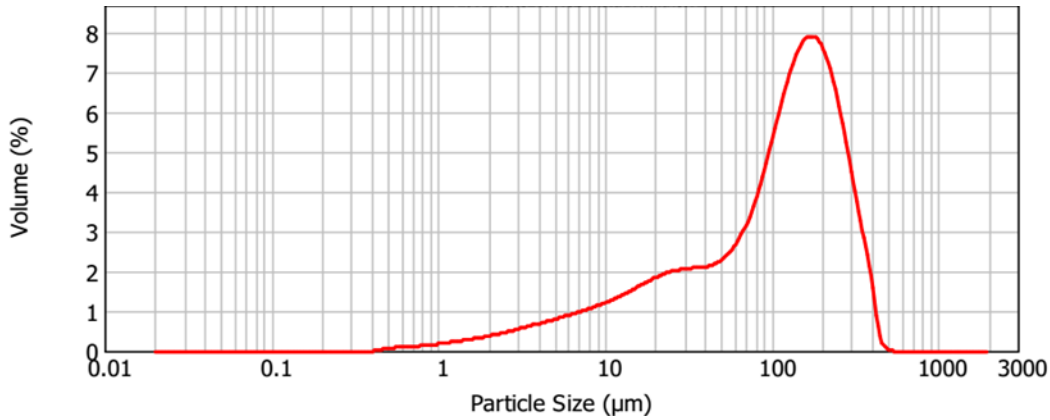

Figure 4.2: Malvern Mastersizer particle size distribution results for Site 1 discards. d(0.1): 10.37µm, d(0.5): 116.47µm, d(0.9): 272.50µm

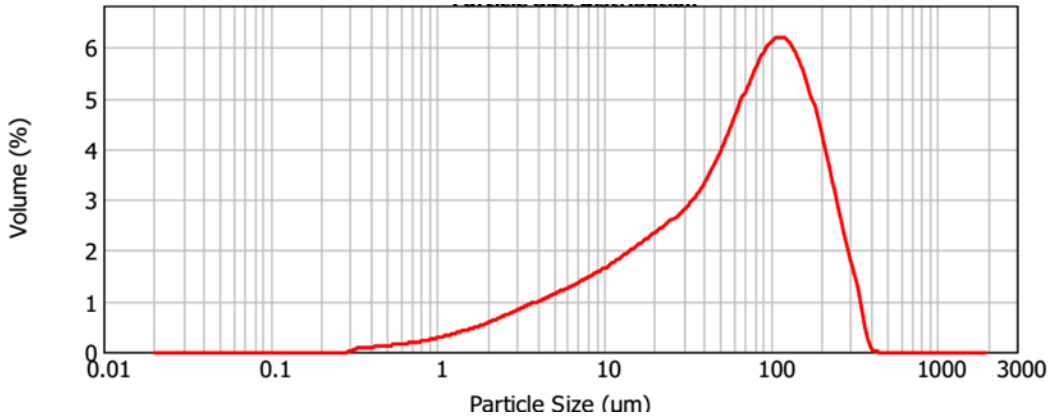

Figure 4.3: Malvern Mastersizer particle size distribution results for Site 2 waste tailings; d(0.1): 6.34µm, d(0.5): 67.77µm, d(0.9): 199.37µm.

4.3.2 Ash and Sulphur analysis

Ash- and sulphur-by-size results for both samples are shown in Table 4.1 and Table 4.2, respectively. It can be seen that coarser particles in Site 1 discards had higher ash content while finer particles were relatively low in ash. The opposite was observed for waste tailings from Site 2– the ash content increased with a decrease in particle size. Sulphur content was high in finer particles than in coarser particles for both samples. The cumulative ash and sulphur contents for Site 1 discards were found to be higher compared to those of Site 2 waste tailings (49.02% ash and 5.71% for Site 1 discards and 25.56% ash and 0.91% sulphur for Site 2 waste tailings).

Table 4.1: Ash and sulphur distribution based on size for the air-dried Waterberg discards from Site 1.

Particle size (µm)	Weight (%)	Ash (%)	Cum. Ash (%)	Sulphur (%)	Cum. Sulphur (%)
-425+212	11.82 ± 0.11	56.73 ± 0.12	56.73	3.14	3.14
-212+150	31.56 ± 0.12	49.84 ± 0.59	51.72	5.06	4.54
-150+106	18.99 ± 0.15	48.03 ± 0.41	50.59	5.76	4.91
-106+75	11.35 ± 0.06	50.34 ± 1.57	50.56	6.02	5.08
-75+25	20.79 ± 0.05	45.35 ± 0.03	49.41	7.32	5.57
-25	5.49 ± 0.03	42.22 ± 0.03	49.02	8.15	5.71

Table 4.2: Ash and sulphur distribution based on size for the air-dried waste tailings from Site 2 in the Witbank area.

Particle size (µm)	Weight (%)	Ash (%)	Cum. Ash (%)	Sulphur (%)	Cum. Sulphur (%)
-212+150	12.41	19.02	19.02	0.55	0.55
-150+106	13.11	21.01	20.04	0.62	0.59
-106+75	17.78	24.03	21.66	0.8	0.67
-75+25	42.5	28.21	24.91	1.11	0.89
-25	14.2	29.48	25.56	1.03	0.91

4.4 Coal flotation results

The performance of the extracted lipids was assessed through flotation experiments which were carried out in batch mode. The flotation cell (Chamic, Barker) was operated at 170 rpm agitation speed and 5 L/min aeration rate as outlined in Section 3.4.2.

The performance indicators for the different collectors were yield (overall mass recovery), recovery of combustibles, ash and sulphur, and product quality in terms of combustibles, ash and sulphur content of concentrates.

4.4.1 Waterberg discards from Site 1

As highlighted earlier in this report, dodecane and oleic acid were used for the positive control experiments. A dosage of 2.8 kg/t was chosen based on the best result obtained by Kazadi Mbamba (2011). Negative control experiments used MIBC only. These were done to see the natural floatability of the coal in the absence of a collector. The results for the control experiments are presented in Figure 4.4.

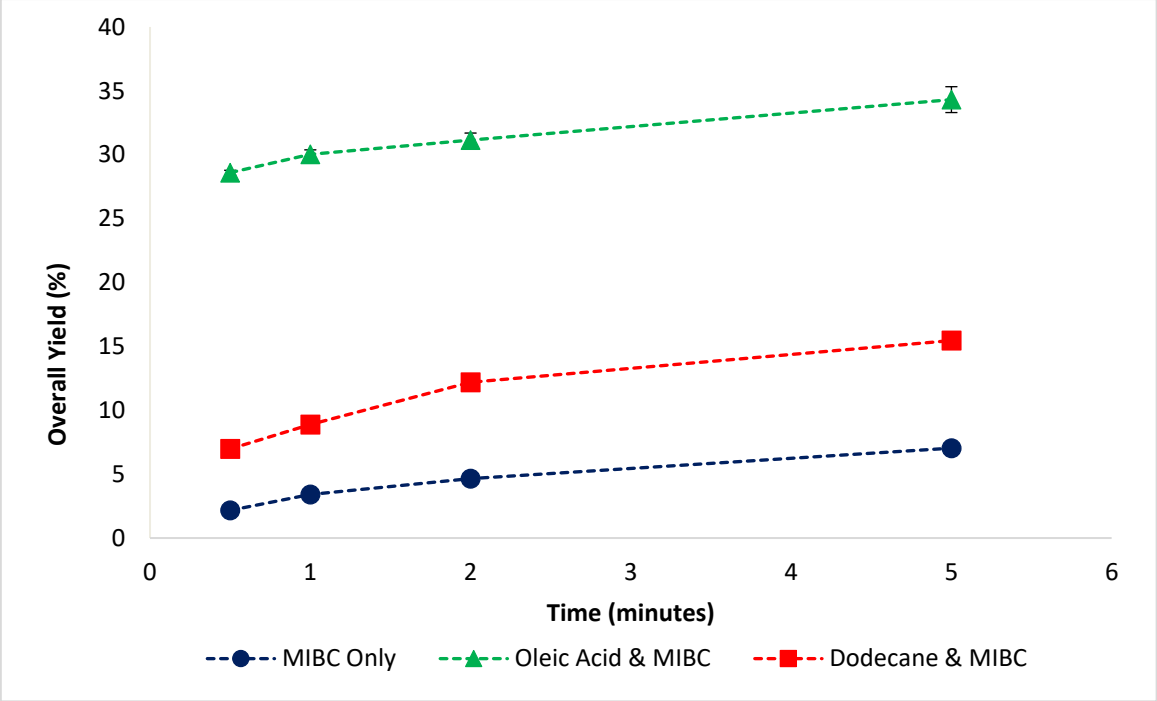

Figure 4.4: Negative and positive control flotation experiment results for Site 1 discards. Collector and MIBC dosage at 2.8 and 0.28 kg/t, respectively. Error bars are standard errors of triplicate repeats.

Only about 7% of the feed was collected in the concentrate when no collector was added. The negative control hence shows that the waste sample was not naturally floatable. This is because of the high ash and sulphur content. Adding dodecane as the collector resulted in approximately twice as much of the material being collected. Oleic acid addition resulted in the best yield of 34.31 ± 0.58%. The positive control results show the marked difference in performance achieved by using non-polar collectors (dodecane) and polar collectors (oleic acid). In a study by Iroala (2014b), it was observed that increasing the dosage of non-polar collector resulted in no significant increase in overall yield. To obtain the same yield, a higher dosage of a non-polar collector is required compared to the dosage of polar collector. Iroala (2014b) tested a dodecane dosage of 27.9 kg/t (10 times the dosage used by Kazadi Mbamba et al. (2013)) on coal samples from Waterberg and Witbank and observed yields of 6.6% for both samples (Table 2.4 in Section 2.2.3).

4.4.1.1 Effect of bioreagent dosage on coal flotation

The dosage of RALs and FAMEs was varied from 1.2 to 3.7 kg/t. The performance of the two bioreagents were assessed in terms of yield, recoveries (combustibles, ash and sulphur) and product quality (ash and sulphur content).

4.4.1.1.1 Yield

The effect of biocollector dosage on yield, determined as the mass fraction of the feed that is collected as concentrate, is shown in Figure 4.5. The observed trend showed that the yield increased as the collector dosage (for both RALs and FAMEs) was increased. At a collector dosage of 1.2 kg/t, RALs had a yield significantly lower than when FAMEs were used as the collector (17.22% yield with RALs and 25.12% with FAMEs). A one-way ANOVA at 95% confidence interval showed that there was no significant difference in performance between FAMEs, RALs and oleic acid at a dosage of 2.8 kg/t. Comparison of the means of yields obtained at dosages of 3.2 and 3.7 kg/t showed no statistical difference in yield for both RALs and FAMEs across these concentrations. This means that collector dosages beyond 3.2 kg/t do not result in better yields.

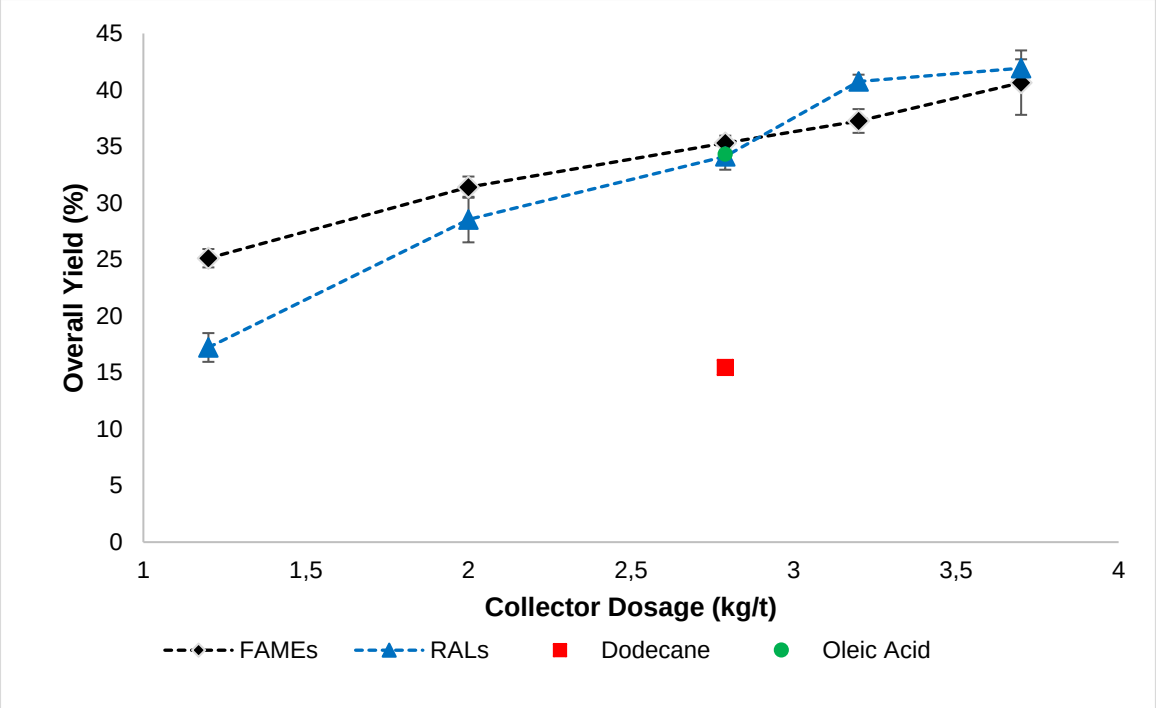

Figure 4.5: Effect of biocollector dosage on final yield for discards from Site 1. MIBC dosage at 0.28 kg/t in all experiments. Each data point is an average of three 5 minute batch flotation experiments. Error bars are standard errors of triplicate repeats.

The general similarity in performance between RALs and FAMEs can be explained as a result of similarities in chemical structure. RALs are triglycerides (esters of glycerol and three fatty acids) with an ester bond that induces negative polarity and a hydrocarbon tail that is hydrophobic (Figure 4.6). FAMEs are derived from the esterification of the triglycerides and therefore retain the ester bond that induces polarity and a hydrocarbon tail that is hydrophobic. It is the polar interactions that results in collector attachment to coal surfaces. The hydrophobic tails render the coal particle hydrophobic, hence it is collected in the concentrate. Oleic acid, represented by the oleate molecule in Figure 2.2 (Section 2.2.2), has the same hydrocarbon chain length as the majority of RALs and FAMEs as shown in the chromatography results presented in Figure 4.1.

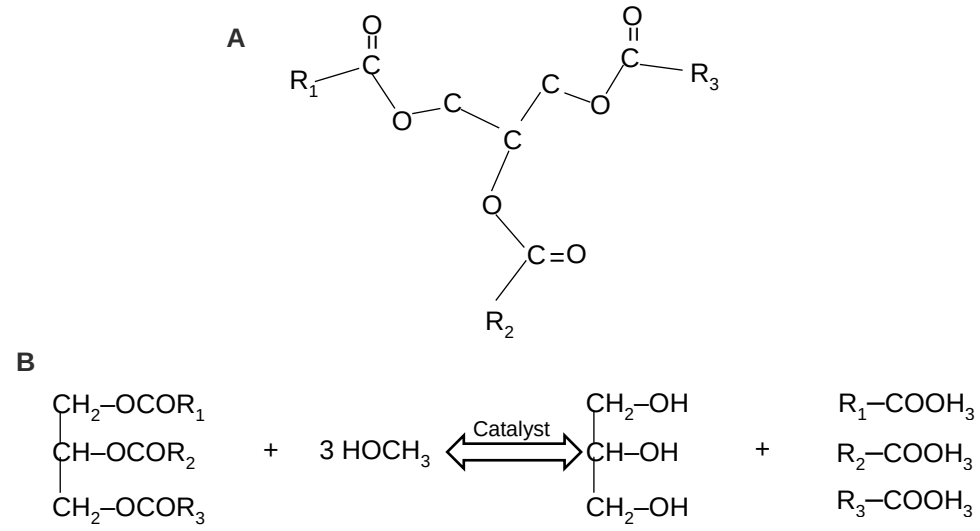

Figure 4.6: A - a triglyceride representing RALs, B - transesterification of a triglyceride to form a fatty acid methyl esters (FAMEs)

4.4.1.1.2 Recoveries

Recovery is a more specific descriptor than yield. For combustibles recovery, for example, it is the fraction of combustible material in the feed that reports to the concentrate. The same applies to ash recovery and sulphur recovery. A well performing coal flotation process has high combustibles recovery and low ash and sulphur recovery. This is dependent on the degree of liberation between coal particles and gangue material. Highly liberated samples show good separation between coal particles and gangue material.

The recovery of combustibles, ash and sulphur was analysed for different collector dosages for RALs and FAMEs. The results are presented in Figure 4.7, Figure 4.8 and Figure 4.10, respectively.

Combustibles recovery follows the same trend that was observed for overall yield (Section 4.4.1.1.1); namely, recovery of combustible material increased with collector dosage. At a dosage of 1.2 kg/t, FAMEs resulted in higher combustibles recovery than RALs (36.98 vs 24.63%). There was no significant difference in performance between the two bioflotation reagents at dosages of 2.0, 2.8 and 3.2 kg/t. These were similar to the oleic acid control at 2.8 kg/t and significantly higher than the dodecane control at the same concentration. FAMEs achieved a recovery of 62.14% at a dosage of 3.7 kg/t while RALs had a significantly lower recovery of 58.59%.

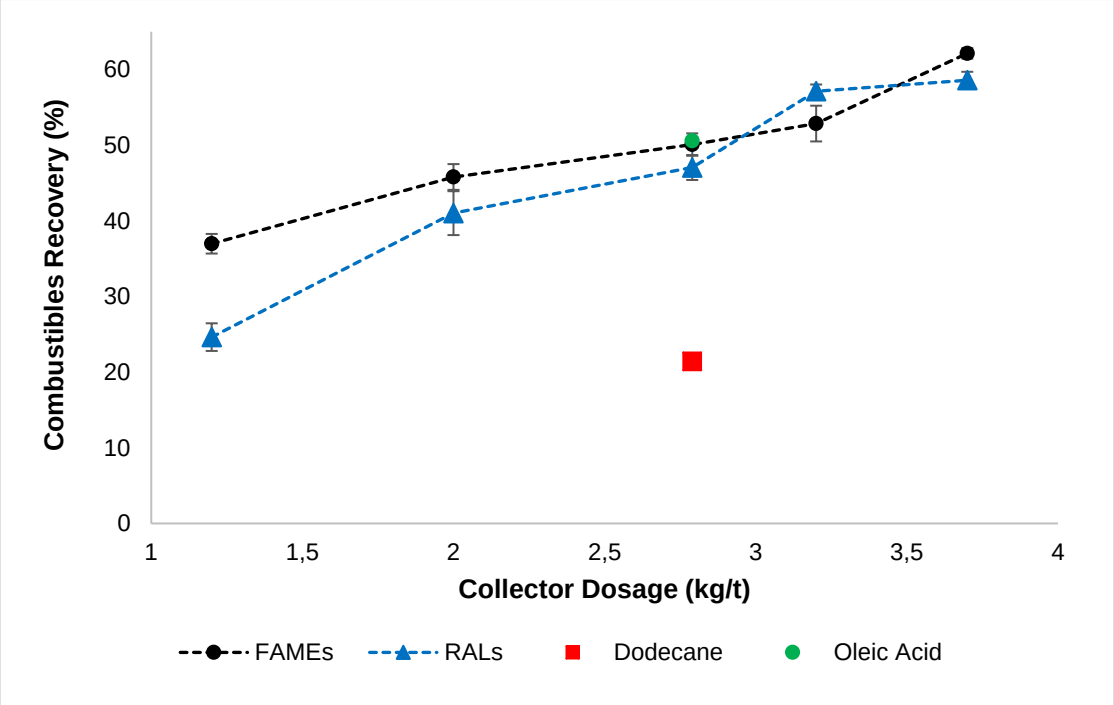

Figure 4.7: Combustibles recovery as a function of biocollector dosage for Waterberg discards from Site 1. MIBC dosage at 0.28 kg/t in all experiments. Error bars are standard errors of triplicate repeats

Figure 4.8 show the effect of collector dosage on ash recovery. Despite differences in combustibles recovery at a collector dose of 3.7 kg/t, both reagents had the same ash recovery. The specificity of the flotation is evaluated by calculating the flotation efficiency index (FEI) which is the difference between combustibles recovery and ash recovery, determined to be 38.78% for FAMEs and 34.82% for RALs. This shows that FAMEs were more specific at rendering combustible particles more hydrophobic than ash particles compared to RALs at the same dosage. The full FEI analysis is presented in Figure 4.9. Here it is shown that there is no significant difference in the FEI for RALs and FAMEs at collector dosages of 2.0, 2.8 and 3.2 kg/t. At collector dosages of 1.2 and 3.7 kg/t, the FEI of FAMEs was significantly higher than that of RALs, meaning FAMEs served as better collectors than RALs at separating combustibles from ash material at these two dosages.

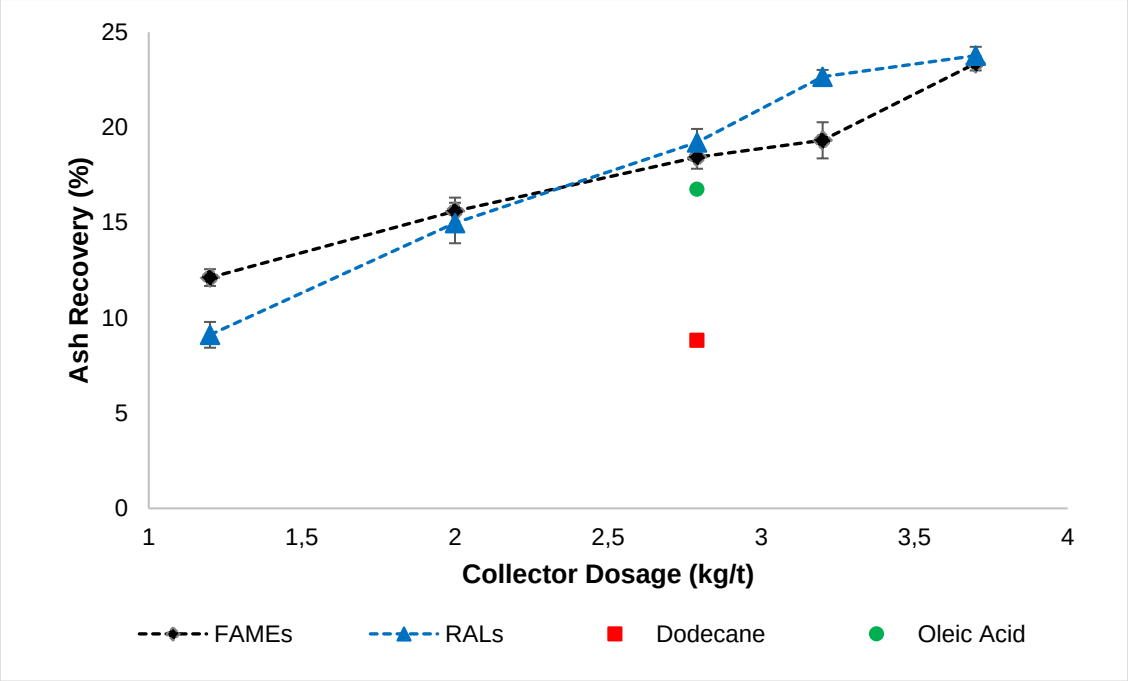

Figure 4.8: Ash recovery as a function of biocollector dosage for Site 1 discards. MIBC dosage at 0.28 kg/t in all experiments. Error bars are standard errors of triplicate repeats.

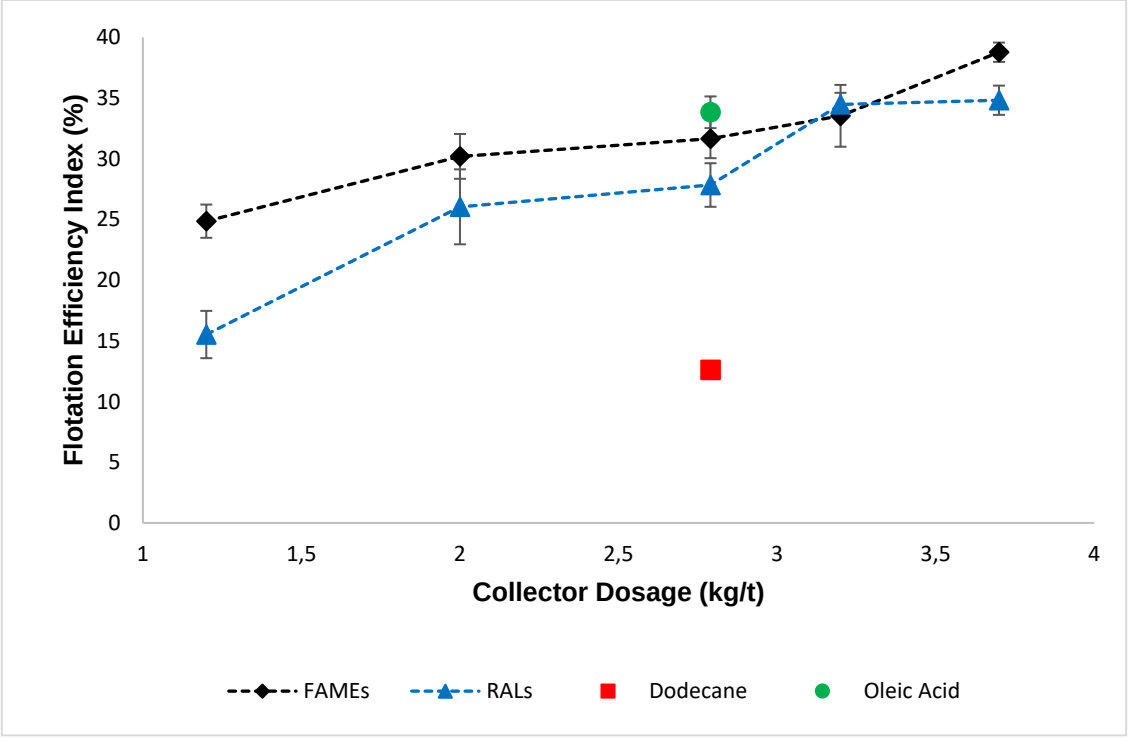

Figure 4.9: Flotation efficiency index results as a function of biocollector dosage for discards from Site 1. Error bars are standard errors of triplicate repeats.

Figure 4.10 shows the sulphur recovery as a function of collector dosage for the two bioreagents tested. In comparison to the positive control with oleic acid, both reagents had higher sulphur recoveries despite having similar combustibles and ash recoveries. This means that oleic acid was more specific at differentiating between combustible material and pyritic sulphur material. This could be ascribed to the

fact that RALs and FAMEs are mixtures of different chemicals with different chain lengths (Figure 4.1). Han (1983) pointed out that collectors with shorter hydrocarbon chain lengths are less specific compared to ones with longer chains, therefore their presence in both RALs and FAMEs results in the whole collector being less specific compared to oleic acid which contains molecules of the same chain length (C18).

For FAMEs, Fisher pairwise comparisons showed that there was no significant difference in sulphur recovery at collector dosages from 1.2 kg/t to 3.2 kg/t. Sulphur recovery at a FAMEs dosage of 3.7 kg/t was significantly higher. Statistical analysis of the sulphur recovery using RALs showed a different trend. Fisher pairwise comparisons showed that a dose of 2.0 kg/t RALs resulted in the same sulphur recovery as at 2.8 kg/t while a dose of 3.2 kg/t caused the same sulphur recovery as 3.7 kg/t. As with the FAMEs, the highest recovery of sulphur with RALs was observed at the highest collector concentration.

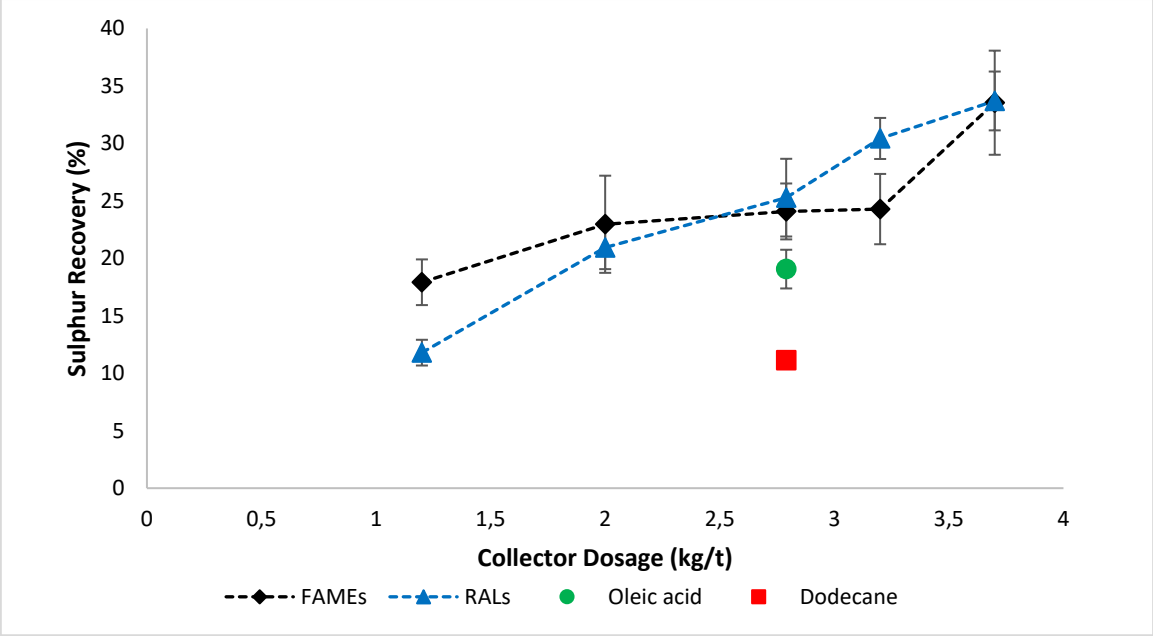

Figure 4.10: Sulphur recovery as a function of biocollector dosage for Site 1 discards. MIBC dosage at 0.28 kg/t in all experiments. Error bars are standard errors of triplicate repeats.

4.4.1.1.3 Product quality

The quality of the recovered concentrates was analysed in terms of ash and sulphur content.

Figure 4.11 and Figure 4.12 show the percentage of ash in the recovered material for the FAMEs and RALs, respectively. Both bioreagents resulted in an increase in the combustibles content of the coal waste feed from 52.60% to more than 70%. For FAMEs, it was observed that increasing the collector dosage from 1.2 kg/t to 2.0 kg/t and from 2.8 kg/t to 3.2 kg/t did not result in a statistically significant increase in the product ash content. The same was observed for RALs at the same collector dosages. This means that the collector dosage can be increased in the range from 1.2 to 2.0 kg/t or from 2.8 to 3.2 kg/t resulting in higher clean coal yields without compromising the product quality in terms of ash content. Increasing the concentration of biocollector from 2.0 kg/t to 2.8 kg/t showed a significant, but small (about 0.6%), increase in ash recovery which was associated with about a 4% increase in overall yield. Hence operating at these collector concentrations may still provide benefit, depending on the specification posed on ash content.

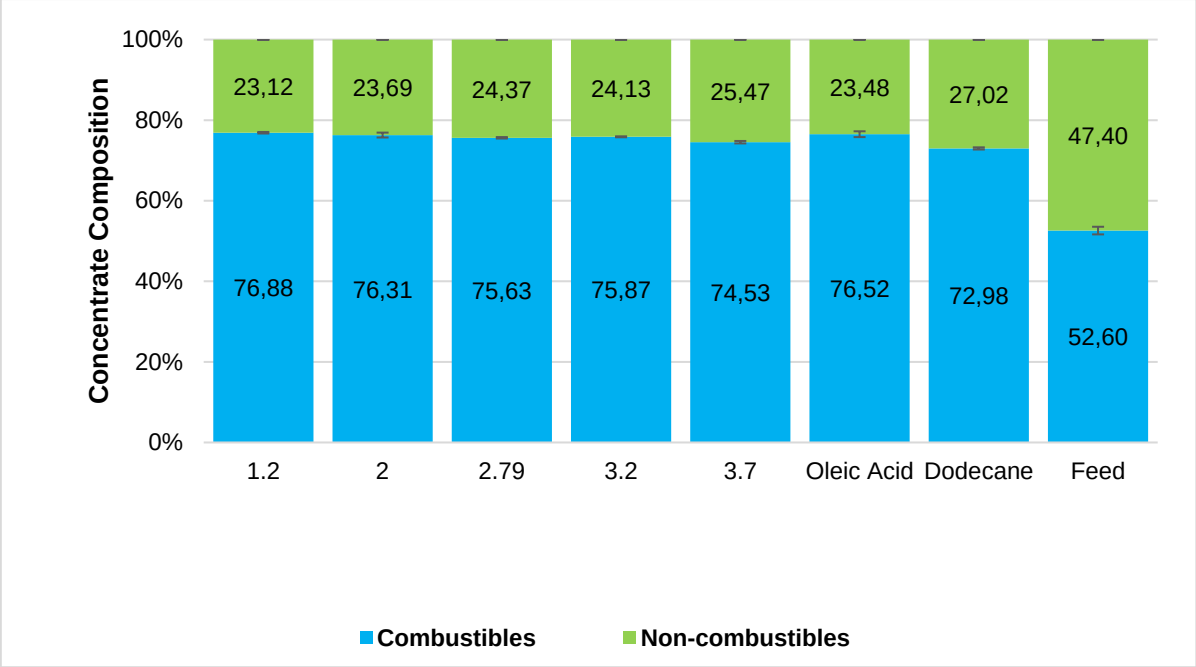

Figure 4.11: Combustibles and ash (non-combustibles) content of the recovered product from discards from Site 1 at different dosages of FAMEs. Error bars are standard errors of triplicate repeats.

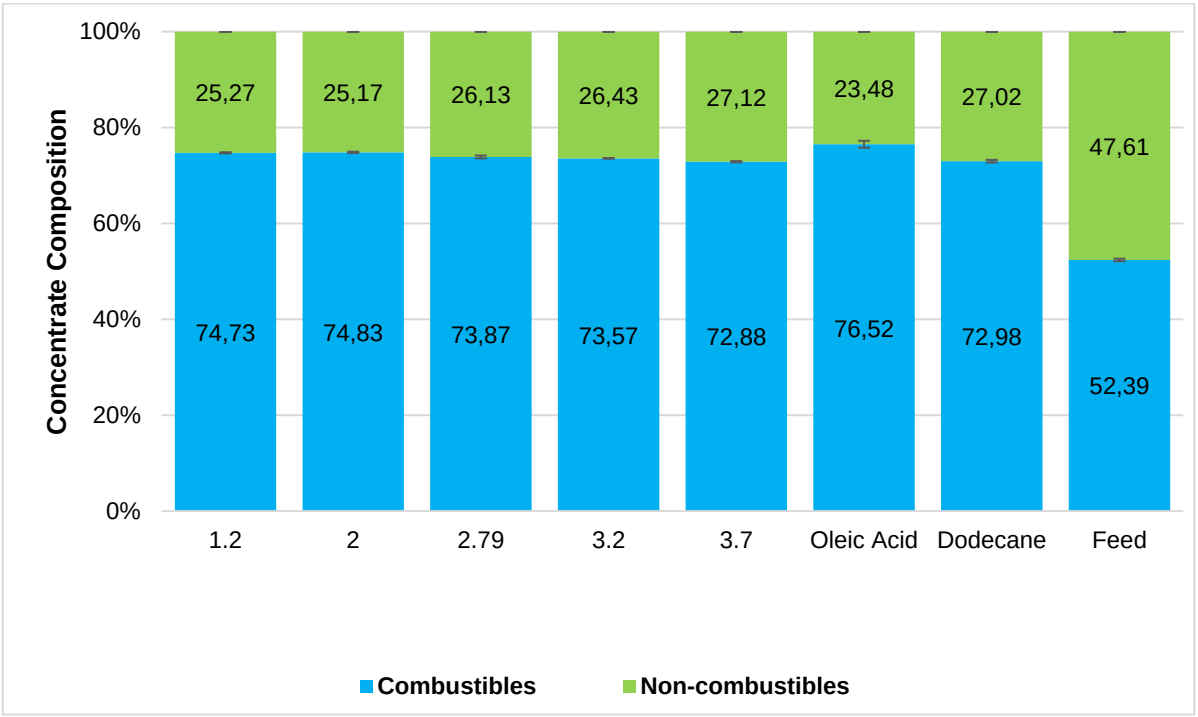

Figure 4.12: Combustibles and ash content (non-combustibles) of the recovered product from Site 1 discards at different dosages of RALs. Error bars are standard errors of triplicate repeats.

When comparing the ash content of products from the two biocollectors, FAMEs achieved a statistically significantly cleaner product compared to RALs across all collector concentrations. The comparisons are summarised in Table 4.3. Considering the concentration of 2.8 kg/t for all the collectors tested, FAMEs and oleic acid gave a product with the same (statistically) and lowest ash content (24.4 and 23.5% respectively). RALs and dodecane resulted in higher ash contents of 26.1% and 27.0% respectively, which were not statistically different. This analysis is shown in Table 4.4.

The poor performance of dodecane, despite low ash recoveries reported in Section 4.4.1.1.2, can be explained based on the mechanism of attachment to coal surfaces. Since dodecane is a non-polar collector, it attaches to surfaces purely by adhesion, as described in Section 2.2.2.1.1. Therefore, dodecane molecules attached to hydrophobic particles only. These hydrophobic particles collected happened to be the relatively coarse particles in the pulp. As observed in Table 4.1 in Section 4.3.2, the distribution of ash is skewed towards the coarser particles, hence the high ash content observed in the concentrate recovered using dodecane.

Table 4.3: Ash content comparisons at different collector dosages for FAMEs, RALs, oleic acid and dodecane for Site 1 discards.

Dosage (kg/t)	Product ash content (%)			
	FAMEs	RALs	Oleic acid	Dodecane
1.2	23.12 ± 0.19	25.27 ± 0.12	-	-
2.0	23.69 ± 0.61	25.17 ± 0.14	-	-
2.8	24.37 ± 0.18	26.13 ± 0.30	23.48 ± 0.72	27.02 ± 0.27
3.2	24.13 ± 0.12	26.43 ± 0.05	-	-
3.7	25.47 ± 0.30	27.13 ± 0.12	-	-

Table 4.4: Fisher Pairwise Comparison for ash content with collectors at a dosage of 2.8 kg/t. Note: means that do not share a letter are significantly different. N in column 2 is the sample size, i.e., triplicates.

Factor	N	Mean	Grouping	
Dodecane	3	27.02	A	
RALs	3	26.13	A	
FAMEs	3	24.37		B
Oleic Acid	3	23.48		B

Figure 4.13 shows the sulphur content of the recovered coal at different biocollector dosages. Both reagents led to a reduction of the sulphur content of the waste from 3.80% to less than 3.30%. Statistical analysis showed that increasing biocollector dosage (either FAMEs or RALs) had no significant effect on the sulphur content of the product recovered at dosages in the range of collector dosage tested. Table 4.5 shows the comparisons of means for the biocollectors compared to oleic acid and dodecane controls at a dosage of 2.8 kg/t. When compared to the oleic acid and dodecane controls, it was observed that FAMEs performance was significantly poor compared to that of oleic acid, while similar to that of dodecane, i.e. FAMEs resulted in a product with more sulphur than when oleic acid was used (Table 4.5). There was no statistically significant difference between the product sulphur content obtained using RALs, oleic acid and dodecane.

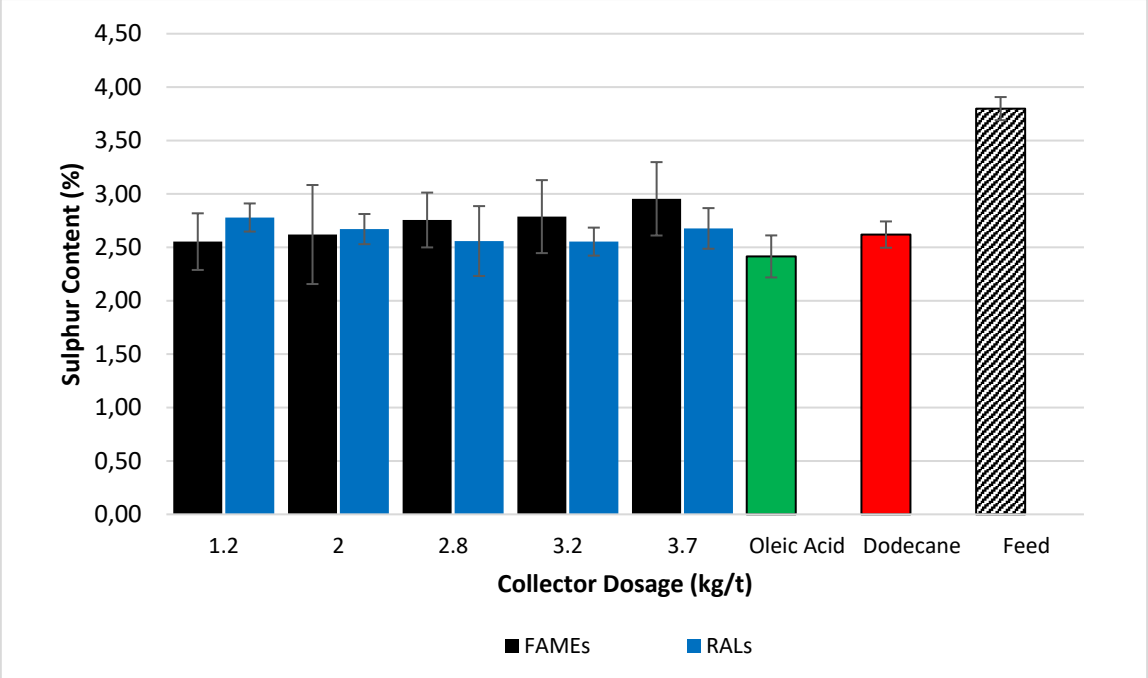

Figure 4.13: Sulphur content of concentrates as a function of collector dosage on flotation experiments for Waterberg discards from Site 1. All test used 0.28 kg/t MIBC. Control collectors were dosed at 2.8 kg/t of coal waste treated. Error bars are standard errors of triplicate repeats.

Table 4.5: Fisher Pairwise Comparison for sulphur content with collectors at a dosage of 2.8 kg/t. Note: means that do not share a letter are significantly different. N in column 2 is the sample size, i.e., triplicates.

Factor	N	Mean	Grouping	
FAMEs	3	2.76	A	
Dodecane	3	2.62	A	B
RALs	3	2.56	A	B
Oleic Acid	3	2.41		B

4.4.1.1.4 Summary of results

As seen in Table 4.6, RALs and FAMEs performance was approximately the same as that of oleic acid (a polar reagent), and better than dodecane (a non-polar collector) in terms of yield and recoveries. When compared to FAMEs, RALs had reduced selectivity with respect to ash material but better selectivity with respect to sulphur. Higher biocollector dosages resulted in higher yields (Section 4.4.1.1.1) at the expense of selectivity.

Table 4.6: Collector performance for 5-minute batch flotation tests on a sample from Site 1 at a collector and MIBC dose of 2.8 and 0.28 kg/t, respectively.

Collector	Yield (%)	Recovery (%)	Ash (%)		Sulphur (%)	
			Product	Tails	Product	Tails
FAMEs	35.31	50.09	24.37	60.82	2.76	5.13
RALs	34.13	47.05	26.13	59.84	2.56	4.68
Dodecane	15.45	21.43	27.02	54.54	2.62	4.20
Oleic acid	34.31	50.58	23.48	58.64	2.41	4.75

4.4.1.2 Effect of pH on collector performance

In the evaluation of pH on collector performance, collectors were dosed of 2.8 kg/t and MIBC at 0.28 kg/t. The results presented in the preceding section were carried out at a natural pH of about 2.7 and were used as the starting pH for the analysis. The pH was then varied to pH 4.0, 6.0 and 7.0. Reagent performance was analysed in terms of product overall yield, recoveries and product quality.

4.4.1.2.1 Yield

Figure 4.14 shows collector performance in terms of yield at pH conditions of 2.7, 4.0, 6.0 and 7.0. RALs, FAMEs and oleic acid achieved the best overall yield at pH 4. For FAMEs, statistical analysis showed that pH 4 and 6 did not result in significantly different overall yield. It was also observed that there was no significant difference in yield for pH 2.7, 6.0 and 7.0 when RALs were used as collector. Overall, the best yield was obtained at a pH around 4 for the two biocollectors and the oleic acid control. At this pH, the biocollectors performed significantly better than the oleic acid control.

For the control experiments, oleic acid showed no significant improvement or decline in yield for the pH pair of 2.7 and 6.0 while there was no significant difference in yield for dodecane collector at pH 4.0, 6.0 and 7.0.

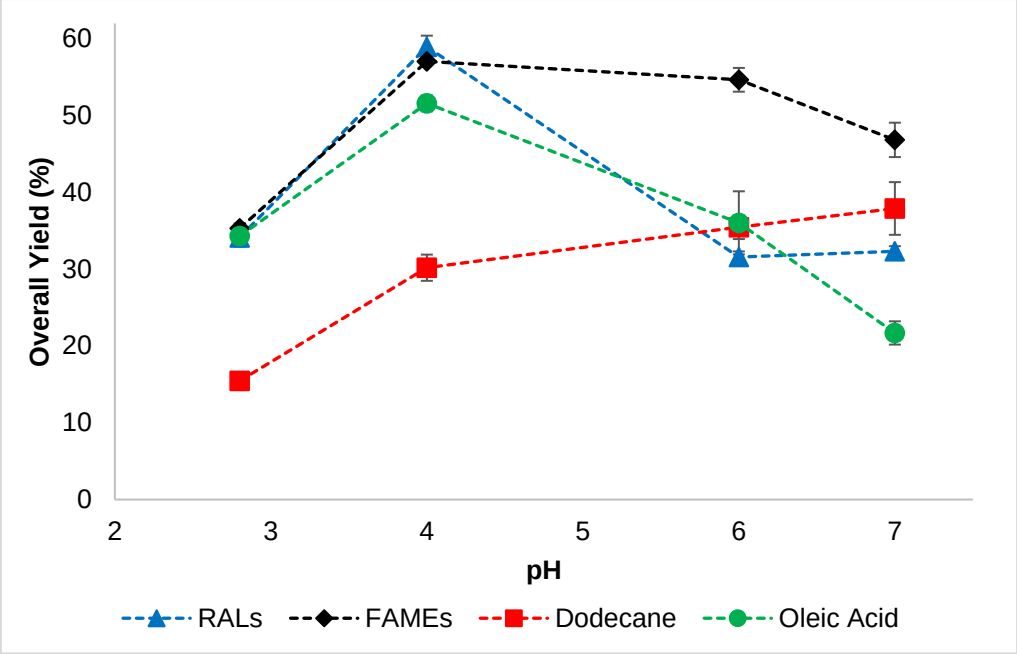

Figure 4.14: Yield at different pH for collectors dosed at 2.8 kg/t from flotation Waterberg discards from Site 1. MIBC dosed at 0.28 kg/t. Error bars are standard errors of triplicate repeats.

When comparing the four collectors at different pH levels, shown in Table 4.7, it was observed that, at pH 2,7, there was no significant difference in performance between FAMEs, RALs and oleic acid. At pH 4.0, there was no significant difference in the product yield obtained using FAMEs or RALs. At pH 6.0, FAMEs outperformed the other three reagents, which showed no significant difference in yield between each other. While FAME performance remained best at pH 7.0, dodecane performed better than at any other pH and the performance of oleic acid and RALs was significantly reduced. The highest yield was obtained at pH 4.0 for FAMEs, RALs and oleic acid (57.06%, 58.95% and 51.59%, respectively) and decreased significantly at higher pH values. The improved yield at pH 4.0 can be attributed to two factors, with both likely to contribute effects.

The first reason is that at this pH, the surface charge coincides with the maximum zeta potential for the coal particles. At this zeta potential value, the coal surfaces are maximally positively charged and hence attach most easily to negatively charged polar heads of the collectors. This creates a more hydrophobic collector-coal particle complex which attaches easily to rising air bubbles. As the pH increases beyond pH 4.0, deprotonation results in the particle charge decreasing towards zero until a pH where the coal particles have no charge. As the positive charge decreases, the coal particles become more hydrophobic and hence do not have as many points of attachment for polar collectors (FAMEs, RALs and oleic acid). Therefore, the yield decreases with increase in pH as more hydrophobic coal particles are produced.

A second reason for decrease in yield with increase in pH after pH 4.0 could be due to the changes in polarity of the collectors themselves. Considering oleic acid, for example, studies have shown that oleic acid in water forms two phases, one with oil or fatty acid crystals (sodium oleate crystals) and the other an aqueous phase at pH below 7.0 (Cistola et al., 1987; Shu et al., 2013). The undissociated acid is dominant at very low pH values. This undissociated acid easily interacts with coal particles, first by hydrophobic interactions of the fatty acid hydrocarbon tail and then by polar interaction of the polar head and charged surfaces on coal surface. As the pH increases, the surface charge of oleic acid increases (becomes more negative) as the carboxylate ion becomes more dominant (Shu et al., 2013). These carboxylate ions are in coexistence with acid soaps in the aqueous phase and fatty acid in the oil phase. Drzymala (1987) pointed out that these carboxylate ions complex with metal ions in solutions. They postulate that the complexing of carboxylate ions with metal ions form stronger bonds than the polar interactions between charged groups on coal surfaces and the carboxylate ion. Therefore, the number

of molecules available for surface modification of the coal decreases as the pH increases and complete dissociation results.

Table 4.7: In each column, Fisher Pairwise Comparison of overall yield is given across four different collectors dosed at 2.8 kg/t. MIBC frother was dosed at 0.28 kg/t in all experiments. The analysis was done for the 4 pH conditions that were tested. Collectors that do not share the same letter have significantly different performance.

Collector type	**pH**			
	2.7	**4.0**	**6.0**	**7.0**
FAMEs	A	C	F	H
RALs	A	C	G	I
Oleic acid	A	D	G	J
Dodecane	B	E	G	H

Even though RALs and FAMEs do not ionise as oleic acid does, the same line of thought can be extended to their behaviour in aqueous solutions at different pH. Increasing pH results in the formation of micelles (Cistola et al., 1987). This is a phenomenon where the lipids distribute themselves in the aqueous phase in tiny droplets, forming an emulsion. However, increasing pH caused a less significant decrease in performance for FAMEs compared to RALs, indicating that pH does not greatly impact the polarity of FAMEs as it does RALs. This is because RALs have more hydrophobic tails per molecule compared to FAMEs. Thus, these tails have stronger hydrophobic interactions and result in the formation of micelles faster than FAMEs at the same pH.

4.4.1.2.2 Recoveries

Figure 4.15 shows that the same trend is observed for combustible recoveries as a function of pH as for yield. The same reasoning is applied to ash recovery (Figure 4.16). It was observed that there was a clear difference in performance between the four reagents at pH 7.0, which is the operating pH for the 2nd stage of the two-stage flotation desulphurisation process. At this pH, FAMEs had the highest combustibles recovery, followed by dodecane, then RALs and lastly oleic acid with the least recovery.

It is observed, however, that the best combustibles recovery is obtained at pH 4 for the two biocollectors and oleic acid. At this pH, the two biocollectors perform significantly better than the oleic acid control. Figure 4.15 shows that FAMEs have a wider range of operation for pH (between 4.0 to 6.0) where the recovery is relatively the same, while RAL and oleic acid performance falls off rapidly when the pH is increased above 4.0.

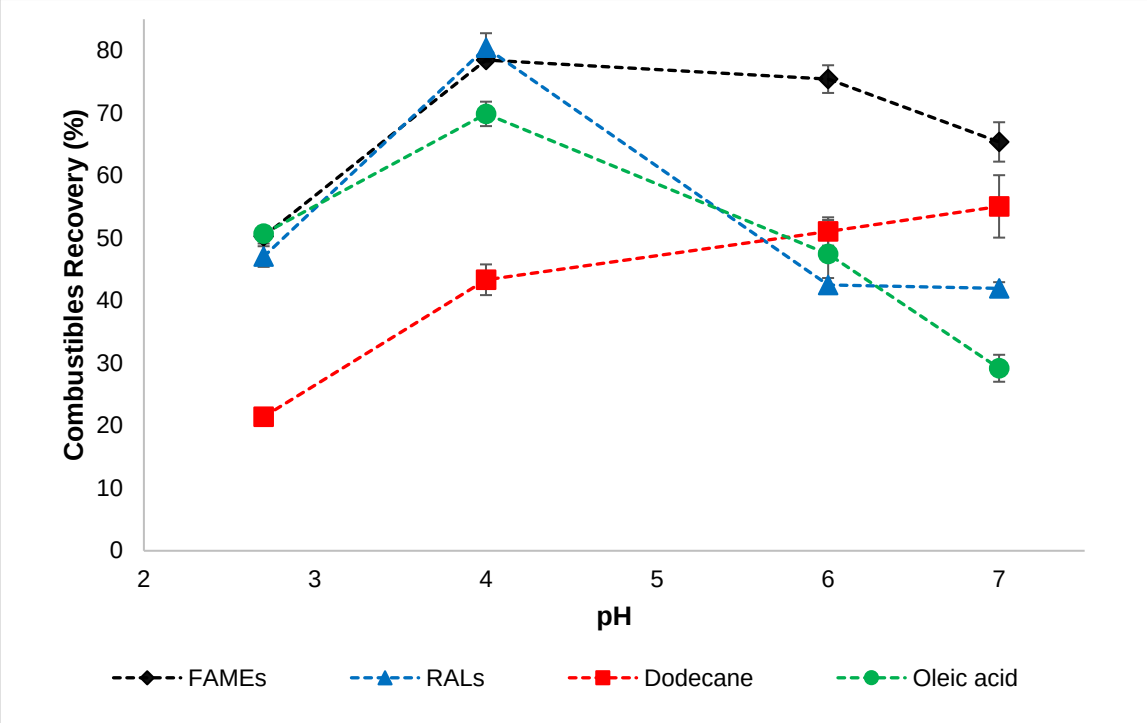

Figure 4.15: Combustibles recovery as a function of pH for different collectors. Collector dosage was maintained at 2.8 kg/t for all experiments and 0.28 kg/t MIBC was used for froth stabilisation. Error bars are standard errors of triplicate repeats.

Ash recovery, presented in Figure 4.16, showed a similar trend to overall yield and combustibles recovery as discussed earlier, where there was significant difference in performance between RALs, FAMEs and oleic acid at pH 7.0, with FAMEs having the highest ash recovery, followed by RALs and oleic acid with the least ash recovery. Superimposing the overall yield and combustibles recovery results onto ash recovery suggest that the differences in ash recovery are, largely, not due to reagent selectivity but due to low degree of liberation between combustible and ash material. Some effect of selectivity is seen between RALs and FAMEs at pH 4.0, where the former was less selective than the latter, i.e. RALs recovered significantly more ash than FAMEs while there was no significant difference between in terms of overall yield and combustibles recovery as shown in Figure 4.14 and Figure 4.15, respectively.

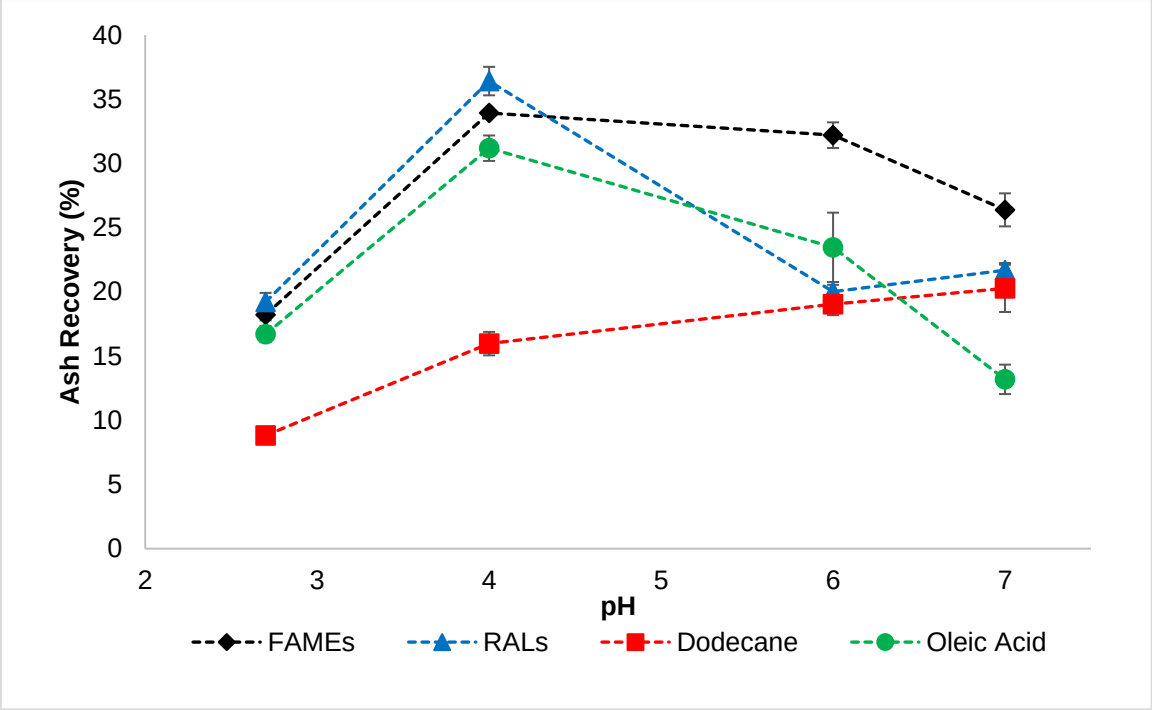

Figure 4.16: Ash recovery as a function of pH on Site 1 discards flotation. A dosage of 2.8 kg/t was used for all collectors and pH. MIBC frother dosed at and 0.28 kg/t. Error bars are standard errors of triplicate repeats.

4.4.1.2.3 Product quality

Figure 4.17 shows how the quality of the product recovered varied with pH. FAMEs performed unexpectedly. The best quality product was obtained at pH 2.7 (75.92%) followed by pH 7.0, followed by pH 4.0 and 6.0. For the latter two, the combustibles content was not significantly different at a 95% confidence interval (71.55 ± 0.14%). For RALs, the product quality decreased from pH 2.7 through pH 4.0 and 6.0 to a lowest at pH 7.0 where the product had the highest ash content.

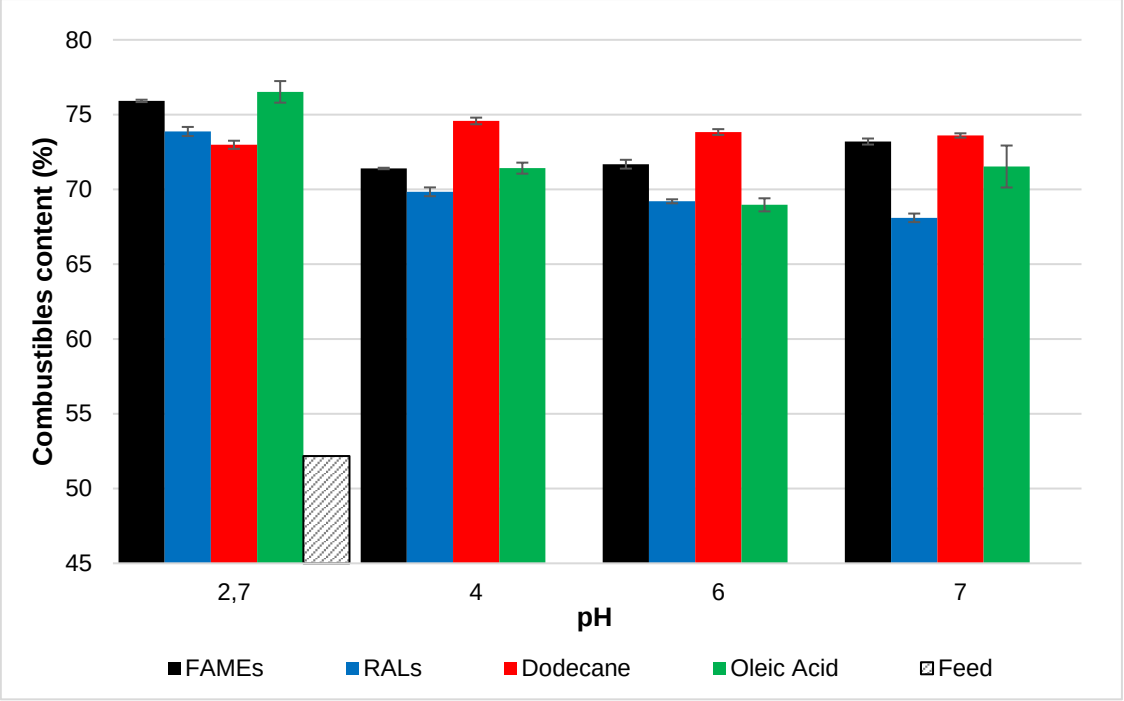

Figure 4.17: Combustible material in product at different flotation pH. Collector and MIBC dosed at 2.8 and 0.28 kg/t, respectively. Error bars are standard errors of triplicate repeats.

Comparing collector performance at each pH level (Table 4.8) showed that at pH 2.7 FAMEs and dodecane resulted in a product with significantly the same ash content, and this was lower than that obtained using RALs or oleic acid, both of which were significantly the same as well. At pH 4.0, 6.0 and 7.0, dodecane resulted in a product higher in combustibles content compared to RALs and FAMEs. FAMEs and oleic acid achieved the same product quality, in terms of combustibles content, at pH 4.0 and 7.0. RALs and oleic acid achieved the same combustibles content at pH 6.0.

Table 4.8: In each column, a Fisher Pairwise Comparison of product ash content is given across four different collectors dosed at 2.8 kg/t. MIBC frother dosed at 0.28 kg/t in all experiments. The analysis was done for the 4 pH conditions tested. Collectors that do not share the same letter have significantly different performance.

Collector	**pH**			
	2.7	**4.0**	**6.0**	**7.0**
FAMEs	A	C	F	I
RALs	B	D	G	J
Oleic acid	A	C	G	I
Dodecane	B	E	H	I

Figure 4.18 show the variation of sulphur content of the product and Table 4.9 shows the comparison of collector performance at different pH values. It was observed that increasing pH for RALs resulted in an increase in the product sulphur. It was observed that each of FAMEs and RALs had the same performance, with statistical significance at the 95% confidence level, across pH 2.7, and 6.0. At pH 7.0, FAMEs performed better than RALs (2.48% sulphur and 2.98% sulphur, respectively), and this is the best condition for FAMEs. The best product using RALs was achieved at the natural pH of the sample (pH 2.7). Overall, the two bioflotation reagents performed similarly to oleic acid at all pH conditions tested except at pH 7.0. The dodecane control results confirmed that, for oily hydrocarbon collectors, selectivity increases as pH increases, as highlighted by (Liu et al., 1993).

The best pH that resulted in a product with the least sulphur content was pH 2.7 for RALs and pH 7.0 for FAMEs,

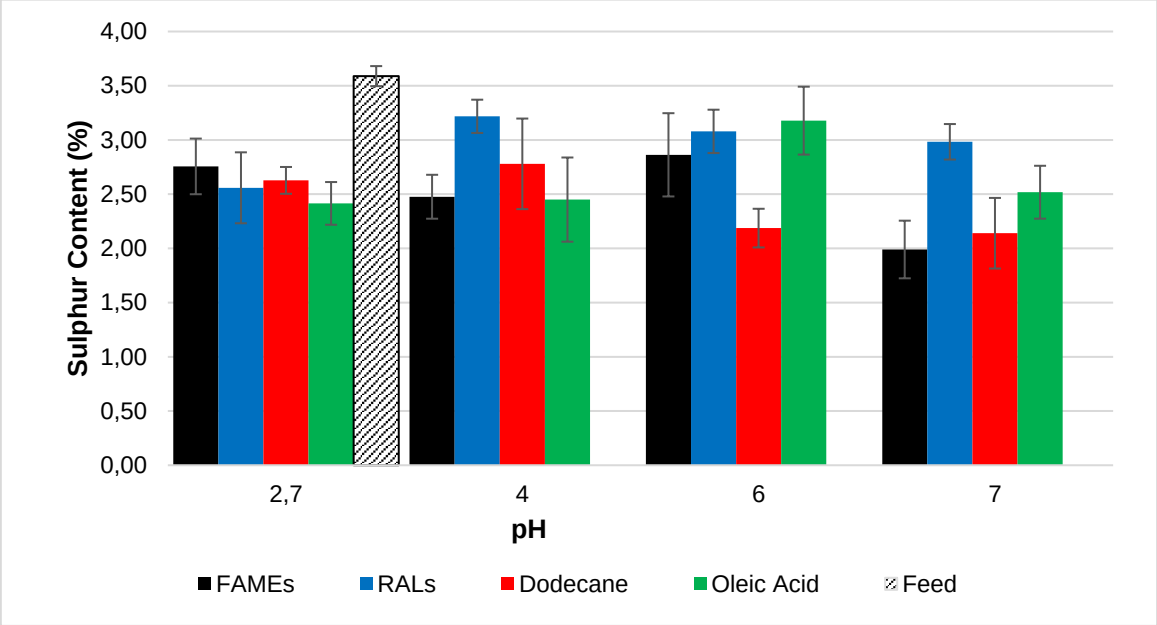

Figure 4.18: Effect of pH on product sulphur content for Site 1 discards flotation. Collector dosage at 2.8 kg/t and MIBC at 0.28 kg/t. Error bars are standard errors of triplicate repeats.

Table 4.9: In each column, a Fisher Pairwise Comparison of product sulphur content is given across four different collectors dosed at 2.8 kg/t. MIBC frother dosed at 0.28 kg/t in all experiments. The analysis was done for the four different pH conditions tested. Collectors that do not share the same letter have significantly different performance. In a particular column, a collector with a letter higher up in the alphabet resulted in the lowest sulphur content.

Collector	**pH**			
	2.7	**4**	**6**	**7**
FAMEs	A	C	E	I
RALs	A B	D	E	G
Oleic acid	B	D	E	H
Dodecane	A B	C D	F	H I

4.4.1.2.4 Summary

Table 4.10 summarises the results from the study of the effect of pH on flotation of Site 1 discards across the four collectors. The best pH for FAMEs, on the basis of the least sulphur content in the recovered coal, is pH 7.0 and for RALs is pH 2.7. Under these conditions, FAMEs will give a product yield of 46.83% and an ash and sulphur content of 26.80% ash and 1.99%, respectively and RALs product yield of 34.13% with an ash and sulphur content of 26.13% and 2.56%, respectively. In comparison at pH 4 both RALs and FAMEs gave an overall coal yield of about 58% which was coupled with high ash and sulphur recoveries, resulting in about 29% ash and 2.5% sulphur for FAMEs and about 30% ash and 3.2% sulphur for RALs.

Table 4.10: Summary of results for pH tests on Site 1 discards. F = FAMEs, R = RALs, D = Dodecane and O = Oleic acid. Collectors and MIBC dosed at 2.8 kg/t 0.28 kg/t, respectively.

pH	Yield (%)				Ash Content (%)				Sulphur Content (%)			
	F	R	D	O	F	R	D	O	F	R	D	O
2.7	35.31	34.13	15.45	34.31	24.08	26.13	27.02	23.48	2.76	2.56	2.63	2.41
4	57.06	58.95	30.19	51.59	28.60	30.16	25.42	28.58	2.48	3.22	2.78	2.45
6	54.66	31.58	35.46	36.03	28.31	30.80	26.17	31.03	2.86	3.08	2.19	3.18
7	46.83	32.33	37.90	21.69	26.80	31.90	26.39	28.47	1.99	2.98	2.14	2.52

4.4.1.3 Frothability of FAMEs and RALs

Additional tests were carried out to evaluate whether biocollectors can induce frothability to the coal suspension during flotation. Visual observations and flotation experiments were used to test this hypothesis.

Figure 4.19 shows that the froth produced by FAMEs in the absence of a frother is not evenly distributed. Over 15 s of this visual test, it was observed that froth formation was poor in the first few seconds after turning on the air. Another observation was that bigger froth bubbles were produced, and they persisted for longer than those produced with RALs. Figure 4.20 shows the froth produced by RALs over a time span of 15 s. RALs resulted in smaller froth bubbles which were evenly distributed. The froth was quickly formed in the test using RALs. These two visual experiments supported the hypothesis that FAMEs and RALs have the potential to induce frothability without addition of MIBC to the flotation system.

Figure 4.19: Froth produced in float cell using only FAMEs, without MIBC frother. (A) 2 seconds, (B) 7 seconds and (C) 15 seconds after turning air on

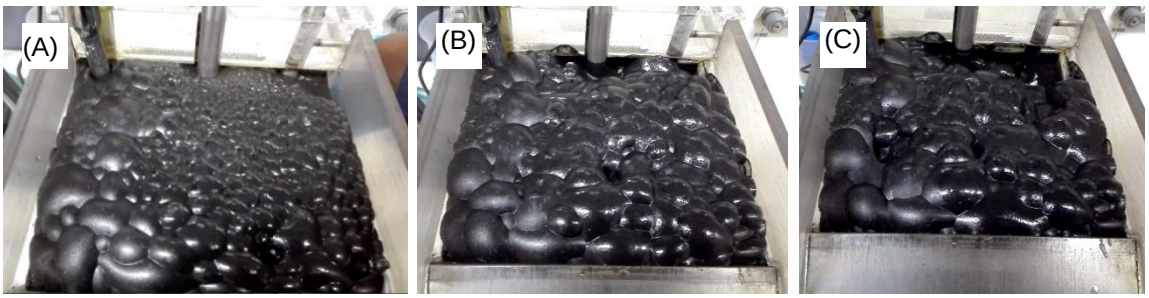

Figure 4.20: Froth produced in a float cell using only RAL, without MIBC frother. (A) 2 seconds, (B) 7 seconds and (C) 15 seconds after turning air on

Figure 4.21 shows results from flotation experiments with and without MIBC. The results show that adding 0.28 kg/t of MIBC increased the overall yield with FAMEs as collector from about 30% to around 35%. For RALs, adding MIBC resulted in a yield increase of 18.70% from 15.43%. The persistent froth produced by FAMEs in the absence of a frother, as shown in Figure 4.19, worked to its advantage as adding MIBC did not result in a big increase in yield as in the case with RALs. The evenly distributed froth bubbles produced by RALs did not persist for long enough to keep the collected coal in the froth. For this reason, adding MIBC resulted in a large increase in yield as it stabilised the froth formed. These results show that the amount of MIBC used in the flotation process can be reduced from the current 0.28 kg/t.

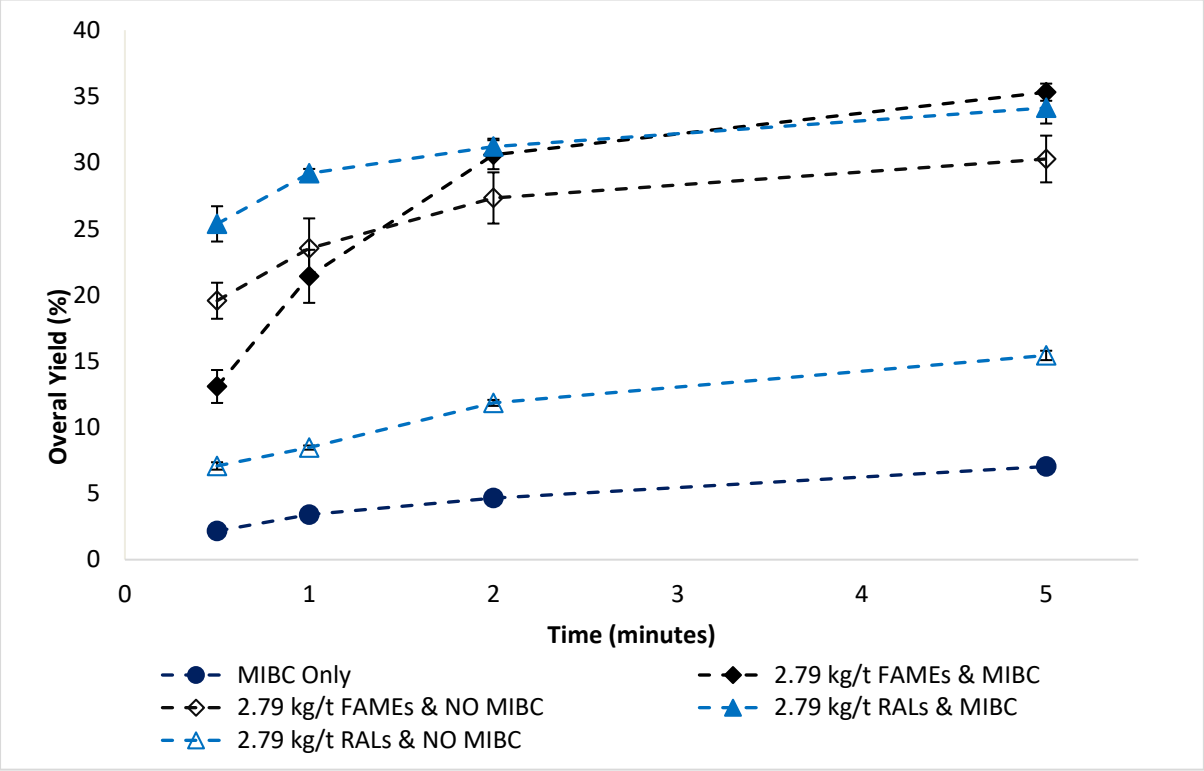

Figure 4.21: Effect of adding MIBC to FAMEs and RALs flotation tests on Waterberg discards from Site 1. MIBC dosage at 0.28 kg/t. Error bars are standard errors of triplicate repeats.

Ash and sulphur analysis of the products from the experiments with and without MIBC showed that adding MIBC resulted in improved selectivity using RALs. This in agreement with the comment made by Han (1983) which says that a reagent that has both collector and frother properties may reduce selective separation of the mineral from the gangue material. Table 4.11 summarises the product quality results.

Table 4.11: Product quality for flotation experiments with and without MIBC at FAMEs and RALs dosage of 2.8 kg/t.

		FAMEs	RALs
Ash	No MIBC	24.70	27.97
	With MIBC	24.08	26.13
Sulphur	No MIBC	2.53	2.96
	With MIBC	2.76	2.56

4.4.2 Witbank waste tailings from Site 2

The same procedure applied to discards from Site 1 was applied to Site 2 waste tailings in order to assess whether the performance of FAMEs and RALs was coal-specific. As shown by the positive and negative control experiments, depicted in Figure 4.22, this sample was easy to float, compared to Site 1 discards. The negative control test achieved a yield of 31.78% compared to 7.04% for Site 1 discards. With 2.8 kg/t oleic acid, a maximum yield of 86.19% was achieved, compared to 34.31% yield for discards from Site 1. Fine coal from Site 2 appeared more naturally floatable due to its low ash and sulphur content (Table 4.2 in Section 4.3.2).

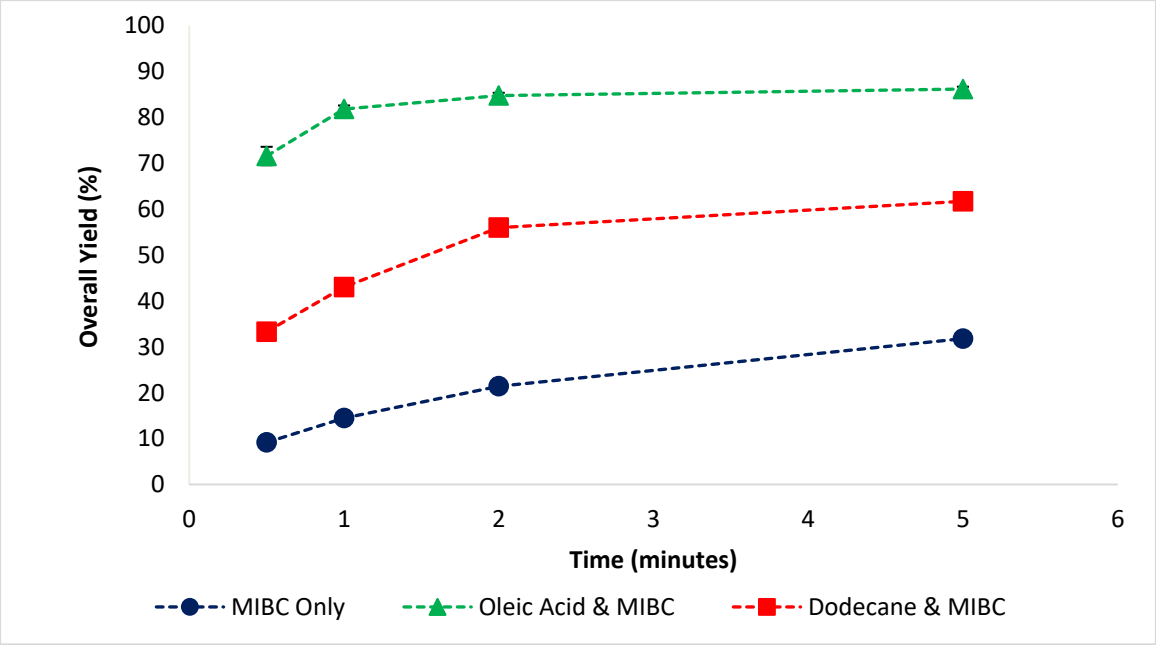

Figure 4.22: Positive and negative control experiments for Site 2 waste tailings using collector and MIBC at doses of 2.8 and 0.28 kg/t, respectively. Error bars are standard errors of triplicate repeats.

4.4.2.1 Effect of biocollector dosage on coal flotation

The dosages of RALs and FAMEs were varied from 1.2 kg/t to 3.7 kg/t and the data collected was analysed in terms of overall yield, recoveries (combustibles, ash and sulphur) and product quality.

4.4.2.1.1 Yield

Figure 4.23 shows the overall yield obtained at different collector dosages using four different collectors. The lowest yield was obtained at a biocollector dosage of 1.2 kg/t. Statistical analysis of FAMEs data using one-way ANOVA at 95% confidence interval, summarised in Table 4.12, showed that there was

no significant difference in yield obtained between collector dosages of 2.8, 3.2 and 3.7. This means that it is not economic to increase the FAMEs dosage beyond 2.8 kg/t. The best FAMEs dosage is therefore 2.8 kg/t of coal waste. For RALs, there was no significant difference in yield obtained at collector dosages of 2, 2.8 and 3.2 kg/t, resulting in a best RALs dosage of 2.0 kg/t coal waste.

At 2.8 kg/t collector dosage, dodecane had the lowest yield (61.72%) followed by oleic acid (86.19%). RALs and FAMEs showed the highest yield of about 96.00%. It is also interesting to note that a lower dosage of 1.2 kg/t of RALs or FAMEs was sufficient to achieve the same yield as the oleic acid control at 2.8 kg/t, showing that RALs and FAMEs are better collectors than oleic acid for this particular coal waste. This is different from the case of Site 1 discards where all three reagents required the same dosage to achieve approximately the same yield (Figure 4.5). This proves that the performance of FAMEs and RALs is coal type specific.

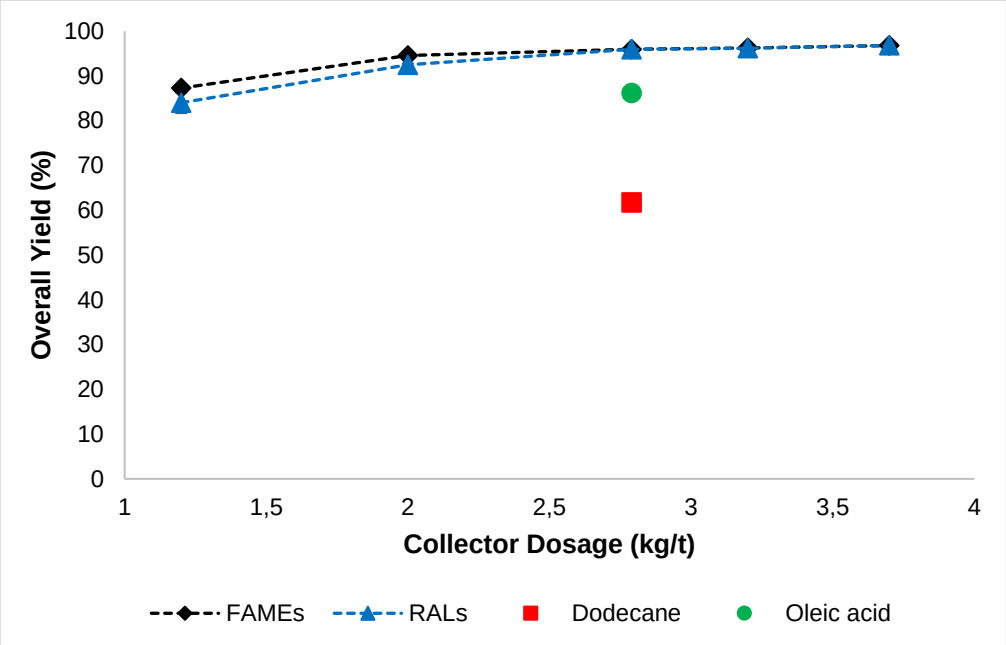

Figure 4.23: Effect of biocollector dosage on final yield for Site 2 waste tailings. MIBC frother dosed at 0.28 kg/t. Error bars are standard errors of triplicate repeats.

Table 4.12: In each column, a Fisher Pairwise Comparison of overall yield is given across different biocollector dosages of FAMEs and RALs. MIBC frother dosed at 0.28 kg/t in all experiments. Collector dosages, under the same collector column, that do not share the same letter have significantly different means. In a particular column, a collector dosage with a letter higher up in the alphabet resulted in the highest yield.

Dosage (kg/t)	Collector	
	FAMEs	RALs
1.2	A	D
2.0	B	E
2.8	C	E F
3.2	C	E F
3.7	C	F

4.4.2.1.2 Recoveries

Figure 4.24 shows the recovery of combustible material at different collector concentrations. It was observed that the best dosage for both FAMEs and RALs with respect to combustibles recovery was 2.0 kg/t with 97.50% of the combustibles in the feed being recovered. Above this concentration, no significant increase in combustibles material recovery with increase in dosage was observed. This is supported by the statistical analysis data summarised in Table 4.13.

The oleic acid and dodecane controls resulted in lower combustible recoveries at a dosage of 2.8 kg/t. This differs from the results for Site 1 discards from the Waterberg area, attributable to differences in coal types. The Site 1 fine coal waste was comprised of high-ash high-sulphur coal waste while the Site 2 tailings comprised low-ash and low-sulphur fine coal waste.

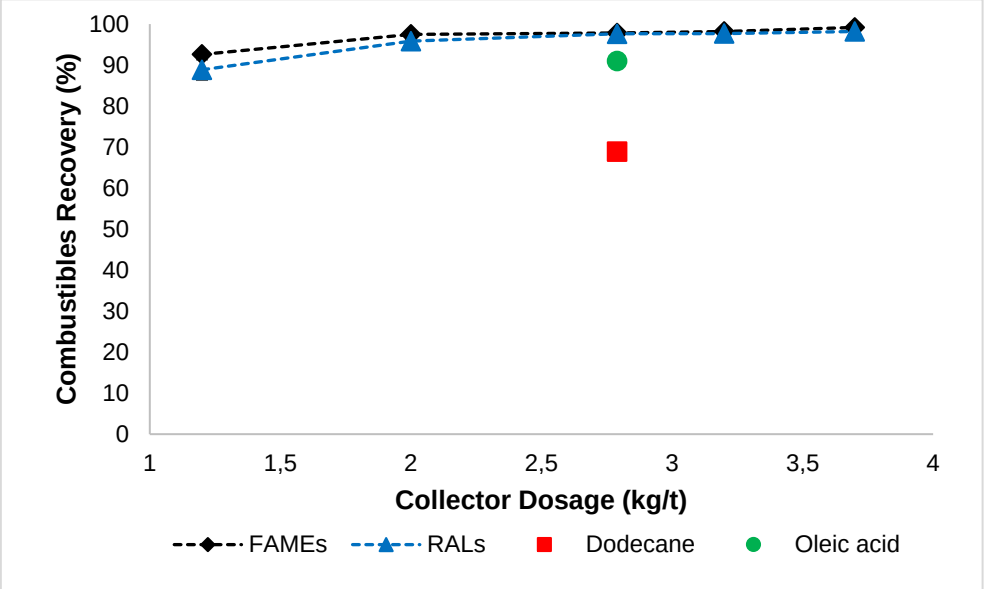

Figure 4.24: Combustibles recovery from Site 2 waste tailings flotation at different collector dosages. MIBC dosed at 0.28 kg/t. Error bars are standard errors of triplicate repeats.

Table 4.13: In each column, Fisher Pairwise Comparison of ash recovery is given across different biocollector dosages using FAMEs and RALs. MIBC frother dosed at 0.28 kg/t in all experiments. Collector dosages, under each collector type, that do not share the same letter have significantly different means. In a particular column, a collector dosage with a letter higher up in the alphabet resulted in the highest ash recovery.

Dosage (kg/t)	**Collector**	
	FAMEs	**RALs**
1.2	A	C
2.0	B	D
2.8	B	D E
3.2	B	E
3.7	B	E

Figure 4.25 showed that higher collector dosages, from 2.8 kg/t to 3.7 kg/t resulted in more than 90% of the ash in the feed being recovered. This is not desirable as the goal of the flotation process is to

separate combustible material from ash. Thus, the best biocollector dosage is 2.0 kg/t at which high combustibles recovery and lower ash recovery were achieved.

High ash recoveries could be attributed to either mechanical entrainment of hydrophilic particles or due to the non-specific nature of the bioflotation reagents as well as collector attachment to ash material or to a lower degree of liberation between coal and gangue material. Owing to the increase in ash recovery without concomitant increase in combustible recovery, increasing ash recovery is not expected to be associated with liberation.

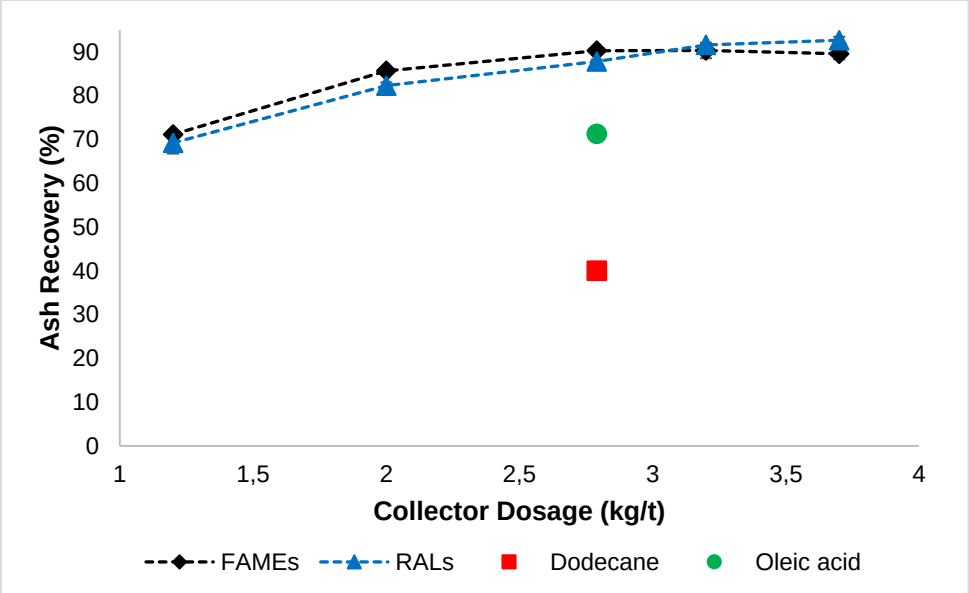

Figure 4.25: Ash recovery at different biocollector dosages for Site 2 waste tailings flotation. MIBC dosed at 0.28 kg/t. Error bars are standard errors of triplicate repeats.

Figure 4.26 shows that the FEI for the flotation of Site 2 discards decreased with increase in biocollector dosage. This is the opposite of what was observed in the flotation of Waterberg discards from Site 1 where the FEI increased with increasing biocollector dosage. It is therefore more efficient to select a biocollector dosage of 1.2kg/t giving the best coal quality or 2.0 kg/ton, giving a higher yield with little compromise on quality. Biocollector dosages above 2.0 kg/ton have a negative impact for Site 2 fine coal waste.

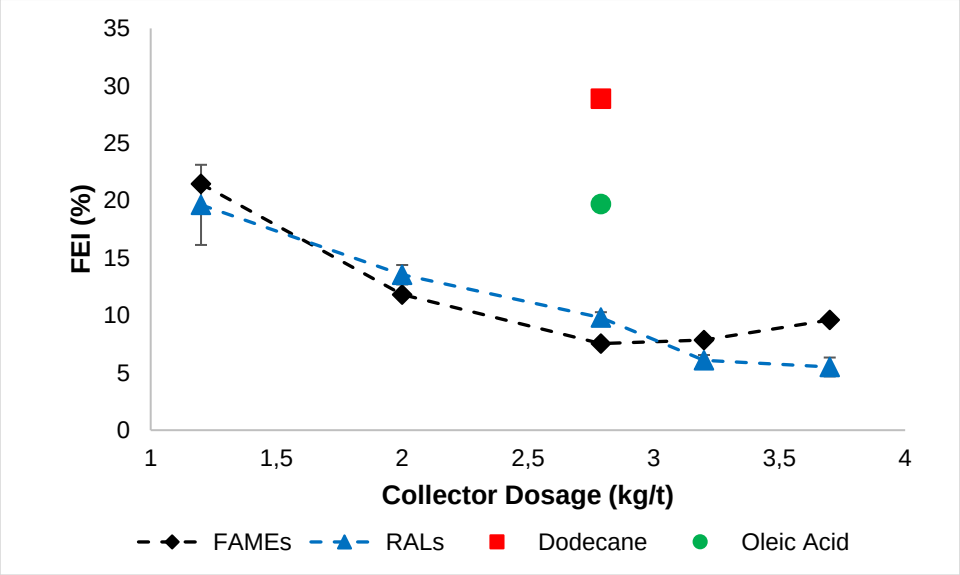

Figure 4.26: Flotation efficiency index (FEI) at different biocollector dosages for Site 2 waste tailings flotation. MIBC dosed at 0.28 kg/t. Error bars are standard errors of triplicate repeats.

Figure 4.27 shows sulphur recovery varied with collector concentration. Again, a low biocollector dosage (1.2 kg/t) resulted in the lowest sulphur recovery. The only increase in sulphur recovery that was statistically significant was between biocollector dosage of 1.2 and 2.0 kg/t. At 2.0 kg/t through 3.7 kg/t there was no significant increase. There was no significant difference in performance between FAMEs and RALs. As with combustibles and ash recovery, a lower dosage of 1.2 kg/t for both RALs and FAMEs achieved the same sulphur recovery as a higher dosage of 2.8 kg/t for oleic acid.

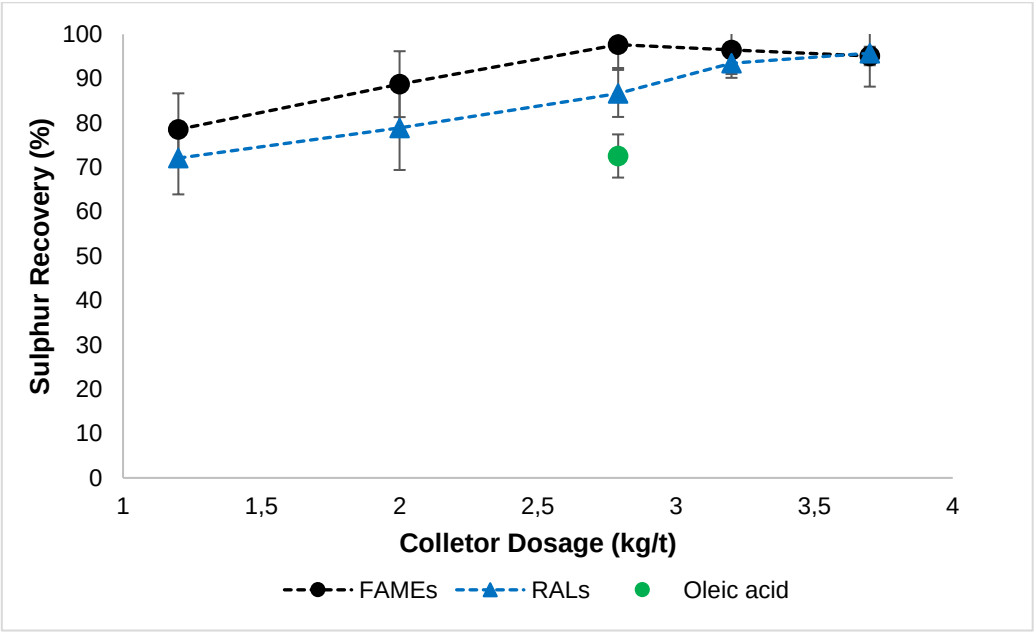

Figure 4.27: Sulphur recovery at different biocollector dosages for Site 2 waste tailings. MIBC frother dosage at 0.28 kg/t. Error bars are standard errors of triplicate repeats.

Table 4.14: In each column, a Fisher Pairwise Comparison of sulphur recovery is given across different biocollector dosages of FAMEs and RALs. MIBC frother dosed at 0.28 kg/t in all experiments. Collector

dosages that do not share the same letter have significantly different means. In a particular column, a collector dosage with a letter higher up in the alphabet resulted in the highest sulphur recovery.

Dosage (kg/t)	Collector	
	FAMEs	RALs
1.2	A	D
2.0	B	D E
2.8	C	E F
3.2	C	F
3.7	C	F

4.4.2.1.3 Product quality

Figure 4.28 and Figure 4.29 show the combustibles content of the concentrate recovered from the flotation process at different FAMEs and RALs dosages, respectively. It was observed that the two bioflotation reagents achieved a similar product quality at the same dosages, with a dosage of 1.2 kg/t achieving the cleanest product. Statistical analysis, results, summarised in Table 4.15, showed that increasing the biocollector dosage of either FAMEs or RALs beyond 2.8 kg/t had no impact on the combustible recovery, yield or ash content of the recovered product. This means that selectivity became independent of collector concentration in the flotation system.

Table 4.15: In each column, a Fisher Pairwise Comparison of product ash content is given across different biocollector dosages for FAMEs and RALs. MIBC frother dosed at 0.28 kg/t in all experiments. Collector dosages that do not share the same letter have significantly different means. In a particular column, a collector dosage with a letter higher up in the alphabet resulted in the highest ash content in the product.

Dosage (kg/t)	Collector	
	FAMEs	RALs
1.2	A	D
2.0	B	E
2.8	C	E F
3.2	B C	F
3.7	B C	F

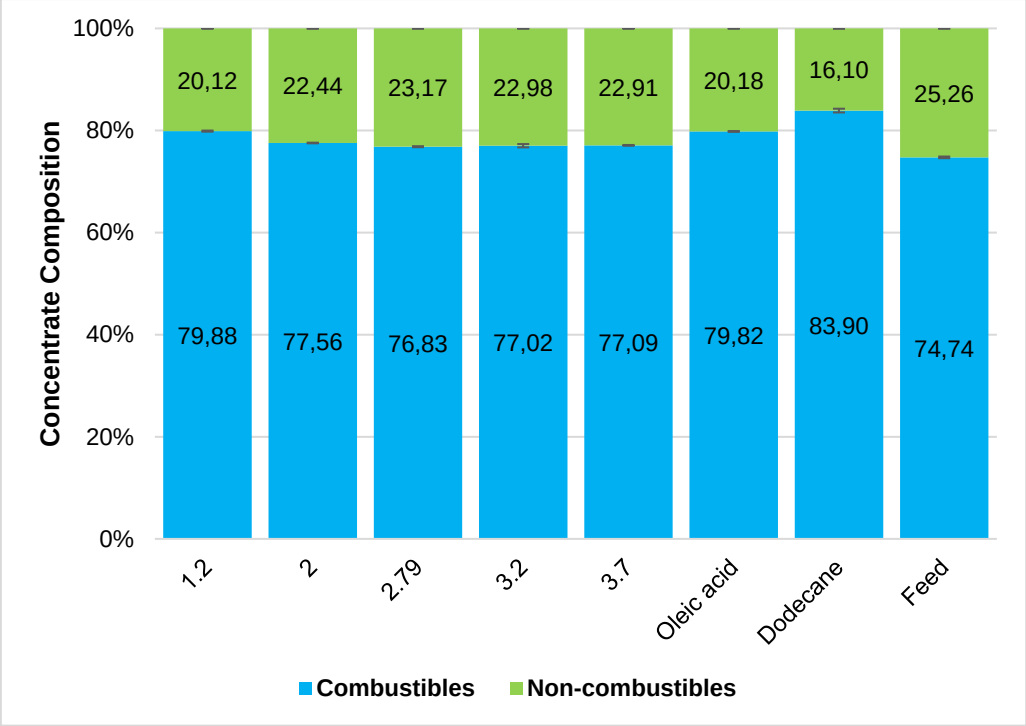

Figure 4.28: Combustibles and ash (non-combustibles) composition for FAMEs test at different biocollector dosages on Site 2 waste tailings flotation. 0.28 kg/t frother used. Error bars are standard errors of triplicate repeats.

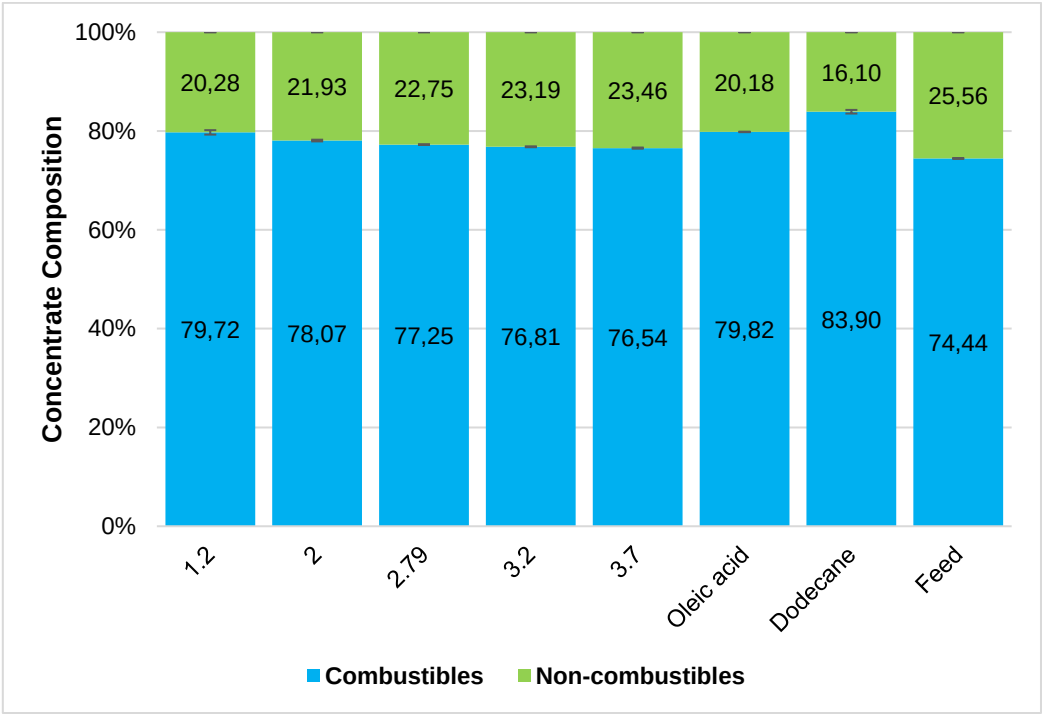

Figure 4.29: Combustibles and ash (non-combustibles) composition for RALs test at different biocollector dosages on Site 2 waste tailings flotation. MIBC frother at 0.28 kg/t. Error bars are standard errors of triplicate repeats.

Figure 4.30 shows that both reagents were able to reduce the feed sulphur content by a statistically significant degree. With FAMEs, the lowest and best sulphur content in the product was achieved at a

collector dosage of 1.2 kg/t. There was no significant difference between the sulphur in the product obtained using 2.0 kg/t and 2.8 kg/t of FAMEs, and similarly between 3.2 and 3.7 kg/t (Table 4.16). It was different case for RALs, where Fisher Pairwise Comparisons showed that there was no significant difference in the sulphur content of the product recovered using RALs at all biocollector dosages. It was also observed that there was no significant performance difference between FAMEs and RALs at all the collector dosages tested as well as between the biocollectors and the oleic acid control which was dosed at 2.8 kg/t.

When harmonised with the flotation efficiency index in Figure 4.26 and product ash content in Figure 4.28 and Figure 4.29, for FAMEs and RALs, respectively, the data shows that selectivity of both bioflotation reagents decreases with increase in collector dosage for this particular type of coal, making 1.2 kg/t the best biocollector dosage to provide a high quality coal product.

Table 4.16: In each column, a Fisher Pairwise Comparison of product sulphur content is given across different biocollector dosages for FAMEs and RALs. MIBC frother dosed at 0.28 kg/t in all experiments. Collector dosages that do not share the same letter have significantly different means. In a particular column, a collector dosage with a letter higher up in the alphabet resulted in the highest sulphur content in the product.

Dosage (kg/t)	**Collector**	
	FAMEs	**RALs**
1.2	A	D
2.0	B	D
2.8	B	D
3.2	C	D
3.7	C	D

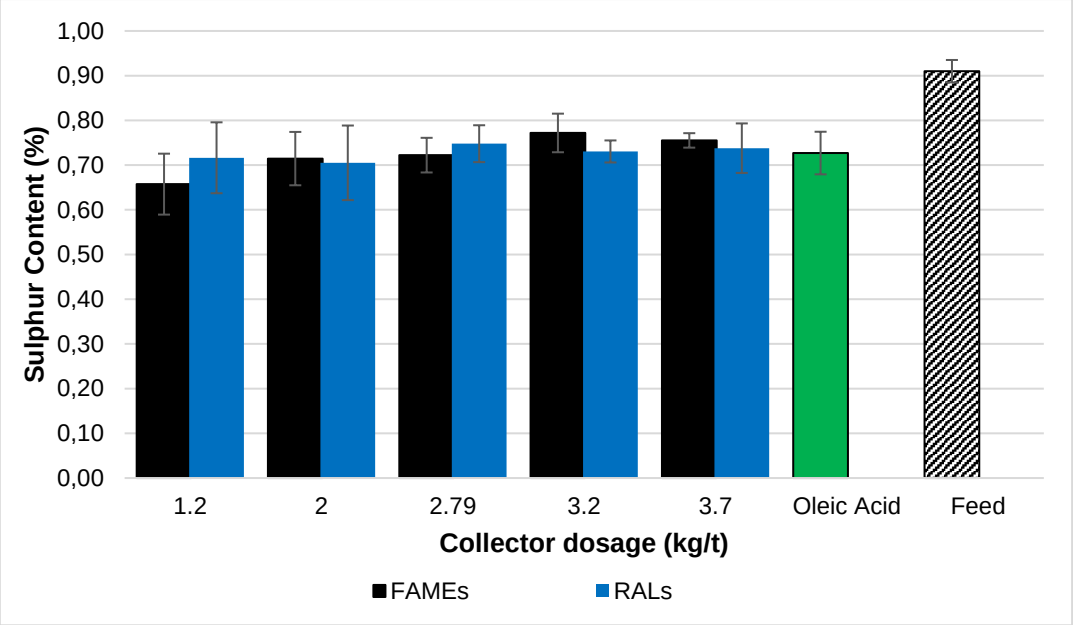

Figure 4.30: Sulphur content of product from Site 2 waste tailings flotation using FAMEs and RALs. MIBC dosage at 0.28 kg/t in all experiments. Error bars are standard errors of triplicate repeats.

4.4.2.1.4 Summary of results

Table 4.17 summarises the results obtained from the flotation experiments using FAMEs and RALs as potential replacements for oleic acid. For this particular fine coal waste sample, less than half the dosage of FAMEs or RALs was required to achieve the same performance as oleic acid. It was also observed that selectivity decreases with increase in reagent concentration.

Table 4.17: Reagent performance at a collector dosage of 2.8 kg/t on Site 2 waste tailings flotation. MIBC dosed at 0.28 kg/t.

Collector	Yield (%)	Recovery (%)	FEI (%)	Ash Content (%)		Sulphur Content (%)	
				Product	Tails	Product	Tails
FAMEs	95.97	97.83	7.54	23.17	72.34	0.72	1.044
RALs	95.20	97.62	9.81	22.75	61.86	0.75	1.15
Dodecane	61.72	68.89	28.87	16.10	37.68		
Oleic acid	86.19	91.00	19.74	20.18	51.75	0.74	1.36

5 Algal Lipids Cost Review

5.1 Introduction

This chapter presents a desktop review of the cost of producing fatty acid methyl esters (FAMEs) and raw algal lipids (RALs). Since there is no literature exclusively covering the production of RALs and FAMEs for the purposes of coal flotation, the analysis presented here is based on biodiesel production from microalgae due to the similarity in process routes and chemical composition of final products. RALs are an intermediate product in biodiesel production, while FAMEs are constituents of biodiesel. Therefore, in this text RALs are synonymous with raw algal oil and FAMEs with biodiesel. Since the effect of purity of RALs and FAMEs on coal flotation was not tested, the cost of both impure and pure products will be presented.

5.2 Literature review

5.2.1 Technical pathways for algae-to-energy

Figure 5.1 shows the pathways that can be adopted in producing biodiesel. This is the framework that has been used in many studies to evaluate the economic viability of biodiesel production from microalgae (Silva et al., 2013; Davis et al., 2013; Zhang et al., 2015). The pathways typically include five steps: (1) Cultivation, (2) Dewatering, (3) Lipid extraction, (4) Lipid upgrading, and (5) Anaerobic digestion (AD) and energy production. These are discussed in detail in Section 5.2.2.

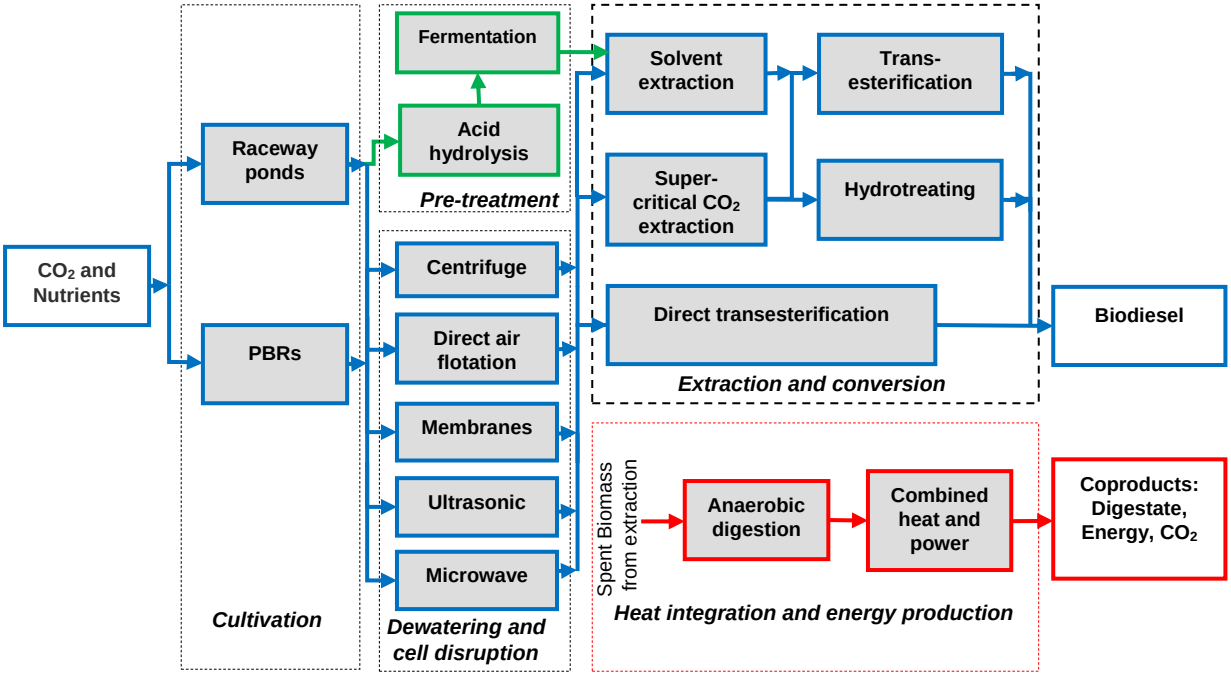

Figure 5.1: Possible routes for oil production from microalgae. Modified from (Silva et al., 2013)

These pathways were designed to maximise resource usage, especially energy and carbon. Energy balances carried out on fuel production from algae biomass showed that the process becomes viable by incorporating a steam generating plant that uses the methane from the anaerobic digestion of spent biomass after lipid extraction (Milledge and Heaven, 2017). Davis et al. (2014) included in their process design two more unit processes (pre-treatment and fermentation) before the lipid extraction process to improve FAMEs extractability. It was reported that including these two steps prior to lipid extraction significantly improved lipid extractability by up to 93%. Another added advantage highlighted was the elimination of the energy intensive cell disruption methods prior to lipid extraction. Depending on the

algal species used, chemical pre-treatment may disrupt the algal cell walls, resulting in high recovery of soluble sugars and enabling effective lipid extraction.

5.2.2 Process design

5.2.2.1 Cultivation

Autotrophic algae production is preferred over heterotrophic production conditions since the latter is resource intensive in terms of reactor design and raw materials needed for the process (Lundquist et al., 2010). Autotrophic biomass production uses CO_2 and light to meet energy demands of the growing cells. Heterotrophic algae use organic carbon sources, glucose and glycerol being the most commonly used. Some researchers suggested the use of a combination of autotrophic growth and heterotrophic growth (termed mixotrophic cultivation) as it was reported to improve productivity (Silva et al., 2013)

Freshwater or saltwater can be used for the medium in microalgae culturing. They both have their advantages and disadvantages. Freshwater has a reduced burden on downstream processing, particularly the oil purification stage, as salts and metals are not accumulated in the biomass in great quantities. These impurities, present is any amount, are carried over to the oil phase during the extraction process and result in catalyst fouling during the upgrading stage (Davis et al., 2014). Therefore, the fewer impurities there are in the biomass to be treated, the less the requirements on the purification step prior to oil upgrading to biodiesel. The advantage of saltwater is that it puts a lower burden on the ecological system. Another source of water which can be used is wastewater. The advantage of wastewater is that it already contains many of the nutrients required for algae growth (nitrogen and phosphorous, for example). The scenario of wastewater integration into biomass production has been hailed as a viable and sustainable route by many researchers (Orfield, 2013; Krishnan, 2013; Lohrey, 2012).

Raceway ponds and closed photobioreactors (PBRs) are the most widely used reactors for algae cultivation. Raceway ponds are the most common method for culturing microalgae because of their improved energy efficiency at large scale, simplicity and low capital requirements. They are closed loop oval channels, typically 0.25 – 0.4 m deep, open to the atmosphere, and with a paddle wheel for mixing and circulation of water and prevention of sedimentation (Slade and Bauen, 2013). Open ponds are susceptible to contamination and evaporative losses; they are also more difficult to control. Low productivities, inefficient use of CO_2 and poor mixing have been reported for raceway ponds (Iqbal, 2012), but net energy recovery from raceways has outstripped closed photobioreactors to date (Richardson, 2011). PBRs offer quite a number of advantages over raceway ponds. With PBRs, there is better control of process parameters such as light (intensity and exposure), temperature, nutrient availability, pH and CO_2 (Krishnan, 2013). They also have lower risk of contamination and reduced evaporative losses, the latter dependent on CO_2 delivery mechanism. However, many PBRs have been found to be unsuitable for microalgae production at large-scale because the system uses more energy than can be recovered in the biomass produced, regardless of high cell densities (Lundquist et al., 2010; Davis et al., 2011; Krishnan, 2013; Slade and Bauen, 2013). They are typically proposed as suitable for inoculum production.

5.2.2.2 Biomass concentration

Literature reports biomass concentrations from the cultivation stage around 0.5 – 1 g/L for raceway ponds and 2 – 6 g/L for PBRs (Davis et al., 2011; Iqbal, 2012). These concentrations are too low for direct economic extraction of lipids since most extraction methods are solvent based. Therefore, there is need for concentrating the biomass before extraction and processing is done.

Many dewatering techniques are available for concentrating algae biomass. Figure 5.1 and Table 5.1 shows the most commonly used methods for dewatering algae. Their selection depends on the microalgal strain, its morphology, size, density, the desired concentration after dewatering and the final product (biomass, intracellular product or extracellular product) (Iqbal, 2012).

Table 5.1: Dewatering techniques categories. Sources: (Krishnan, 2013; Iqbal, 2012).

Technique	Description	Concentration factor (efficiency)	Examples
Chemical	Chemicals are added to coagulate or flocculate algae	100 – 800 times (90%)	Flocculation Coagulation Combined flocculation.
Electrical	Algal cells are negatively charged and are concentrated by passing through an electrical field.	(80 – 95%)	Electrocoagulation Electroflocculation.
Mechanical	Uses settling velocities or cell sizes to concentrate cells	250 – 2500 times	Gravity sedimentation Centrifugation Filtration Flotation.
Biological	pH is increased to 8.5 – 9. Ca^{2+} and PO_4^{2-} precipitate. Positively charged precipitate is attracted to negatively charged algae	(90%)	Autoflocculation Bioflocculation Biofilms Microbial flocculation.

Dewatering techniques are normally combined because a single technique cannot effectively achieve the desired concentration (around 200 g/L). The dewatering process presented by Davis et al. (2013) had three steps: primary settling which increased the concentration to 10 g/L, direct air flotation (DAF) with addition of chitosan which concentrated the biomass further to 60 g/L and the final step concentrating the biomass to about 200 g/L by centrifugation. A similar design philosophy has been adopted by many authors (Krishnan, 2013; Iqbal, 2012; Milledge and Heaven, 2017; Milledge, 2013; Lundquist et al., 2010).

5.2.2.3 Lipid extraction

Kumar et al. (2015) reviewed the methods available for lipid extraction and the data presented in their report is summarised in Table 5.2. Most of the methods presented in the review are still under development and have not been tested at industrial scale. Of the methods tested at lab scale, the microwave method was found to be the most simple and effective method for extracting lipids (Lee et al., 2010).

Mechanical disruption methods and solvent extraction (commonly using hexane) are the most often used techniques for lipid extraction. Environmentally friendly and cheap to operate, mechanical methods have reported low lipid yields and result in product degradation; however, this is species specific. Solvent extraction tends to be the default method for lipid extraction because of high lipid recoveries. Mubarak et al. (2015) suggested using ultrasonication or microwave-assisted methods as pre-treatment prior to solvent extraction to improve yield.

During solvent extraction, an organic solvent is contacted with the wet biomass. The lipids partition into the organic phase while the spent biomass remains in the aqueous phase. The phases are separated, and the solvent is stripped from the oil. The solvent is then recycled to the extraction process where it is supplemented with fresh solvent to make up for system losses. Davis et al. (2013) reported that this step of the process carries a lot of uncertainties with regards to process performance and efficiency due to unavailability of literature data at industrial scale.

5.2.2.4 Product upgrading

Transesterification converts fatty acids into alkyl esters using an alcohol (typically methanol). Commercial transesterification requires dry biomass with ruptured cell walls. This has been shown to be energy intensive for economic exploitation of the method at large scale (Milledge, 2013). To overcome these hurdles, Griffiths et al. (2010) recommended using *in situ* transesterification. This

eliminates some unit operations thus making the process simple and more economic. In *in situ* transesterification, the extraction solvent is added together with the reagent (methanol) and catalyst. Transesterification was used in economic evaluations by Krishnan (2013), Chisti (2007), Brownbridge et al. (2013), Silva et al. (2013) and Richardson et al. (2010).

Table 5.2: Lipid extraction methods. Source: Kumar et al. (2015).

Method	Extraction efficiency	Efficiency rating	Cost	Energy consumption	Comments
Solvent extraction (e.g. chloroform / methanol, hexane, and ether)	The extraction efficiency depends on a lot of design parameters, biological, physical and chemical.	Moderate	High due to high cost of solvents. Solvent recovery lowers operating cost a little since recycling is energy-intensive	High energy demand	Safety, health and environmental issues (fire, toxic vapours), regulatory issues
Pressurized solvent extraction		High	Pressurised nitrogen plus solvents increase the operating cost	High energy demand	
Isotonic extraction		Moderate – high	Synthetic non-volatile solvents increase the cost of operation	High energy demand	Less hazardous
Supercritical CO_2		High	High	High operating pressure results in high energy demand	Health, safety and environmental issues
Expeller press		Low - moderate	High	High energy demand	Product degradation due to heat generation
Bead beating		Moderate	Cost-effective	High energy demand but efficient reactor design can lower it	Difficulties with scaling up
Microwave		Very high	High capital and maintenance cost	Very intensive energy requirements as additional energy is required for cooling	Only tested at pilot scale. Yet to be standardised at industrial scale
Sonication		High	High capital and maintenance cost	High energy requirements (for both sonication and cooling)	Degradation results in a poor quality product
Osmotic shock		Moderate - high	Low	Less demanding	
Electroporation		Very high	High capital and maintenance cost but low operating cost	Less demanding	

5.2.2.5 Spent biomass utilisation

Anaerobic digestion (AD) is a well-established technique which has been used particularly in the wastewater treatment field. It is used to recover nutrients (nitrogen and phosphorous) in liquid form and residual carbon in the form of methane. Lundquist et al. (2010) reported that AD recycles about 90% of the nutrients in the process and Yang et al. (2011) reported that recycling water from the AD process back to the cultivation stage reduces nutrient requirements by 55%. Incorporating AD into the algae-to-fuel pathway has been found to be a plausible approach from an energy balance perspective (Milledge, 2013). It results in a positive net energy, making the whole process energetically and economically viable.

Combustion of biogas from the digestion process produces low pressure and high pressure steam which are used for electricity generation and as a process utility, respectively. The flue gas from biogas combustion is recycled to the cultivation process to supply carbon dioxide for the growing algae. This recycling of carbon reduces the amount of externally sourced carbon, which is one of the cost driving factors in algae production (Davis et al., 2016).

5.2.3 Factors affecting the 'algae-to-energy' process

Algal biomass generation has been shown to be more productive compared to terrestrial biomass. An economic evaluation by Zhang et al. (2015) analysed biomass productivities varying from 20 to 60 g/m^2/day and lipid content from 15% to 50%. A sensitivity analysis by Davis et al. (2016) showed a biomass productivity of 25 g/m^2/day as the minimum biomass productivity that would result in an economically feasible operation. The range tested in the sensitivity analysis was from 7 to 35 g/m^2/day. Figure 5.2 shows the sensitivity of algal oil cost to biomass productivity.

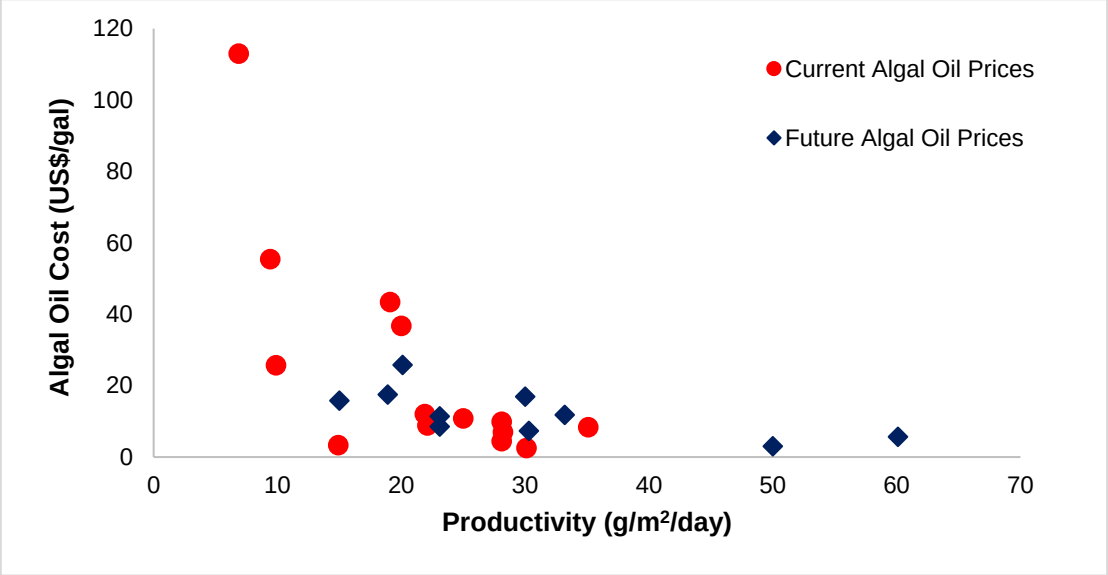

Figure 5.2: Cost of algae biomass and algal oil based on current and projected biomass productivities. Current algal oil cost determined using currently achievable design parameters such as productivity, lipid content, etc. and future algal oil prices based on expected developments in near future in terms of reactor design, process optimisation, etc. Data points adapted from Davis et al. (2016)

Lipid content has also been correlated to algal cost broadly in the literature. However, lipid productivity provides a more relevant approach to evaluation. Lipid content and productivity are related as follows (Griffiths and Harrison, 2009):

Lipid productivity = lipid content * biomass productivity

= lipid content * biomass concentration * specific growth rate

(Davis et al., 2013) report that the influence of lipid content on the economics of algae cultivation and oil production is stronger than productivity; however, this is not supported by all researchers as a baseline productivity is essential for cost-effective production (Harrison et al., 2013; Louw et al., 2016). The challenge that has been observed is that lipid content and biomass productivity cannot be simultaneously optimised, resulting in a compromise in both typically required to maximise lipid productivity. Griffiths and Harrison (2009) and Griffiths (2011), using literature and experimental data respectively, showed that increasing the lipid content in algae to its maximum typically resulted in reduced productivities and vice versa.

Cultivation costs are predominantly driven by feedstock prices and reactor design. Davis et al. (2016) showed that the source of carbon dioxide did not make much difference on the overall cost of biomass cultivation. The text analysed the effect of using purified and pressurised CO_2 from flue gas versus direct sparging of low pressure, non-purified flue gas and found, for the latter, that the cost of biomass production reduced by 10% from a base case cost of $491/ dry ton. As mentioned earlier, open ponds result in better economics than PBRs. The presence of liners in ponds significantly increased the cultivation cost by over 25% (Davis et al., 2016; Silva et al., 2013; Orfield, 2013).

The values of productivity and lipid content found in literature are from laboratory experiments which are controlled environments. These do not truly reflect what is to be expected in actual large scale processes for algal oil production. However, Griffiths and Harrison (unpublished data) demonstrated that the biomass productivity of Spirulina could be maintained on scale up from 2000 litre to 500 000 litre raceways, provided adequate raceway management was implemented.

5.2.4 Algae production economics

Many studies have been conducted to estimate algal oil prices under different scenarios. Due to the lack of real industrial data, simulation, pilot scale results in the public domain, equipment supplier quotations and patent data were used in the estimation process (Davis et al., 2011).

A study by Silva et al. (2013), which simulated the process in Aspen Plus, pegged the price of biodiesel to $4.34/gal, in 2011 US dollars (2011-$) for a plant designed to produce 175 million gal/year using estimates from industrial quotes and cost estimates reported in literature. This was based on mixotrophic growth conditions which the authors mentioned yielded lipid contents well above 50% (on a dry cell basis). For the algae cultivation, open raceway ponds with liners to reduce water loss by percolation were used. Microwave extraction process was used as the cheapest option, although the authors expressed doubt about its reliability at large scale since it was only tested at pilot scale. Sensitivity analysis showed that eliminating pond liners would reduce the selling price to $3.20/gal (2011-$) while changing the harvesting method from direct air flotation to ultrasonic harvesting would reduce the selling price to $3.51/gal (2011-$).

A study by Richardson et al. (2010) considered two different scenarios. The simulation for Scenario 1 used an annual production capacity of 2 300 gal/acre, a productivity of 30 g/m^2/day, 30% algal oil content (dry weight), and an average CO_2 consumption of 1.83 g CO_2/g biomass. Scenario 2 had an annual algae oil production capacity of 4 500 gal/acre. They estimated the total cost of algal oil to range from $6.20 to $26.79/gal (average value $11.68/gal) for Scenario 1 and $1.09 to $3.21/gal (average value $1.82/gal) for Scenario 2. This cost considered the by-products credit. This result was based on a Monte Carlo simulation methodology using stochastic figures for the key input variables (Frost, 2017).

A techno-economic model developed by Brownbridge et al. (2013) presented the cost of algal biodiesel in the range $4.39 – $8.77/gal (2013-$) for a plant producing 100 000 tonnes/year of biodiesel. The analysis showed that the 5 year return on investment (ROI) is predominantly sensitive to lipid content, the prevailing crude oil price at plant start-up, and annual productivity. The 30 year ROI was sensitive to the rate of crude oil price increase, on top of the factors affecting the 5 year ROI.

Davis et al. (2011) carried out a techno-economic analysis for a production capacity of 10 million gal/year which compared the cost of biodiesel produced via the open raceway ponds route to PBR route. The study used the assumed parameters in Table 5.3. The study gave the price of raw oil via the open raceway ponds as $8.52/gal and $18.10/gal via the PBR route. Hydro-treating to produce biodiesel

increased the production cost to $9.84/gal and $20.53/gal of algal biofuel, respectively. These costs considered by-product credits. The by-products were naphtha from hydro-treating, digestate from AD and excess energy from the combined heat and power plant. A sensitivity analysis showed that lipid content had a significant contribution to the cost of the final product as compared to productivity. Increasing the algal oil content to 50% algal dry weight resulted in a cost reduction of 50% in both reactor configurations.

Table 5.3: Assumed variables in the techno-economic analysis comparing open raceway ponds and PBRs for algal biodiesel production. Source: (Davis et al., 2011).

	Raceway pond	**PBR**
Productivity	25 g/m^2/day	1.25 kg/m^3/day
Lipid content	25%	25%
Biomass concentration	0.5 g/L	4 g/L

Davis et al. (2014) improved the process design in the 2011 study by adding a pre-treatment and fermentation stage that took advantage of soluble carbohydrates. This gave a selling price of fuel of $4.57/gal (2011-$). The improved cost was due to a subsidy offered by ethanol as one of the main products, naphtha, digestate, biogas and CO_2 credits.

A more recent study by Zhang et al. (2015) harmonised previously published data on algal biodiesel production cost in a meta-analysis. The study had two scenarios: a base case scenario which assumed moderate algal oil yields that were attainable at the current technologies, and a projected scenario which assumed higher algal lipid yields based on future technological advancements. The base case yielded a production cost ranging from $5.00 to $10.31/gal. The projected case had a much lower production cost ($2.76 – 4.92/gal).

5.3 Methodology

The literature review on algal oil production economics showed that the study by Davis et al. (2014) was more comprehensive compared to other studies and offered more realistic assumptions. The technology pathway chosen in their study differed from many researchers in that it included a pre-treatment and fermentation process to convert carbohydrates into fuel, in addition to algal-derived fuel oil. For this reason, this study adopted the economic analysis by Davis et al. (2014) as a framework for the current economic analysis for RALs and FAMEs production. To maintain consistency, all cost and prices are quoted in 2011-$. The price of oleic acid and other collectors used in coal flotation will be quoted in 2011-$ for an accurate comparison.

Figure 5.3 shows the block flow diagram used for the production of RALs and FAMEs. This was modified from the process flow presented by Davis et al. (2014). The hydro-treating step was swapped out for a transesterification step. Two routes for FAMEs production were analysed. One route was transesterification after solvent extraction and the other route was direct transesterification of the biomass coming from the fermentation and distillation process.

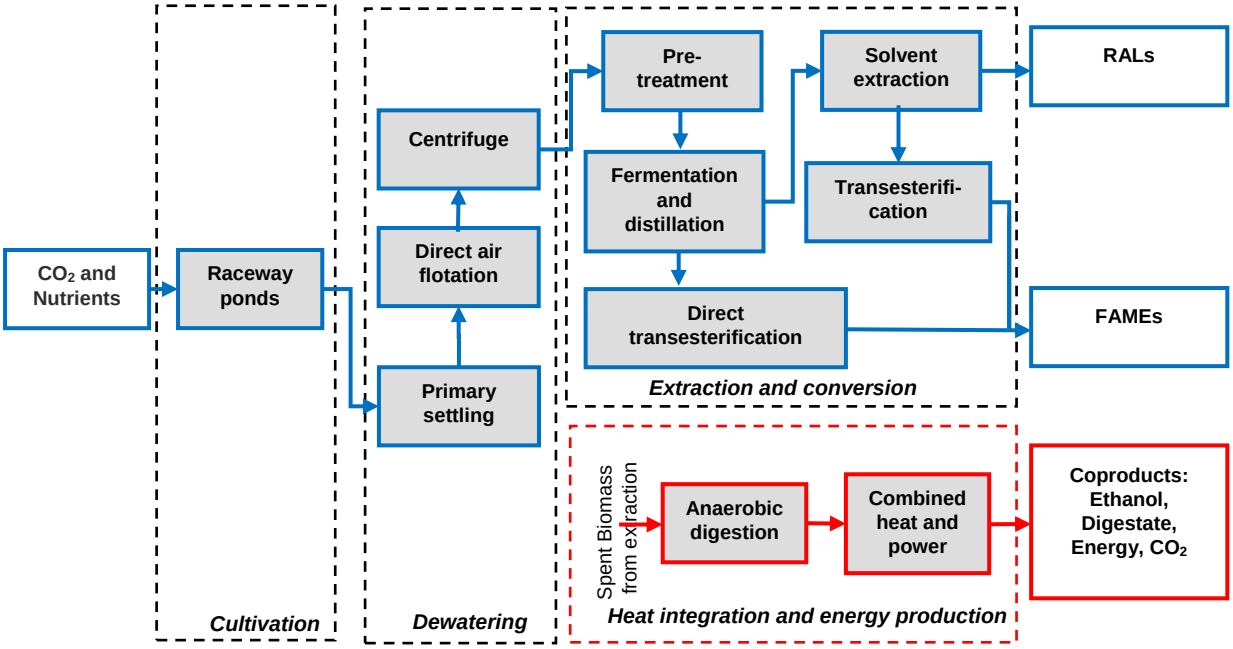

Figure 5.3: Block flow diagram for RALs and FAMEs production.

The economic analysis was done using the framework from Davis et al. (2014). The economic analysis was first replicated on an MS Excel sheet and then the necessary changes were performed on the Excel spreadsheet to determine the minimum selling price (MSP) for RALs and FAMEs.

5.3.1 Design parameters

Davis et al. (2014) used hydrotreating for upgrading algal oil to straight chain paraffins. This process was eliminated from this study and replaced by direct transesterification which produces FAMEs. This means that one of the process by-products changed from naphtha to glycerol. The option of using PBRs was not considered as literature has already suggested that it is not economically feasible at large scale (Davis et al., 2013; Davis et al., 2011; Lundquist et al., 2010; Slade and Bauen, 2013)

The parameters used for algal lipids cost review are presented in Table 5.4.

Table 5.4: Design parameters used in the cost review for RALs and FAMEs production. Source: (Davis et al., 2014).

Parameter	Value	Units
Physical parameters		
Plant capacity (biomass)	441 870	Ash-free dry ton/year
Operation	330	days
Productivity	30	$g/m^2/day$
Biomass	*Scenedesmus* sp.	
Lipid content	41	%
Biomass concentration	20	wt% after dewatering
Operating parameters		
Lipid extraction efficiency	95	%
Glucose-ethanol conversion	55	%
Purified lipid product rate	22 120	kg/hr
Biogas composition (CH_4)	67	vol%
Economic parameters		
Plant life	30	years
Internal rate of return	10	%
Tax rate	35	%
Depreciation	7	Years (Modified Accelerated Cost Recovery System – MACRS)

5.3.2 Assumptions

The algal processing plant was designed on the assumption that excess summer capacity is diverted, dried and stored for winter time when biomass production is low. The ponds are designed without liners. Make-up water is added to cover for loses due to evaporation, blow-down, percolation and water in products (digestate, lipids). 2% of the water in the aqueous phase is carried over to the organic phase during lipid extraction.

The densities of RALs and FAMEs were assumed to be 0.9 kg/L and 0.864 kg/L (Schlagermann et al., 2012; Oilgae, 2018). The densities of methanol and glycerol were obtained from Sigma-Aldrich® and were assumed to be of 99% purity. Density of methanol was taken as 0.792kg/L (Sigma-Aldrich, 2018b) and 1.26 kg/L for glycerol (Sigma-Aldrich, 2018a)

FAMEs were modelled as C16 ($C_{17}H_{34}O_2$), C18:2 ($C_{19}H_{34}O_2$) and C20 ($C_{21}H_{42}O_2$) with mass fractions of 0.32, 0.56 and 0.12, respectively. These mass fractions were derived from Figure 4.1 by merging minor peaks. The methanol required for transesterification and the glycerol product were determined based on these values. The yield of FAMEs in the transesterification stages was assumed as 95%. Literature has reported more than 98% conversion for vegetable oil (Schuchardt et al., 1998). However, 95% was chosen because of the presence of wet biomass in the reaction. Griffiths et al. (2010) highlighted that the presence of water affects the efficiency of the transesterification process.

5.4 Results and discussion

The adapted process flowsheet designs were used to calculate the minimum selling price (MSP) of the RALs and FAMEs (full costing data shown in Appendix D). For a payback period of 10 years, a tax rate of 35%, and a 10% IRR, the MSP of RALs was found to be $4.73/gal. The FAMEs MSP for a process that has separate lipid extraction and transesterification was $5.06/gal. When *in situ* transesterification is considered, the expensive solvent extraction column is eliminated. This reduces the MSP to about $4.78/gal, which is close to the MSP of RALs.

Lipid upgrading to FAMEs included the purification stage for de-gumming and removing other impurities. This step was included by Davis et al. (2014) in order to prevent fouling of the catalyst used in the hydro-treating process. Although there is no literature evidence to support the technical feasibility of large-scale homogeneous direct transesterification using aqueous catalyst, the effect of salts and other impurities can be ignored thus eliminating the purification stage. This results in an MSP of FAMEs of $4.63/gal.

These cost estimates are comparable with data presented in literature. The MSP for biodiesel via the hydrotreating route from an economic evaluation by Davis et al. (2014) was $4.57/gal while that obtained by Silva et al. (2013) using transesterification was $4.34/gal. Diesel and kerosene, which are the commonly used coal collectors, retailed at $3.52/gal and $3.09/gal, respectively (U.S. Energy Information Administration, 2012; U.S. Energy Information Administration, 2018). Oleic acid sold at $5.96/gal in 2011 (Taylor and ICIS, 2013). The price of dodecane ranged from as low as $4.54/gal for bulk orders to $47.30/gal (Alibaba.com, 2018).

As with Davis et al. (2014)'s economic analysis, the MSP for both RALs and FAMEs were heavily driven by the cost of algae cultivation. This analysis was done using a conservative cost of biomass of $430/US dry ton. An increase in biomass cost to $550/ton increased the MSP by about 26% and a biomass cost of $300/ton reduced the MSP by a similar factor. Davis et al. (2014) considered the currently achievable lipid content of about 27% and found that the MSP of their product increased by 15.86%. This similar analysis was not done in this review since there was no proper mass balance to achieve that. However, the author believes that same effect will be observed in the RALs and FAMEs cost if the lipid content is reduced to an attainable value of 27%.

6 Conclusions and recommendations

6.1 Conclusions

The investigations performed and reported herein were aimed at testing algal-derived lipids as biocollectors in the desulphurisation of coal by froth flotation. The objective of the investigation was to evaluate the technical and economic feasibility of the use of algal-derived lipids in coal flotation. Technical assessment was done through batch flotation experiments with 6% solids loading. The variables tested in the flotation experiments were biocollector type, biocollector dosage and coal flotation pH. Biocollector performance was referenced to the performance of oleic acid and dodecane, which were dosed at 2.8 kg/t, based on the work by Kazadi Mbamba (2011), Kazadi Mbamba et al. (2012) and Harrison et al. (2013). The data from the flotation experiments were analysed in terms of overall yield (equivalent to total mass recovery), recoveries of combustibles, ash and sulphur, and product quality in terms of ash and sulphur content.

The first hypothesis put forward for this study was that raw algal lipids (RALs) and their derivatives (fatty acid methyl esters - FAMEs) have the necessary functional groups (–OH, $–COO^-$, $–C_nH_{2n-1}$, $–C_nH_{2n+1}$) to perform as polar collectors. They contain an ester head which is polar and hydrocarbon tails with varying carbon chain lengths in the range from 12 to 22, a chemical structure which is similar to commonly used polar collectors such as oleic acid. The flotation experiments showed that it is technically feasible to desulphurise fine coal waste using algal lipids and their derivatives by froth flotation. For difficult-to-float fine coal waste, exemplified by the Site 1 coal fines from the Waterberg area, there is no significant difference in performance between the algal lipids and oleic acid. On the other hand, algal lipids have better performance compared to oleic acid when dealing with easy-to-float coal waste, represented by Site 2 tailings from the Witbank area, thus requiring lower dosages compared to oleic acid to achieve similar yields and product quality. RALs were generally more selective at low dosages compared to FAMEs as they resulted in low sulphur recoveries. Dodecane was used to represent non-polar collectors and its performance was significantly lower than that of RALs and FAMEs for the two types of fine coal waste samples tested. The similarity in performance of RALs and FAMEs to oleic acid was due to similarities in chemical structure. Both bioreagents have polar heads which can attach to coal and hydrocarbon tails with carbon lengths ranging from 12 to 20 atoms which offer hydrophobicity to the coal particles once the bioreagents are attached.

In terms of the effect of pH on collector performance, dodecane showed the trend reported in literature, where the overall yield increased with increase in pH. For this study, a significantly different pH trend was observed for flotation using RALs and FAMEs as collector. The difference in chemical composition and structure between RALs and FAMEs resulted in pH impacting their performance differently at pH values above 4. Despite high yield and combustibles recovery being obtained at pH 4, the starting pH for further optimisation should be pH 7 for FAMEs and pH 2.7 for RALs as they resulted in the lowest sulphur content in the recovered product.

It was also hypothesised that algal-derived lipids have the potential to act as dual flotation reagents, that is, they have both collecting and frothing properties. This was confirmed visually and experimentally through flotation. At a biocollector dosage of 2.8 kg/t RALs, in the absence of MIBC frother, resulted in a coal yield of 15.43% while the experiment with both RALs and MIBC frother had 34.13% yield. This significant increase in yield between the two scenarios was due to the presence of low molecular weight compounds in the RALs that have surface active properties. However, the presence of both collecting and frothing ability in RALs resulted in reduced selectivity (product had 2.96% sulphur for RALs only experiments and 2.56% sulphur when MIBC frother was added). With proper optimisation, it is possible to eliminate or reduce the amount of MIBC frother in the process, thus reducing the operating expenses. Overall, RALs and FAMEs are suitable replacements of chemical collectors in the desulphurisation of coal by froth flotation because their performance matches or surpass, depending on the coal type, that of oleic which has been demonstrated to be one of the best polar collectors.

The third hypothesis that was tested stated that RALs and their derivatives (FAMEs) present an economically cheaper and environmentally friendly alternative to oleic acid and other currently used chemical collectors in coal desulphurisation by froth flotation. The algal lipids cost review was based on adaptation of a comprehensive economic evaluation by Davis et al. (2014) to the biocollector production requirements. In particular, hydrotreating of RALs was swapped out for transesterification for production of FAMEs. The evaluation yielded minimum selling prices for RALs and FAMEs at $4.73/gal and $4.63/gal in 2011-$, respectively. FAMEs came out cheaper than RALs because the FAMEs production process excluded lipid extraction and purification steps. When compared to the equivalent 2011 price of oleic acid, the cost of the two bioreagents is 20 – 21% cheaper.

It is important to note that the minimum selling price for RALs and FAMEs does not include transport costs for a case where the algal lipid processing plant is not located near the site of coal waste disposal. Locating the algae cultivation and lipid processing plant at the site of coal waste disposal will make the use of RALs and FAMEs more economically favourable. This may be feasible for coal waste disposal sites close to coal-fired power plants as the power plant can provide both flue gas for algae cultivation and fine coal waste for treatment to upgrade it to a saleable and combustible product.

Based on the above mentioned conclusions, RALs and FAMEs present a technically and economically sound option, comparable to or offering advantage over traditional chemical collectors. From a technical standpoint, there is no significant difference between the performance of RALs and FAMEs under the best operating conditions; however, differing responses to operating variables such as pH were observed. The choice of bioflotation reagent can be made based on cost. From the current analysis, FAMEs are the cheaper option of the two when they are made via the direct transesterification route, which is the economically viable route.

6.2 Recommendations

The positive technical and economic results motivate further process optimisation studies for the two bioreagents. These optimisation tests should include variables such as pulp density, particle size, frother dosage, agitation speed and aeration rate.

Future work should also consider the presence of impurities and free fatty acids in the FAMEs. Studies have shown that oils extracted from microalgae may contain free fatty acids in proportions as high as 10% (Lohrey, 2012; Silva et al., 2013). Chisti (2007) stated that, in the presence of water, the free fatty acids result in the formation of soap (saponification). The effects of the saponified free fatty acids, unconverted RALs were not decoupled from the results of FAMEs since they were not purified. Hence it is recommended that future experiments be carried out with purified FAMEs to evaluate their performance as biocollectors.

A comprehensive up-to-date economic evaluation for the South African context needs to be carried out. This will take into account of location of algae cultivation and lipid extraction plants, biomass productivities and lipid contents attainable in South African environments, equipment and local labour costs.

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Appendix A: Calculations

The following equations were used to calculate yield, recoveries and flotation efficiency index.

Yield: $$Y = \frac{(T_A - F_A)}{(T_A - C_A)} \times 100\% \quad \text{(eqn 1)}$$

Combustibles recovery: $$R_C = Y \times \frac{(100 - C_A)}{(100 - F_A)} \quad \text{(eqn 2)}$$

Ash recovery: $$R_A = Y \times \frac{(C_A)}{(F_A)} \quad \text{(eqn 3)}$$

Sulphur recovery: $$R_S = Y \times \frac{(C_S)}{(F_S)} \quad \text{(eqn 4)}$$

FEI: $$FEI = \frac{(1 - R_A)}{(100 - F_A)} \quad \text{(eqn 5)}$$

Where: Y is yield, R_C is combustibles recovery, R_A is the ash recovery, R_S is sulphur recovery, T_A is tails ash, F_A is feed ash, C_A is concentrate ash, C_S is concentrate sulphur, and F_S is feed sulphur.

Appendix B: Media Preparation, and lipid extraction procedures

B.1 Modified Bold's basal medium (3N BBM)

This 3N BBM is modified by reducing the nitrogen concentration from the normal 750 mg/l as per original recipe to 150 mg/l based on a study by Griffiths et al. (2012).

Recipe for 1 l

- *Add 3 ml of each macro-element stock*
- *Add 6 ml PIV metal solution*
- *Add deionised water to make up to 1 L*
- *Autoclave and let it cool*
- *Add 1 ml of each of the two vitamin stocks (NOTE: the vitamins should not be autoclaved as they degenerate at high temperature)*

The macro-elements stocks are made by adding the appropriate amounts indicated in Table 7.1

Table 7.1: Composition of macro-elements per L.

Substance	**Chemical formula**	**Quantity (g)**
Sodium nitrate	$NaNO_3$	25.0
Calcium chloride	$CaCl_2.2H_2O$	2.5
Magnesium sulphate	$MgSO_4.7H_2O$	7.5
Potassium phosphate (dibasic)	$K_2HPO_4.3H_2O$	7.5
Potassium phosphate (monobasic)	KH_2PO_4	17.5
Sodium chloride	NaCl	2.5

The PIV solution is made by adding the minerals in Table 7.2 in the order in which they are listed in deionised water containing 0.75 g Na_2EDTA. The final solution is autoclaved and stored in the dark.

Table 7.2: Composition of micro-elements per L.

Substance	Chemical formula	Quantity (mg)
Iron (III) chloride	$FeCl_3.6H_2O$	97.0
Manganese chloride	$MnCl_2.4H_2O$	41.0
Zinc Chloride	$ZnCl_2$	5.0
Cobalt chloride	$CoCl_2.6H_2O$	2.0
Sodium molybdate	$Na_2MoO_4.2H_2O$	4.0

The vitamins are prepared as follows:

- *Add 0.12 g vitamin B1 (Thiamin HCl) to 100 mL deionised water and filter sterilise.*
- *Add 0.1 g vitamin B12 (cyanocobalamin) to 1 L deionised H_2O. Take 1 mL of this and add to 99 ml of deionised water.*
- *Filter sterilise and store in the dark when not in use.*

B.2 Raw algal lipids extraction

The method used for the extraction of raw algal lipids from wet algae is Axelsson and Gentili (2014)'s two-step method. It is noteworthy that the method described by Axelsson and Gentili (2014) used chloroform as the non-polar solvent. This was replaced with hexane for health and safety reasons.

The extraction is done as follows:

- Prepare a 2:1 hexane-methanol mixture.
- Suspend microalgal paste in 2:1 parts of Hex:Meth (v/v).
- Vigorously shake the container for a few minutes or until the algae paste is thoroughly distributed in the solvent.
- Finally, add a 0.73% $NaCl_{(aq)}$ to give a volume ratio of 2:1:0.8 (Hex:Meth:H_2O).
- Separate the hexane phase from the methanol phase.
- Use an evaporator to recover hexane and the raw lipids. Lipids are less volatile than hexane.

Care must be taken when working with organic solvents. Work should be done in a fume hood. The recovered hexane can be used in successive extraction. Methanol is also recoverable by means of distillation and can be reused for successive extraction processes.

B.3 Fatty acid methyl ester extraction

FAMEs are extracted in situ by direct transesterification of the raw algal lipids. This means that the step described in Appendix B.2 is not necessary. The raw algal lipids are converted to methyl esters by reacting with methanol as shown in Figure 7.1

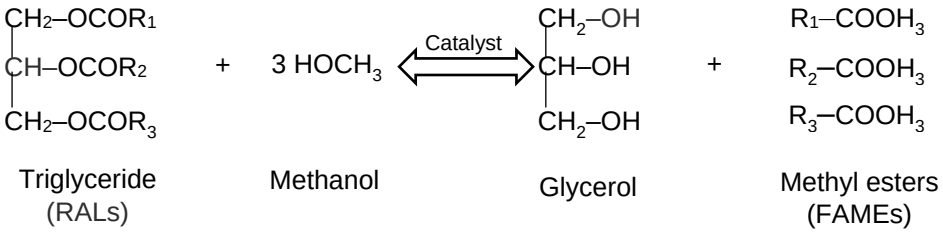


Figure 7.1: Conversion of fatty acids to fatty acid methyl esters using methanol. The reaction is done in two steps where the first step is alkali hydrolysis followed by acid hydrolysis

The procedure is done as follows:

- To 100 g of wet algae paste[1], add 600 ml hexane.
- Add 1 000 ml of basic catalyst.
- Incubate at 80°C for 20 min while shaking at 300 rpm.
- Allow to cool at room temperature after the 20 min.
- Add 1 000 ml of acid catalyst and repeat the incubation under the same conditions.
- Add 400 ml deionised water followed by 400 ml hexane.
- Separate the hexane phase from the methanol phase and recover the FAMEs and hexane by distillation.

The catalysts are made as follows:

Basic catalyst:

The basic catalyst which can be used is either sodium methoxide or 0.5N sodium hydroxide in methanol. The former can be ordered from a chemicals supplier and the later can be prepared in the lab. To prepare 0.5N NaOH in methanol, dissolve 2 g NaOH pellets in 100 ml methanol and allow to dissolve completely.

Acid catalyst:

The acid catalyst can either be boron trifluoride in 14% methanol which can be ordered from a reputable laboratory chemicals supplier or 5% hydrochloric acid. 5% HCl is made by adding 13.5 ml of 37% HCl to 86.5 ml methanol.

[1] The water content of the wet algae paste ha to be controlled to below 10% of the total reaction volume for reasons mentioned elsewhere (Griffiths et al., 2010).

Appendix C: Flotation Results

C.1 Flotation experiment results for Waterberg discards from Site 1

MIBC frother dosed at 0.28 kg/t, unless otherwise indicated.

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.38 g No collector pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	0.61 0.35 0.35 0.67 26.03 28.00	0.61 0.95 1.30 1.97	All concentrates were used up by sulphur analysis	-	2.61 2.39 1.88 2.27 4.19 3.56	2.61 2.53 2.36 2.33
Feed – 31.32 g Oleic acid – 2.8 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	7.99 0.40 0.31 0.88 18.35 27.93	7.99 8.39 8.70 9.58	22.69 23.07 24.19 30.62 58.01 48.09	19.24 20.33 21.25 24.10	2.43 1.96 2.00 2.64 4.75 4.35	2.43 2.41 2.39 2.41
Feed – 31.57 g Dodecane – 2.8 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	1.90 0.52 0.90 0.89 23.07 27.28	1.90 2.42 3.33 4.22	24.22 23.39 35.06 40.70 63.87 49.34	17.88 20.10 23.03 26.51	2.53 2.25 2.89 2.8 4.20 3.43	2.53 2.47 2.58 2.63
Feed – 31.64 g FAMEs – 1.20 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	1.67 1.64 2.37 1.32 20.87 27.86	1.67 3.30 5.67 6.99	20.41 19.56 21.83 33.25 56.51 47.85	4.87 9.53 17.01 23.52	1.74 1.60 2.51 4.85 5.07 3.57	1.74 1.67 2.02 2.55

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.45 g FAMEs – 2.00 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	3.43 2.46 1.44 1.52 19.31 28.15	3.43 5.89 7.32 8.84	22.20 20.70 21.70 32.15 59.50 47.68	8.81 14.88 18.66 24.31	2.31 2.05 2.18 4.67 4.76 3.58	2.31 2.20 2.20 2.62
Feed – 31.23 g FAMEs – 2.8 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	3.67 2.33 2.57 1.32 18.11 28.00	3.67 6.00 8.57 9.89	22.75 21.96 22.94 33.77 60.82 46.68	8.60 13.80 19.83 24.51	2.59 2.04 2.75 4.48 4.79 4.04	2.59 2.38 2.49 2.76
Feed – 31.50 g FAMEs – 2.8 kg/t MIBC – 0.00 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	5.52 1.12 1.07 0.83 19.67 28.20	5.52 6.63 7.71 8.54	24.16 21.96 23.56 33.79 59.39 48.17	15.66 19.00 22.01 25.34	2.45 2.06 2.44 3.88 4.73 3.43	2.45 2.38 2.39 2.53
Feed – 31.34 g FAMEs – 3.20 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	4.53 1.95 2.20 1.77 17.59 28.04	4.53 6.48 8.68 10.45	23.16 21.62 21.49 29.99 63.23 46.52	10.87 16.72 21.56 26.63	2.52 2.34 2.38 4.47 5.24 4.28	2.52 2.47 2.45 2.8
Feed – 31.31 g FAMEs – 3.70 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	5.79 1.96 2.99 1.54 15.88 28.16	5.79 7.75 10.74 12.29	23.88 23.26 24.56 35.89 66.01 47.61	11.32 15.12 21.27 25.90	2.82 2.39 2.62 4.81 5.81 3.85	2.82 2.71 2.69 2.95

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.72 g RALs – 1.20 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	3.29 0.42 0.44 0.68 23.29 28.11	3.29 3.70 4.14 4.82	23.11 26.90 29.67 31.71 53.68 47.75	15.73 18.07 20.76 25.31	2.62 3.16 3.22 3.01 4.86 4.04	2.62 2.68 2.74 2.78
Feed – 31.56 g RALs – 2.00 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	6.22 0.60 0.51 0.67 20.05 28.05	6.22 6.83 7.33 8.00	23.46 27.09 32.97 32.97 57.62 47.94	18.36 20.42 22.81 25.66	2.48 3.18 3.53 3.34 4.90 3.63	2.48 2.54 2.61 2.67
Feed – 31.84 g RALs – 2.8 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	7.07 1.06 0.56 0.82 18.36 27.87	7.07 8.14 8.70 9.52	24.14 28.26 33.12 35.85 59.84 46.41	17.95 21.75 23.88 27.30	2.38 2.99 3.25 3.09 4.41 3.43	2.38 2.46 2.51 2.56
Feed – 31.33 g RALs – 2.8 kg/t MIBC – 0.00 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	2.02 0.40 0.96 1.02 24.14 28.54	2.02 2.42 3.38 4.40	23.35 25.21 31.06 35.11 51.56 48.01	10.77 13.28 20.10 28.27	2.22 2.38 3.61 4.02 3.95 3.25	2.22 2.25 2.64 2.96
Feed – 31.71 g RALs – 3.20 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	9.15 0.98 0.60 0.68 16.60 28.01	9.15 10.13 10.73 11.41	24.69 29.06 35.54 37.80 63.30 47.52	19.80 22.29 24.21 26.47	2.42 3.02 3.34 2.99 4.60 3.41	2.42 2.48 2.53 2.55

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.40 g RALs – 3.70 kg/t pH – 2.7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	9.56 0.94 0.73 0.82 16.69 28.74	9.56 10.50 11.24 12.05	25.23 29.92 35.85 38.25 63.19 47.84	20.00 22.35 24.53 27.13	2.55 3.18 3.33 2.94 4.65 3.41	2.55 2.61 2.66 2.68

C.2 The pH test results for Waterberg discards from Site 1 flotation experiments

MIBC frother dosed at 0.28 kg/t, unless otherwise indicated.

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.20 g Oleic acid – 2.8 kg/t pH – 4.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	11.00 2.08 1.31 0.87 14.32 29.58	11.00 13.08 14.39 15.26	27.06 26.38 36.29 41.14 69.24 47.26	19.60 23.38 27.01 29.36	2.17 2.59 3.92 3.39	2.17 2.24 2.39 2.45
Feed – 31.22 g Oleic acid – 2.8 kg/t pH – 6.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	7.34 1.23 1.31 0.85 19.04 29.77	7.34 8.58 9.89 10.74	30.45 28.44 34.40 34.65 58.52 47.64	20.72 24.05 28.88 32.05	3.37 2.96 2.88 2.31	3.37 3.31 3.25 3.18
Feed – 31.55 g Oleic acid – 2.8 kg/t pH – 7.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	2.98 1.02 1.42 0.65 21.86 27.92	2.98 3.99 5.41 6.06	26.03 28.20 31.74 32.17 55.18 46.84	12.54 17.29 24.77 28.39	2.62 2.19 2.64 2.26	2.62 2.51 2.55 2.52

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.41 g Dodecane – 2.8 kg/t pH – 4.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	5.71 0.82 1.09 1.05 20.06 28.73	5.71 6.53 7.62 8.67	22.09 23.69 32.82 36.86 58.73 48.05	14.56 17.22 21.66 26.25	2.40 2.73 3.79 3.84	2.40 2.44 2.63 2.78
Feed – 31.26 g Dodecane – 2.8 kg/t pH – 6.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	7.90 0.73 0.83 0.96 18.96 29.37	7.90 8.63 9.46 10.42	23.79 24.00 35.56 39.33 61.37 48.72	18.02 19.70 22.57 26.25	1.93 1.94 3.29 3.55	1.93 1.93 2.05 2.19
Feed – 31.38 g Dodecane – 2.8 kg/t pH – 7.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	8.25 1.09 0.91 0.91 18.26 29.41	8.25 9.34 10.25 11.16	24.22 23.39 35.06 40.70 63.87 49.34	17.88 20.10 23.03 26.51	2.03 1.71 2.66 3.10	2.03 2.00 2.05 2.14
Feed – 31.49 g FAMEs – 2.8 kg/t pH – 4.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	11.91 2.51 0.90 0.73 12.08 28.14	11.91 14.42 15.32 16.05	27.47 28.57 32.04 43.04 77.01 48.09	20.40 24.87 26.84 28.80	2.31 2.44 2.88 4.85	2.31 2.33 2.36 2.48
Feed – 31.38 g FAMEs – 2.8 kg/t pH – 6.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	10.36 2.60 1.18 1.16 12.69 27.99	10.36 12.96 14.14 15.30	26.84 28.44 31.97 37.18 73.98 48.06	18.27 23.10 25.60 28.44	2.84 2.90 2.80 3.09	2.84 2.85 2.84 2.86

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.42 g FAMEs – 2.8 kg/t pH – 7.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	5.98 3.06 2.37 2.71 13.90 28.01	5.98 9.04 11.41 14.12	23.98 25.82 28.31 32.71 71.53 47.57	10.18 16.08 20.86 27.26	1.83 2.02 2.10 2.22	1.83 1.89 1.94 1.99
Feed – 31.43 g RALs – 2.8 kg/t pH – 4.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	13.39 1.97 1.03 0.52 10.67 27.58	13.39 15.36 16.39 16.91	28.10 30.69 45.40 51.18 78.22 48.82	22.17 25.78 28.57 30.15	2.87 3.68 6.00 4.87 4.71 3.58	2.87 2.98 3.17 3.22
Feed – 31.52 g RALs – 2.8 kg/t pH – 6.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	5.36 1.01 1.63 0.89 19.27 28.16	5.36 6.36 8.00 8.89	29.34 27.30 35.07 35.58 56.75 48.59	17.69 20.80 27.30 30.87	3.22 2.68 3.06 2.74 3.93 3.41	3.22 3.13 3.12 3.08
Feed – 31.57 g RALs – 2.8 kg/t pH – 7.0	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	5.52 1.31 1.54 0.66 18.90 27.93	5.52 6.83 8.37 9.03	31.73 29.42 34.44 32.32 57.33 47.54	19.43 23.69 29.58 31.97	3.15 2.72 2.97 2.11 4.08 3.38	3.15 3.07 3.05 2.98

C.3 Flotation experiment results for Site 2 waste tailings

MIBC frother dosed at 0.28 kg/t, unless otherwise indicated.

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.48 g No collector pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	2.84 1.64 2.15 3.22 21.15 31.00	2.84 4.49 6.64 9.86	15.54 15.73 17.37 19.72 28.58 24.72	4.50 7.12 10.91 17.38	0.57 0.61 0.65 0.74 1.05 0.94	0.57 0.58 0.61 0.65
Feed – 31.25 g Oleic acid – 2.8 kg/t pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	22.03 3.16 0.90 0.43 4.25 30.77	22.03 25.18 26.09 26.52	19.67 21.49 22.61 31.91 51.69 24.41	16.35 18.92 19.69 20.22	0.69 0.71 1.36 1.17 1.36 0.86	0.69 0.70 0.72 0.73
Feed – 31.46 g Dodecane – 2.8 kg/t pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	9.80 2.86 3.82 1.69 11.28 29.45	9.80 12.66 16.48 18.17	14.01 14.87 19.37 24.25 37.68 24.83	7.49 9.84 13.88 16.19	0.44 0.49 0.59 0.73	0.51 0.51 0.55 0.58
Feed – 31.39 g FAMEs – 1.20 kg/t pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	22.48 2.42 0.85 0.05 3.75 29.54	22.48 24.90 25.74 25.80	19.67 22.92 24.50 25.11 55.23 24.69	17.14 19.33 20.14	0.65 0.70 0.66 0.00 1.20 0.73	0.65 0.66 0.66 0.66
Feed – 31.28 g FAMEs – 2.00 kg/t pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	24.61 2.77 0.85 0.00 1.62 29.85	24.61 27.38 28.23 28.23	21.51 29.86 25.25 25.64 68.48 24.77	18.75 21.68 22.44	0.70 0.86 0.63 0.56 1.13 0.76	0.70 0.72 0.71 0.71

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.23 g	C1	0.5	25.81	25.81	21.88	19.00	0.70	0.70
FAMEs – 2.8 kg/t	C2	1.0	2.96	28.76	33.24	22.33	0.89	0.72
pH - 7	C3	2.0	0.96	29.73	26.56	23.20	0.68	0.72
	C4	5.0	0.00	29.73	25.24		0.00	0.72
	Tails		1.25		72.34		1.07	
	Feed		30.97		24.63		0.71	
Feed – 31.29 g	C1	0.5	23.91	23.91	21.06	18.57	0.69	0.69
FAMEs – 2.8 kg/t	C2	1.0	2.49	26.40	27.57	21.10	0.89	0.71
MIBC – 0.00 kg/t	C3	2.0	0.58	26.98	22.59	21.59	0.44	0.70
pH - 7	C4	5.0	0.13	27.11	23.12		0.00	0.70
	Tails		2.46		59.77		1.20	
	Feed		29.57		24.68		0.77	
Feed – 31.20 g	C1	0.5	24.79	24.79	21.37	17.82	0.75	0.75
FAMEs – 3.20 kg/t	C2	1.0	3.40	28.19	33.51	21.67	0.94	0.77
pH - 7	C3	2.0	1.56	29.75	26.26	23.18	0.75	0.77
	C4	5.0	0.00	29.75	26.83		0.00	0.77
	Tails		1.15		76.09		0.69	
	Feed		30.90		24.49		0.77	
Feed – 31.36 g	C1	0.5	21.59	21.59	20.87	15.78	0.71	0.71
FAMEs – 3.70 kg/t	C2	1.0	4.18	25.77	32.43	20.55	0.96	0.75
pH - 7	C3	2.0	2.78	28.55	24.46	22.94	0.77	0.76
	C4	5.0	0.00	28.55	23.73		0.00	0.76
	Tails		0.94		78.68		0.61	
	Feed		29.49		24.76		0.77	
Feed – 31.24 g	C1	0.5	21.96	21.96	19.99	16.93	0.72	0.72
RALs – 1.20 kg/t	C2	1.0	2.53	24.50	20.78	19.05	0.66	0.71
pH - 7	C3	2.0	0.93	25.43	22.86	19.92	0.72	0.71
	C4	5.0	0.38	25.80	26.69	20.37	0.88	0.72
	Tails		4.89		49.26		1.27	
	Feed		30.69		24.61		0.84	

Conditions	Sample	Time (min)	Mass (g)	Cumulative mass (g)	Ash (%)	Cumulative Ash (%)	Sulphur (%)	Cumulative Sulphur (%)
Feed – 31.45 g RALs – 2.00 kg/t pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	24.00 2.55 0.79 0.06 2.22 29.63	24.00 26.56 27.34 27.41	21.41 26.40 24.48 28.94 59.13 24.65	18.74 21.21 21.91	0.70 0.81 0.63 0.00 1.22 0.83	0.70 0.71 0.71 0.71
Feed – 31.48 g RALs – 2.8 kg/t pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	24.96 1.82 1.56 0.04 1.43 29.81	24.96 26.78 28.34 28.38	22.02 29.28 26.01 27.03 61.86 24.66	19.37 21.24 22.60	0.74 0.84 0.81 0.76 0.96 0.82	0.74 0.74 0.75 0.75
Feed – 31.41 g RALs – 2.8 kg/t MIBC – 0.00 kg/t pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	23.11 1.82 0.64 0.19 3.76 29.52	23.11 24.93 25.57 25.76	21.00 23.15 24.18 27.73 48.62 24.39	18.84 20.48 21.08	0.68 0.71 0.65 0.73 1.13 0.75	0.68 0.69 0.68 0.68
Feed – 31.38 g RALs – 3.20 kg/t pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	25.35 2.81 0.70 0.04 1.14 30.05	25.35 28.16 28.86 28.91	22.31 30.30 26.71 28.86 68.54 24.36	19.53 22.51 23.17	0.72 0.86 0.69 0.00 0.97 0.75	0.72 0.73 0.73 0.73
Feed – 31.38 g RALs – 3.70 kg/t pH - 7	C1 C2 C3 C4 Tails Feed	0.5 1.0 2.0 5.0	26.04 2.53 0.68 0.01 0.95 30.22	26.04 28.58 29.26 29.27	22.59 30.76 29.35 29.84 69.65 24.52	20.08 22.76 23.45	0.73 0.83 0.63 0.00 1.22 0.75	0.73 0.74 0.74 0.74

Appendix D: Statistical Analysis

The two statistical methods used for data analysis were the One-way analysis of variance (ANOVA) and the t-test. Presented in this appendix are the equations used, the underlying assumptions and the raw data they were applied to.

Definition of terms:

σ^2	Standard deviation
a	Number of levels or treatments in a single experiment.
F_0	The test statistic. The calculated *f* value for an *F*-distribution, which is the ratio of $MS_{Treatments}$ to MS_E
$f_{\alpha,a-1,a(n-1)}$	The critical value of an *F*-distribution with a-1 and a(n-1) degrees of freedom. A is the significance level.
H_0	Null hypothesis
H_1	Alternative hypothesis
MS_E	Error mean square
$MS_{Treatments}$	Mean square for treatments.
n	The number of replicates. For an experiment done in triplicates, n = 3
N	The population size. N=an; the total number of all observations for data that has more than two levels of a single factor
SS_E	Sum of squares of differences of observations within a treatment from the treatment mean
SS_T	Total sum of squares
$SS_{Treatments}$	Sum of squares of differences between treatment means and the grand mean
t	The test statistic for a t-test. $\|t\|$ means the modulus of the t-value, i.e., the positive value.
$\bar{y}_i$	The average of the data taken from the *i*th treatment
y_{ij}	The *j*th observation taken under treatment *i*

D.1 t-Test

This statistical method is used to compare the means of data with small samples (population size less than 30) that has two levels of a single factor. FAMEs and RALs performance was compared using this tool. The null hypothesis is that means of the two levels or treatments are equal and the alternative hypothesis is that the means are not equal.

H_0: $\bar{y}_1 - \bar{y}_2 = 0$

H_1: $\bar{y}_1 - \bar{y}_2 \neq 0$

The t-value for a t-test is calculated as:

$$|t| = \frac{\bar{y}_1 - \bar{y}_2}{\sqrt{\left(\frac{\sigma_1^2}{N_1} + \frac{\sigma_2^2}{N_2}\right)}}$$

Where the standard deviation, σ^2, of the population is estimated from the standard deviation of the population with the Bessel correction applied (Bird, 2006).

$$\sigma^2 = s^2\left(\frac{N}{N-1}\right)$$

D.2 One-Way ANOVA

This is used to compare the means of data that has more than two levels of a single factor under consideration (Montgomery and Runger, 2003). Under this test, the null hypothesis (H_0) is that all means are equal, while the alternative hypothesis (H_1) assumes that not all means are equal, for at least one treatment.

D.2.1 Equations

The following equations apply to ANOVA with equal sample sizes in each treatment. Table 7.3 shows how the data is presented for analysis;

Table 7.3: Typical Data from a Single-Factor Experiment for ANOVA. Treatment is the variable under test, e.g. concentration, different collectors, in the case of this research. Observations are the results obtained from the experiments.

Treatment	Observations				Totals	Averages
1	y_{11}	y_{12}	…	y_{1n}	$y_{1'}$	$\bar{y}_{1'}$
2	y_{21}	y_{22}	…	y_{2n}	$y_{2'}$	$\bar{y}_{2'}$
.	.	.	…	.	.	.
.	.	.	…	.	.	.
.	.	.	…	.	.	.
a	y_{a1}	y_{a2}	…	y_{an}	$y_{a'}$	$\bar{y}a'$
					$y_{''}$	$\bar{y}_{''}$

$$SS_T = \sum_{i=1}^{a}\sum_{j=1}^{n} y_{ij}^2 - \frac{y_{..}^2}{N}$$

$$SS_{Treatments} = \sum_{i=1}^{a} \frac{y_i^2}{n} - \frac{y_{..}^2}{N}$$

$$MS_{Tretaments} = \frac{SS_{Treatments}}{a-1}$$

$$MS_E = \frac{SS_E}{a(n-1)}$$

The error sum of the squares is the difference between SS_T and $SS_{Treatments}$:

$$SS_E = SS_T - SS_{Treatments}$$

The results obtained from the above equations are presented in a tabular form as shown in Table 7.4.

Table 7.4: Typical Presentation of Results for Analysis of Variance for a Single-Factor Experiment, Fixed-Effects Model.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F_O
Treatments	$SS_{Treatments}$	$a-1$	$MS_{Treatments}$	$\frac{MS_{Treatments}}{MS_E}$
Error	SS_E	$a(n-1)$	MS_E	
Total	SS_T	$an-1$		

All the data was analysed using MS Excel® and Minitab®. Both software use the above equations for their One-way ANOVA. Section D.2.2 is a sample output from Minitab®. MS Excel calculates the F_{crit}, while Minitab does not. Both software give the P-value of the test statistic, which when compared to the confidence level, either supports or does not support the conclusion made on the null hypotheses. For example, a P-value that is considerably smaller than the confidence interval chosen provides strong evidence that the decision made on the H_0 is correct.

D.2.2 One-way ANOVA: Site 1 Sample – FAMEs Dosage (kg/t)

Method

Null hypothesis, H_0	All means are equal
Alternative hypothesis, H_1	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	5	1.2, 2, 2.8, 3.2, 3.7

Analysis of Variance

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Factor	4	591.4	85.28%	591.4	147.85	14.49	0.000
Error	10	102.1	14.72%	102.1	10.21		
Total	14	693.4	100.00%				

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
3.19470	85.28%	79.39%	229.637	66.88%

Means

Factor	N	Mean	StDev	95% CI
1.2	3	25.08	1.74	(20.97, 29.19)
2	3	31.40	1.99	(27.29, 35.51)

2.8	3	35.313	1.374	(31.203, 39.423)
3.2	3	37.26	2.23	(33.15, 41.37)
3.7	3	44.02	6.10	(39.91, 48.13)

Pooled StDev = 3.19470

D.3 Fisher Least Significant Difference (LSD)

The Fisher LSD, also known as the Fisher Pairwise Comparisons, uses the t-distribution to compare all pairs of means with the null hypothesis $H_0: \bar{y}_i = \bar{y}_j$ (for $i \neq j$) using the test statistic

$$t = \frac{\bar{y}_{i'} - \bar{y}_{j'}}{\sqrt{\frac{2MS_E}{n}}}$$

When a two-sided alternative hypothesis is assumed, the pair of means $\bar{y}_i$ and $\bar{y}_j$ would be declared significantly different if

$$\left|\bar{y}_{i'} - \bar{y}_{j'}\right| > LSD$$

Where LSD, the least significant difference, is

$$LSD = t_{\frac{a}{2},a(n-1)}\sqrt{\frac{2MS_E}{n}}$$

Minitab® has an option of performing a Fisher Pairwise Comparison for data that is analysed by One-way ANOVA. Section D.3.1 is a Minitab output for Site 1 sample using FAMEs with the dosage varied from 1.2 kg/t to 3.7 kg/t. The same result is obtained by using an ordinary t-test as presented in Section D.1.

D.3.1 Fisher Pairwise Comparisons for Site 1 discards using FAMEs

Grouping Information Using the Fisher LSD Method and 95% Confidence

Factor	N	Mean	Grouping		
3.7	3	44.02	A		
3.2	3	37.26		B	
2.8	3	35.313		B	C
2	3	31.40			C
1.2	3	25.08			D

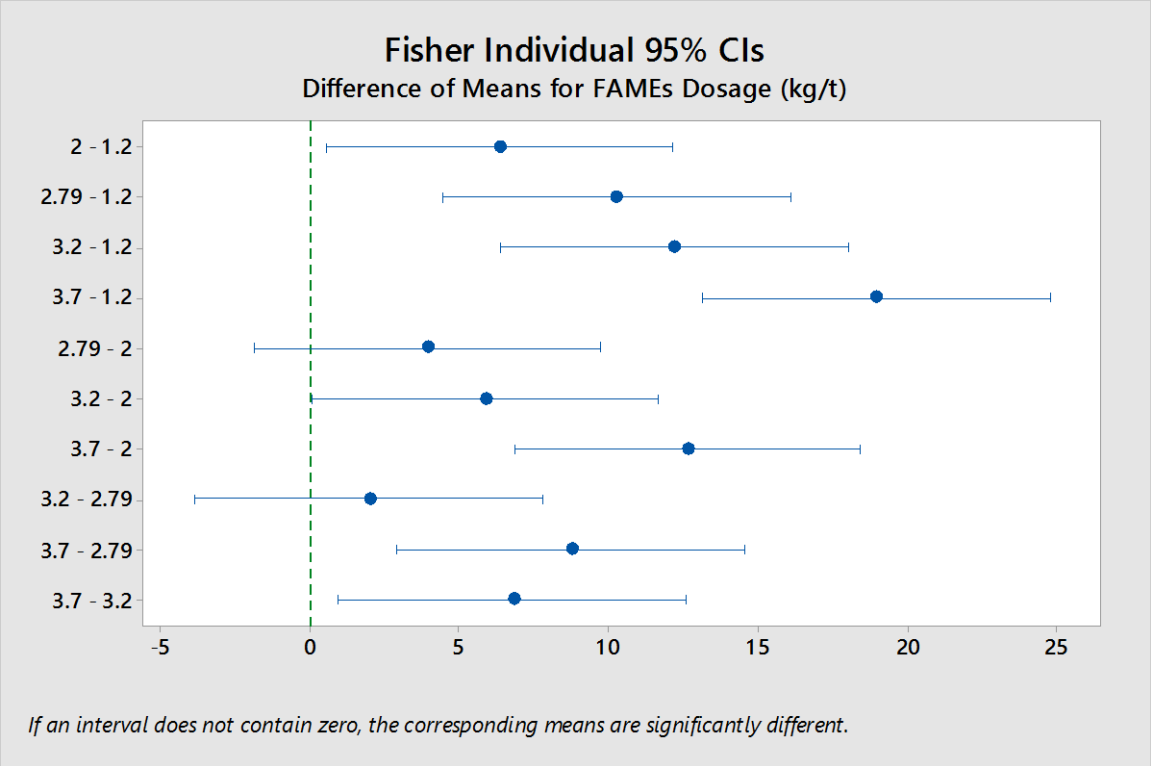
Means that do not share a letter are significantly different.

Fisher Individual Tests for Differences of Means

Difference of Levels	Difference of Means	SE of Difference	95% CI	T-Value	Adjusted P-Value
2 - 1.2	6.32	2.61	(0.51, 12.13)	2.42	0.036
2.8 - 1.2	10.23	2.61	(4.42, 16.04)	3.92	0.003
3.2 - 1.2	12.18	2.61	(6.36, 17.99)	4.67	0.001
3.7 - 1.2	18.94	2.61	(13.13, 24.75)	7.26	0.000

2.8 - 2	3.91	2.61	(-1.90, 9.72)	1.50	0.165
3.2 - 2	5.85	2.61	(0.04, 11.67)	2.24	0.049
3.7 - 2	12.62	2.61	(6.80, 18.43)	4.84	0.001
3.2 - 2.8	1.95	2.61	(-3.87, 7.76)	0.75	0.473
3.7 - 2.8	8.71	2.61	(2.90, 14.52)	3.34	0.008
3.7 - 3.2	6.76	2.61	(0.95, 12.57)	2.59	0.027

Simultaneous confidence level = 75.51%



All the Minitab outputs are found **here**.

D.4 Raw Data

The experiments were randomised to balance out nuisance variables. This was done by not increasing the concentration or pH linearly from low to high, or vice versa.

D.4.1 Site 1 Discards – Effect of Collector Type and Collector Dosage

Yield

Table 7.5: Overall Yield Data from Effect of Collector Dosage Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	**2**	**2.8**	**3.2**	**3.7**
FAMEs	27.01	29.65	36.80	39.36	47.63
	23.63	33.57	35.06	34.92	36.98
	24.61	30.99	34.08	37.50	47.46
RALs	17.79	33.39	36.89	42.23	40.45
	14.29	26.88	31.96	39.98	41.61
	19.59	25.34	33.55	40.06	43.74

Table 7.6: Overall Yield Data from Effect of Collector Type Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage (kg/t)	Collector			
	FAMEs	**RALs**	**Oleic Acid**	**Dodecane**
2.8	36.80	36.89	35.57	15.21
	35.06	31.96	34.27	15.77
	34.08	33.55	33.09	15.38

Combustibles Recovery

Table 7.7: Combustibles Recovery Data from Effect of Collector Dosage Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	**2**	**2.8**	**3.2**	**3.7**
FAMEs	40.11	43.47	53.63	58.46	67.67
	35.27	47.93	48.49	49.55	53.59
	35.64	46.51	48.84	51.24	67.94
RALs	25.27	47.96	50.57	59.07	56.95
	20.28	39.00	43.82	55.49	57.78
	28.43	36.12	46.75	56.87	61.03

Ash Recovery

Table 7.8: Ash Recovery Data from Effect of Collector Dosage Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	**2**	**2.8**	**3.2**	**3.7**
FAMEs	12.96	14.34	18.48	19.27	25.44
	11.20	17.05	18.65	18.17	18.93
	12.13	14.91	17.54	20.15	24.94
RALs	9.53	17.48	21.22	23.57	22.59
	7.57	13.91	18.04	22.52	23.17
	10.22	13.53	18.41	22.66	24.95

Table 7.9: Ash Recovery Data from Effect of Collector Type Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage (kg/t)	Collector			
	FAMEs	**RALs**	**Oleic Acid**	**Dodecane**
2.8	18.48	21.22	16.12	8.55
	18.65	18.04	17.74	9.06
	17.54	18.41	16.35	8.82

Sulphur Recovery

Table 7.10: Sulphur Recovery Data from Effect of Collector Dosage Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	**2**	**2.8**	**3.2**	**3.7**
FAMEs	17.72	20.07	28.78	26.43	42.11
	18.82	24.54	23.14	21.75	28.91
	17.29	24.69	20.80	24.62	33.46
RALs	12.81	22.74	29.28	34.76	30.39
	9.93	19.96	24.45	29.27	33.87
	12.70	20.29	22.84	27.97	34.69

Table 7.11: Sulphur Recovery Data from Effect of Collector Type Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage	Collector			
	FAMEs	RALs	Oleic Acid	Dodecane
2.8	28.78	29.28	18.57	11.52
	23.14	24.45	21.06	11.53
	20.80	22.84	17.71	12.35

Product Ash Content

Table 7.12: Product Ash Content Data from Effect of Collector Dosage Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	2.00	2.8	3.2	3.7
FAMEs	23.16	22.92	24.05	23.87	25.36
	22.92	23.62	23.93	24.25	24.54
	23.13	23.63	24.26	23.76	25.03
RALs	25.48	25.02	26.83	26.47	26.83
	25.00	24.98	25.98	26.50	27.21
	25.32	25.50	25.57	26.31	27.33

Product Sulphur Content

Table 7.13: Product Sulphur Content Data from Effect of Collector Dosage Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	2	2.8	3.2	3.7
FAMEs	2.36	2.65	2.90	2.89	3.55
	2.71	2.60	2.83	2.62	3.06
	2.61	2.62	2.53	2.84	3.07
RALs	2.74	2.47	2.69	2.67	2.64
	2.73	2.78	2.54	2.48	2.65
	2.85	2.81	2.43	2.51	2.74

Table 7.14: Product Sulphur Content Data from Effect of Collector Type Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage (2.8 kg/t)	Collector			
	FAMEs	RALs	Oleic Acid	Dodecane
2.8	2.90	2.69	2.18	2.56
	2.83	2.54	2.58	2.65
	2.53	2.43	2.49	2.65

D.4.2 Site 1 Discards: pH Tests

Yield

Table 7.15: Overall Yield Data from Effect of pH on Collector Performance Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

pH	Collector			
	FAMEs	RALs	Oleic Acid	Dodecane
2.7	36.80	36.89	35.57	15.21
	35.06	31.96	34.27	15.77
	34.08	33.55	33.09	15.38
4	56.87	60.78	51.93	33.85
	56.98	60.69	53.59	30.12
	57.32	55.39	49.24	26.61
6	57.39	33.35	25.99	31.70
	55.56	30.97	40.51	37.59
	51.02	30.41	41.59	37.10
7	51.15	32.30	25.40	42.89
	41.75	30.93	19.73	41.27
	47.60	33.75	19.94	29.55

Combustibles Recovery

Table 7.16: Combustibles Recovery Data from Effect of pH on Collector Performance Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	pH			
	2.7	**4**	**6**	**7**
FAMEs	53.63	78.30	79.82	72.31
	48.49	78.37	76.38	58.28
	48.84	78.77	70.15	65.63
RALs	50.57	85.04	44.67	42.53
	43.82	80.95	40.86	40.25
	46.75	75.49	42.00	43.10
Oleic Acid	53.46	68.67	35.07	32.92
	48.87	75.40	52.56	27.04
	49.48	65.84	54.29	27.33
Dodecane	21.08	49.18	45.54	62.48
	21.87	43.10	53.39	60.18
	21.33	37.86	54.30	42.67

Ash Recovery

Table 7.17: Ash Recovery Data from Effect of pH on Collector Performance Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	pH			
	2.7	**4**	**6**	**7**
FAMEs	18.48	33.77	33.87	28.46
	18.65	33.96	33.01	23.28
	17.54	34.06	29.75	27.43
RALs	21.22	37.05	21.13	21.40
	18.04	38.37	20.09	20.85
	18.41	33.90	18.85	22.84
Oleic Acid	53.46	68.67	35.07	32.92
	48.87	75.40	52.56	27.04
	16.12	31.72	16.27	16.80
Dodecane	8.56	17.44	16.87	22.95
	9.07	16.11	20.58	22.11
	8.82	14.29	19.72	15.78

Sulphur Recovery

Table 7.18: Sulphur Recovery Data from Effect of pH on Collector Performance Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	pH			
	2.7	**4**	**6**	**7**
FAMEs	28.78	39.87	48.56	30.04
	23.14	40.24	48.73	24.44
	20.80	42.99	42.04	22.59
RALs	29.28	50.16	31.34	30.22
	24.45	54.25	27.06	27.76
	22.84	54.45	27.09	27.70
Oleic Acid	18.57	30.68	21.80	21.35
	21.06	39.81	32.69	14.72
	17.71	37.14	40.50	17.23
Dodecane	11.52	25.84	18.76	21.64
	11.63	22.69	22.69	26.74
	12.35	20.74	28.97	19.13

Product Ash Content

Table 7.19: Product Ash Content Data from Effect of pH Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

pH	Collector			
	FAMEs	**RALs**	**Oleic Acid**	**Dodecane**
2.7	24.05	26.83	21.71	26.35
	23.93	25.98	24.29	27.37
	24.26	25.57	24.43	27.33
4	28.59	30.82	27.68	24.88
	28.71	30.08	28.94	25.73
	28.51	29.58	29.12	25.65
6	28.81	30.48	30.24	25.70
	28.53	30.88	30.81	26.35
	27.61	31.02	32.05	26.45
7	26.86	32.05	30.84	26.52
	26.34	32.41	29.44	26.61
	27.20	31.23	25.13	26.04

Product Sulphur Content

Table 7.20: Product Sulphur Content Data from Effect of pH Experiments on Site 1 Discards. MIBC frother dosed at 0.28 kg/t in all experiments.

pH	Collector			
	FAMEs	**RALs**	**Oleic Acid**	**Dodecane**
2.7	2.90	2.69	2.18	2.56
	2.83	2.54	2.58	2.67
	2.53	2.43	2.49	2.65
4	2.45	3.01	2.01	2.66
	2.51	3.32	2.70	3.07
	2.46	3.32	2.64	2.60
6	2.90	3.25	2.94	2.08
	3.11	3.01	3.03	2.12
	2.55	2.97	3.48	2.35
7	2.13	3.15	2.72	1.87
	1.96	2.97	2.34	2.21
	1.88	2.83	2.43	2.44

D.4.3 Site 2 Tailings from the Witbank Area

Yield

Table 7.21: Overall Yield Data from Effect of Collector Dosage Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	**2**	**2.8**	**3.2**	**3.7**
FAMEs	86.61	94.69	95.98	96.95	96.89
	87.89	94.74	95.74	96.35	96.70
	87.43	94.29	96.20	95.53	96.81
RALs	78.59	92.78	95.14	96.34	96.77
	85.37	91.78	95.48	96.44	96.94
	88.11	92.93	95.00	95.84	96.83

Table 7.22: Overall Yield Data from Effect of Collector Type Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage	Collector			
	FAMEs	RALs	Oleic Acid	Dodecane
2.8	95.98	95.14	85.53	60.83
	95.74	95.48	86.76	60.41
	96.20	95.00	86.27	63.93

Combustibles Recovery

Table 7.23: Combustibles Recovery Data from Effect of Collector Dosage Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	2	2.8	3.2	3.7
FAMEs	92.35	97.88	97.87	97.45	98.03
	93.09	97.74	97.73	98.82	99.13
	92.37	96.88	97.90	98.33	99.39
RALs	84.24	95.78	97.66	97.45	98.09
	90.16	95.83	97.68	97.99	97.74
	92.03	95.88	97.53	97.63	98.76

Table 7.24: Combustibles Recovery Data from Effect of Collector Type Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage (kg/t)	Collector			
	FAMEs	RALs	Oleic Acid	Dodecane
2.8	97.87	97.66	90.51	68.48
	97.73	97.68	91.70	66.81
	97.90	97.53	90.79	71.39

Ash Recovery

Table 7.25: Ash Recovery Data from Effect of Collector Dosage Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	**2**	**2.8**	**3.2**	**3.7**
FAMEs	69.28	85.02	90.17	95.32	93.27
	72.14	85.70	89.65	89.03	86.63
	72.06	86.34	91.05	86.88	89.03
RALs	61.33	83.59	87.52	92.88	92.67
	70.76	79.49	88.72	91.66	94.43
	76.02	83.85	87.21	90.27	91.01

Table 7.26: Ash Recovery Data from Effect of Collector Type Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage (kg/t)	Collector			
	FAMEs	**RALs**	**Oleic Acid**	**Dodecane**
2.8	90.17	87.52	90.51	68.48
	89.65	88.72	91.69	66.81
	91.05	87.21	90.79	71.39

Sulphur Recovery

Table 7.27: Sulphur Recovery Data from Effect of Collector Dosage Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	**2**	**2.8**	**3.2**	**3.7**
FAMEs	80.79	88.49	98.74	90.99	97.21
	77.86	88.60	96.60	98.84	91.98
	77.11	89.19	97.75	99.86	96.37
RALs	63.72	81.45	80.23	92.09	89.85
	76.98	81.09	88.36	95.44	96.10
	75.21	74.49	92.16	92.88	101.86

Table 7.28: Sulphur Recovery Data from Effect of Collector Type Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage	Collector		
	FAMEs	RALs	Oleic Acid
2.8	98.74	80.23	85.66
	96.60	88.36	86.84
	97.75	92.16	86.36

Product Ash Content

Table 7.29: Ash Content Data from Effect of Collector Dosage Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	2	2.8	3.2	3.7
FAMEs	19.92	22.28	23.07	23.46	23.10
	20.37	22.54	23.04	23.30	22.77
	20.06	22.50	23.41	22.18	22.87
RALs	19.25	22.18	22.87	23.39	23.24
	20.46	21.51	22.82	23.18	23.73
	21.12	22.10	22.56	23.01	23.42

Table 7.30: Ash Content Data from Effect of Collector Type Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage (kg/t)	Collector			
	FAMEs	RALs	Oleic Acid	Dodecane
2.8	23.07	22.87	20.13	15.31
	23.04	22.82	20.11	16.12
	23.41	22.56	20.31	16.86

Product Sulphur Content

Table 7.31: Sulphur Content Data from Effect of Collector Dosage Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Collector	Dosage (kg/t)				
	1.2	**2**	**2.8**	**3.2**	**3.7**
FAMEs	0.67	0.72	0.70	0.75	0.75
	0.65	0.71	0.74	0.80	0.77
	0.64	0.72	0.72	0.77	0.75
RALs	0.67	0.70	0.74	0.70	0.73
	0.77	0.71	0.74	0.76	0.74
	0.70	0.70	0.76	0.73	0.75

Table 7.32: Sulphur Content Data from Effect of Collector Type Experiments on Waste Tailings from Site 2 in the Witbank Area. MIBC frother dosed at 0.28 kg/t in all experiments.

Dosage (kg/t)	Collector		
	FAMEs	**RALs**	**Oleic Acid**
2.8	0.70	0.74	0.78
	0.74	0.74	0.72
	0.72	0.76	0.70

Appendix E: Algal Lipids Costing

E.1 RALs costing

Raw Algal Lipids	Years to recover capital			10	
Lipid Production Capacity	GGE/yr		51 492 695.21	514 926 952.13	
	gal/yr		51 422 665.00	514 226 650.00	
Cost			**Per year**	**Total**	
Pretreatment and Conditioning			**$65 564 413**	**$65 564 413**	
Dryer		*$18 612 122*			
PT Flash/Solvent Dist Preheat HX		*$181 960*			
Pretreatment Feed-Effluent HX		*$864 140*			
Pretreatment Reactor		*$43 887 372*			
Pretreatment Rest of Plant		*$2 018 819*			
Fermentation and Distillation			**$19 560 322**	**$19 560 322**	
Ethanol Fermentor		*$5 683 052*			
Fermentor agitator		*$353 507*			
Fermentor cooler		*$48 777*			
Fermentor recirculation pump		*$26 485*			
Ethanol seed train agitator		*$27 093*			
Ethanol seed train agitator		*$44 808*			
1st ethanol seed fermentor		*$94 284*			
2nd "		*$145 802*			
3rd "		*$197 071*			
4th"		*$489 064*			
5th "		*$1 639 476*			
Fermentation: Balance of plant		*$752 450*			
Vent scrubber		*$350 977*			
Ethanol distilation equipment		*$5 522 345*			
Reboilers					
Rectification ondensor					
beer condenser		*$1 020 820*			
Beer column HX economiser					
Ethanol Molecular seive		*$3 164 311*			
Lipid Extraction and Solvent Recovery			**$71 480 821**	**$71 480 821**	
Extraction Column		*$63 479 220*			
Solvent Recovery Column		*$6 208 251*			
Solvent Recovery Reboiler		*$1 793 350*			
Product Purification and Upgrading			**$18 521 319**	**$18 521 319**	
Hydrotreating Unit		*$0*			
PSA Unit		*$11 887 836*			
Bleaching/Degumming Unit		*$6 633 483*			
Anaerobic Digestion/CHP			**$21 558 209**	**$21 558 209**	
Anaerobic Digestor		*$11 025 544*			
Generator set		*$10 532 666*			
Storage			**$4 379 479**	**$4 379 479**	
Diesel Product Storage Tank		*$1 742 898*			
Ethanol Product Storage Tank		*$1 149 444*			
Naphtha Storage Tank		*$0*			
Firewater Storage Tank		*$728 838*			
Tankage BOP		*$758 299*			
Dried algae storage (3 months)					

Utilities			**$5 700 840**	**$5 700 840**	
Cooling Tower System		*$988 281*			
Plant Air Compressor		*$37 760*			
Chilled Water Package		*$677 303*			
CIP System		*$1 111 212*			
Cooling Water pump		*$300 617*			
Makeup Water Pump		*$13 975*			
Process water circulating pump		*$11 877*			
Instrument Air dryer		*$24 018*			
Plant Air Receiver		*$44 121*			
Process Water Tank 1		*$148 392*			
Steam Boiler HP Steam HRSG		*$576 610*			
Steam Boiler HP Steam HRSG		*$825 283*			
Steam Boiler HL Steam HRSG		*$875 083*			
HP Steam Economiser 1 HX		*$35 603*			
HP Steam Economiser 2 HX		*$30 705*			
Installed Equipment Cost			**$206 765 403**	**$206 765 403**	
Direct and Indirect Cost (48% of TCI)			**$190 860 372**	**$190 860 372**	
Total Capital Investment (TCI)			**$397 625 775**	**$397 625 775**	
Manufacturing Cost					
Feedstock	305.0	$206 133 751.36	$206 133 751.36		
Sulphuric acid	3.1	$2 095 373.55	$2 095 373.55		
Ammonia	5	$3 379 634.76	$3 379 634.76		
Hexane	13.8	$9 327 791.94	$9 327 791.94		
Natural gas	8.5	$5 745 379.09	$5 745 379.09		
Hydrogen	0	$0.00	$0.00		
Other raw mats	3.2	$2 162 966.25	$2 162 966.25		
AD nutrients, digestate, and CO2 recylcle credit	-24.5	-$16 560 210.33	-$16 560 210.33		
Ethanol	-99.653		-$67 358 148.56		
Net electricity	-5	-$3 379 634.76	-$3 379 634.76		
Naphtha credit	0	$0.00	$0.00		
Fixed cost	22	$14 870 392.95	$14 870 392.95		
Capital deprication	23.3	$15 749 097.98	$15 749 097.98		
Average income tax	13.3	$8 989 828.46	$8 989 828.46		
Total Manufacturing Cost			**$181 156 222.70**	**$1 811 562 226.98**	
Total Cash flow				2 430 106 802.18	
RAL cost/Gasoline gallon equivalent (GGE)				**4.72**	**/GGE**
RAL cost/gallon				**4.73**	**/gal**

E.2 FAMEs costing

E.2.1 FAMEs via normal process

Fatty Acid Methyl Esters	Yeas to recover capital			10	
Lipid Production Capacity	GGE/yr		48 918 060.45	489 180 604.53	
	gal/yr		48 851 531.75	488 515 317.50	
Cost			**Per year**	**Total**	
Pretreatment and Conditioning			**$65 564 413**	**$65 564 413**	
Dryer		*$18 612 122*			
PT Flash/Solvent Dist Preheat HX		*$181 960*			
Pretreatment Feed-Effluent HX		*$864 140*			
Pretreatment Reactor		*$43 887 372*			
Pretreatment Rest of Plant		*$2 018 819*			
Fermentation and Distillation			**$19 560 322**	**$19 560 322**	
Ethanol Fermentor		*$5 683 052*			
Fermentor agitator		*$353 507*			
Fermentor cooler		*$48 777*			
Fermentor recirculation pump		*$26 485*			
Ethanol seed train agitator		*$27 093*			
Ethanol seed train agitator		*$44 808*			
1st ethanol seed fermentor		*$94 284*			
2nd "		*$145 802*			
3rd "		*$197 071*			
4th"		*$489 064*			
5th "		*$1 639 476*			
Fermentation: Balance of plant		*$752 450*			
Vent scrubber		*$350 977*			
Ethanol distilation equipment		*$5 522 345*			
Reboilers					
Rectification ondensor					
beer condenser		*$1 020 820*			
Beer column HX economiser					
Ethanol Molecular seive		*$3 164 311*			
Lipid Extraction and Solvent Recovery			**$71 480 821**	**$71 480 821**	
Extraction Column		*$63 479 220*			
Solvent Recovery Column		*$6 208 251*			
Solvent Recovery Reboiler		*$1 793 350*			
Product Purification and Upgrading			**$28 493 035**	**$28 493 035**	
Transesterification Unit		*$9 971 716*			
PSA Unit		*$11 887 836*			
Bleaching/Degumming Unit		*$6 633 483*			
Anaerobic Digestion/CHP			**$21 558 209**	**$21 558 209**	
Anaerobic Digestor		*$11 025 544*			
Generator set		*$10 532 666*			
Storage			**$4 549 792**	**$4 549 792**	
Diesel Product Storage Tank		*$1 742 898*			
Ethanol Product Storage Tank		*$1 149 444*			
Naphtha Glycerol		*$170 313*			
Firewater Storage Tank		*$728 838*			
Tankage BOP		*$758 299*			
Dried algae storage (3 months)					

Utilities			**$5 700 840**	**$5 700 840**	
Cooling Tower System		*$988 281*			
Plant Air Compressor		*$37 760*			
Chilled Water Package		*$677 303*			
CIP System		*$1 111 212*			
Cooling Water pump		*$300 617*			
Makeup Water Pump		*$13 975*			
Process water circulating pump		*$11 877*			
Instrument Air dryer		*$24 018*			
Plant Air Receiver		*$44 121*			
Process Water Tank 1		*$148 392*			
Steam Boiler HP Steam HRSG		*$576 610*			
Steam Boiler HP Steam HRSG		*$825 283*			
Steam Boiler HL Steam HRSG		*$875 083*			
HP Steam Economiser 1 HX		*$35 603*			
HP Steam Economiser 2 HX		*$30 705*			
Installed Equipment Cost			**$216 907 432**	**$216 907 432**	
Direct and Indirect Cost (48% of TCI)			**$200 222 245**	**$200 222 245**	
Total Capital Investment (TCI)			**$417 129 677**	**$417 129 677**	
Manufacturing Cost					
Feedstock	304.9645	$195 827 063.79	$195 827 063.79		
Sulphuric acid	3.1	$1 990 604.87	$1 990 604.87		
Ammonia	5	$3 210 653.02	$3 210 653.02		
Sodium methoxide catalyst	5.1	$3 246 571.52	$3 246 571.52		
Hexane	13.8	$8 861 402.34	$8 861 402.34		
Natural gas	8.5	$5 458 110.14	$5 458 110.14		
Methanol	12.9	$8 291 182.96	$8 291 182.96		
Other raw mats	3.2	$2 054 817.93	$2 054 817.93		
AD nutrients, digestate, and CO2 recylcle credit	-24.5	-$15 732 199.81	-$15 732 199.81		
Ethanol	-99.7		-$63 990 241.13		
Net electricity	-5	-$3 210 653.02	-$3 210 653.02		
Glycerol credit	-1.2	-$784 896.76	-$784 896.76		
Fixed cost	22	$14 126 873.30	$14 126 873.30		
Capital deprication	23.3	$14 961 643.09	$14 961 643.09		
Average income tax	13.3	$8 540 337.04	$8 540 337.04		
Total Manufacturing Cost			**$182 851 269.28**	**$1 828 512 692.80**	
Total Cash flow				2 470 206 606.70	
FAMEs cost/Gasoline Gallon Equivalent (GGE)				**5.05**	**/GGE**
FAMEs cost/gal				**5.06**	**/gal**

E.2.2 FAMEs via direct transesterification

Fatty Acid Methyl Esters via Direct Transesterification	Years to recover capital			10	
Lipid Production Capacity	GGE/yr		48 918 060.45	489 180 604.53	
	gal/yr		48 851 531.75	488 515 317.50	
Cost			**Per year**	**Total**	
Pretreatment and Conditioning			**$65 564 413**	**$65 564 413**	
Dryer		*$18 612 122*			
PT Flash/Solvent Dist Preheat HX		*$181 960*			
Pretreatment Feed-Effluent HX		*$864 140*			
Pretreatment Reactor		*$43 887 372*			
Pretreatment Rest of Plant		*$2 018 819*			
Fermentation and Distillation			**$19 560 322**	**$19 560 322**	
Ethanol Fermentor		*$5 683 052*			
Fermentor agitator		*$353 507*			
Fermentor cooler		*$48 777*			
Fermentor recirculation pump		*$26 485*			
Ethanol seed train agitator		*$27 093*			
Ethanol seed train agitator		*$44 808*			
1st ethanol seed fermentor		*$94 284*			
2nd "		*$145 802*			
3rd "		*$197 071*			
4th"		*$489 064*			
5th "		*$1 639 476*			
Fermentation: Balance of plant		*$752 450*			
Vent scrubber		*$350 977*			
Ethanol distilation equipment		*$5 522 345*			
Reboilers					
Rectification ondensor					
beer condenser		*$1 020 820*			
Beer column HX economiser					
Ethanol Molecular seive		*$3 164 311*			
Lipid Extraction and Solvent Recovery			**$8 001 601**	**$8 001 601**	
Extraction Column					
Solvent Recovery Column		*$6 208 251*			
Solvent Recovery Reboiler		*$1 793 350*			
Product Purification and Upgrading			**$28 493 035**	**$28 493 035**	
Transesterification Unit		*$9 971 716*			
PSA Unit		*$11 887 836*			
Bleaching/Degumming Unit		*$6 633 483*			
Anaerobic Digestion/CHP			**$21 558 209**	**$21 558 209**	
Anaerobic Digestor		*$11 025 544*			
Generator set		*$10 532 666*			
Storage			**$4 549 792**	**$4 549 792**	
Diesel Product Storage Tank		*$1 742 898*			
Ethanol Product Storage Tank		*$1 149 444*			
Glycerol		*$170 313*			
Firewater Storage Tank		*$728 838*			
Tankage BOP		*$758 299*			
Dried algae storage (3 months)					

Utilities			**$5 700 840**	**$5 700 840**	
Cooling Tower System		*$988 281*			
Plant Air Compressor		*$37 760*			
Chilled Water Package		*$677 303*			
CIP System		*$1 111 212*			
Cooling Water pump		*$300 617*			
Makeup Water Pump		*$13 975*			
Process water circulating pump		*$11 877*			
Instrument Air dryer		*$24 018*			
Plant Air Receiver		*$44 121*			
Process Water Tank 1		*$148 392*			
Steam Boiler HP Steam HRSG		*$576 610*			
Steam Boiler HP Steam HRSG		*$825 283*			
Steam Boiler HL Steam HRSG		*$875 083*			
HP Steam Economiser 1 HX		*$35 603*			
HP Steam Economiser 2 HX		*$30 705*			
Installed Equipment Cost			**$153 428 212**	**$153 428 212**	
Direct and Indirect Cost (48% of TCI)			**$141 626 042**	**$141 626 042**	
Total Capital Investment (TCI)			**$295 054 254**	**$295 054 254**	
Manufacturing Cost					
Feedstock	304.7	$195 657 195.20	$195 657 195.20		
Sulphuric acid	3.1	$1 990 604.87	$1 990 604.87		
Ammonia	5	$3 210 653.02	$3 210 653.02		
Sodium methoxide catalyst	5.1	$3 246 571.52	$3 246 571.52		
Hexane	13.8	$8 861 402.34	$8 861 402.34		
Natural gas	8.5	$5 458 110.14	$5 458 110.14		
Methanol	12.9	$8 291 182.96	$8 291 182.96		
Other raw mats	3.2	$2 054 817.93	$2 054 817.93		
AD nutrients, digestate, and CO2 recylcle credit	-24.5	-$15 732 199.81	-$15 732 199.81		
Ethanol	-99.7		-$63 990 241.13		
Net electricity	-5	-$3 210 653.02	-$3 210 653.02		
Glycerol credit	-1.2	-$784 896.76	-$784 896.76		
Fixed cost	22	$14 126 873.30	$14 126 873.30		
Capital deprication	23.3	$14 961 643.09	$14 961 643.09		
Average income tax	13.3	$8 540 337.04	$8 540 337.04		
Total Manufacturing Cost			**$182 681 400.69**	**$1 826 814 006.88**	
Total Cash flow				2 334 055 086.79	
FAMEs cost/Gasoline Gallon Equivalent (GGE)				**4.77**	**/GGE**
FAMEs cost/gal				**4.78**	**/gal**