

Desulphurisation of fine coal waste tailings using algal lipids

Kudzai Chiodza¹, Susan TL Harrison¹, Marijke A Fagan-Endres¹

¹Centre for Bioprocessing Engineering Research (CeBER), Department of Chemical Engineering, University of Cape Town, South Lane, Upper Campus, Rondebosch, Cape Town, 7700.

CHDGOD002@myuct.ac.za, sue.harrison@uct.ac.za, marijke.fagan-endres@uct.ac.za

Abstract

Flotation desulphurisation experiments were performed using algal lipids (raw algal lipids (RALs) and their derivatives, fatty acid methyl esters (FAMES)) as biocollectors for recovering saleable clean coal from waste. The results from batch flotation experiments on a coal sample from a site in the Waterberg region in South Africa were evaluated in terms of overall yield, recoveries (combustibles, ash and sulphur) and product quality (ash and sulphur content). The product yield using the lipids was between 34 and 35%, with a combustible matter recovery between 40 and 50%. The lipids reduced the ash content of the discards from 49% to less than 27%, and the sulphur content from 5.7% to less than 2.8%. These results were comparable to those obtained using oleic acid under similar conditions.

Keywords: Algal lipids, fatty acid methyl esters (FAMES), oleic acid, coal, bioflotation

Introduction

The amount of coal waste generated annually in South Africa is estimated to be around 60 million tonnes (Chamber of Mines Of South Africa 2018, Department of Energy South Africa 2018). This has resulted in over a billion tonnes of coal waste accumulated in mine dumps in South Africa to date. Apart from its land footprint, the coal waste contains pyritic sulphur which, when oxidised, results in the formation of acid mine drainage (AMD) (Kazadi Mbamba et al. 2012). AMD, once started, has been known to persist for decades, resulting in the contamination of surface and ground water.

Various methods have been developed to prevent AMD forming. One such technique is the two-stage coal flotation for desulphurisation, developed at the University of Cape Town (Harrison et al. 2010, Kazadi Mbamba 2011). The first separation stage recovers clean coal using oleic acid as the collector, and the second stage recovers pyrite using the potassium amyl xanthate (PAX) collector. Applying the two-stage flotation process to coal cleaning showed that it was technically feasible to recover valuable coal from waste tailings (Iroala 2014, Kazadi Mbamba et al. 2012). An economic evaluation of the overall process (Jera 2013) showed greatest sensitiv-

ity to operating costs, primarily the reagent costs, including the oleic acid reagent used in the first stage of the process. The aim of this work was to investigate alternative reagents that will enhance the process economics, while being environmentally benign.

Algal lipids, raw or modified into methyl esters, have physical and chemical properties that are similar to commonly used coal collectors. They have the carboxyl group (-COOH), for the raw algal lipids (RALs) are triglycerides containing three long chain fatty acids (C12 – C22) linked by ester bonds to glycerol. The fatty acid methyl esters (FAMES) are comprised of the single fatty acid chain linked to an alcohol via the ester bond. Both have polar heads and hydrophobic hydrocarbon tails of C12 to C22. These functional groups that make algal lipids of interest in coal cleaning by froth flotation.

Materials and methods

The algal lipids used in this evaluation were extracted from *Scenedesmus* sp. The algae was subcultured in 500 mL aerated and illuminated Erlenmeyer flasks before inoculating into 3.2 L batch photobioreactors. The reactor design, inoculation and cultivation procedure were carried out according to Langley et al. (2012). The algae culture in the airlift



reactors was carried out for at least 25 days to maximise lipid production, based on a recommendation by Mandal and Mallick (2009). The algal suspension was harvested on day 30 of each batch and dewatered using high speed centrifugation (Beckman Coulter Avanti® J-E with JA-10 rotors) at $10\,000 \times g$ for 15 minutes. Raw algal lipids (RALs) were extracted using the Axelsson and Gentili (2014) method. A portion of the dewatered algae was used to produce fatty acid methyl esters (FAMES), which are products of transesterification, using the protocol detailed by Griffiths et al. (2010). The RALs and FAMES were recovered from the solvent phase using a rotary evaporator (Heidolph Hei-VAP Value) and stored in absolute ethanol. Ethanol was used as the carrier solvent for the lipids since it does not interfere with the flotation process, i.e. it does not have any collecting or frothing properties (Klassen and Vlasova 1967).

Fine coal waste from the Waterberg area, South Africa, was used for the coal recovered by batch flotation as the first stage of the two-stage desulphurisation process. Samples were prepared by representative sampling and size reduction as outlined by Kazadi Mbamba et al. (2012). The freshly milled coal had a particle size distribution of 11.8% +212 μm , 31.6% +150 μm to -212 μm , 19.0% +106 μm to -150 μm , 11.4% +75 to -106 μm , 20.8% +25 to -75 μm and 5.5% -25 μm . About 56% of the particles passed through the 150 μm sieve. The sample comprised 49.0% ash and 5.71% sulphur.

In each batch flotation experiment, 34 g milled fine coal waste was added to water at a pH of 2.7 (the natural pH of the coal waste sample) in a 500 mL Leeds-type flotation cell

to produce 6% solids loading. The aeration rate and impeller speed were set at 5 L/min (10 vvm) and 170 rpm, respectively, for all experiments. All experiments used a methyl isobutyl carbinol (MIBC) frother at a dosage of 0.28 kg/t. For the control experiments, oleic acid was used as the collector at a dosage of 2.79 kg/t, based on the results of Kazadi Mbamba et al. (2013). Collector and frother conditioning times were 5 min and 1 min, respectively.

For each batch flotation experiment, the following samples were taken: 2 mL feed slurry; concentrate samples after 0.5 min, 1 min, 2 min and 5 min operation and the residual tails at the end of experiment. These samples were filtered and dried at 80 °C to constant mass (for at least 24 hours), weighed and analysed for ash and sulphur content. Ash analysis was performed according to the South African National Standard SANS 131:2011 and sulphur analysis was done using the LECO S632 (LECO Corporation 2010).

The results obtained were used to determine the following performance indicators: yield – the total mass recovery to the concentrate, combustibles recovery – the amount of combustibles material in the concentrate expressed as a percentage of the combustibles material in the feed, ash recovery – the percentage of ash in the feed that is recovered in the concentrate, sulphur recovery – the percentage of sulphur in the feed that is recovered in the concentrate, and flotation efficiency index – the ability of a collector to effect separation between combustible material and ash. The determination of these is detailed in Equations 1 to 4:

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

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

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

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

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



where Y is the yield (%), R_C is combustibles recovery (%), R_A is the ash recovery (%), R_S is sulphur recovery (%), M_C is the mass of concentrate (g), M_F is the mass of the feed (g), T_A is tails ash composition (%), F_A is feed ash composition (%), C_A is concentrate ash composition (%), C_S is concentrate sulphur (%), and F_S is feed sulphur (%).

Results and discussion

Table 1 summarises the results obtained using RALs, FAMEs and oleic acid on the coal waste from the Waterberg area. Under the

conditions of investigation, the summary shows that there was no statistically significant difference in performance of the two bioflotation reagents in comparison to oleic acid.

In terms of flotation yield and recovery, both RALs and FAMEs gave similar results as oleic acid at the same dosage of 2.79 kg/t (Figure 1). Both reagents recovered about 34% of the waste coal with an increase in combustible material from 52% to 74% and 76% for RALs and FAMEs, respectively, compared to 77% for oleic acid.

Table 1 Collector performance for flotation of sample from the Waterberg area at a collector and MIBC dose of 2.79 and 0.28 kg/t, respectively. Feed had 49.0% ash, 5.71% sulphur.

Collector	Yield (%)	Recovery (%)	Ash (%)		Sulphur (%)	
			Product	Tails	Product	Tails
FAMEs	35.3 ± 0.65	50.1 ± 1.48	24.4 ± 0.18	60.8 ± 1.04	2.76 ± 0.26	5.13 ± 0.17
RALs	34.1 ± 1.18	47.1 ± 1.65	26.1 ± 0.30	59.8 ± 0.20	2.56 ± 0.33	4.68 ± 0.08
Oleic acid	34.3 ± 0.58	50.6 ± 1.15	23.5 ± 0.72	58.6 ± 2.28	2.41 ± 0.20	4.75 ± 0.14

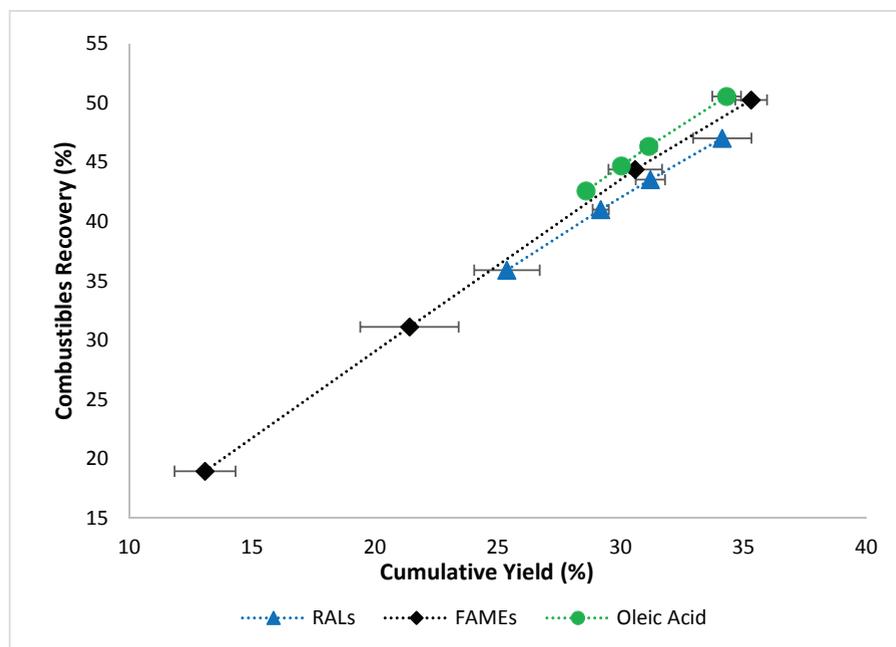


Figure 1 Cumulative yield vs combustibles recovery to the concentrate for flotation of Waterberg discards at a collector dosage of 2.79 kg/t and MIBC dosage at 0.28 kg/t. All points are an average of three experiments. The lowest yield point for each reagent is for concentrate recovered after 0.5 min, subsequently increasing for concentrate recovered at 1 min, 2 min and finally 5 min.



The similarities in performance between the algal lipids and the oleic acid is attributable to the similarities in the chemical structure of the three reagents. As shown in Figure 2, all three reagents have a polar head and a hydrocarbon tail that is hydrophobic.

Figure 3 shows that the selectivity of both bioflotation reagents towards sulphur is similar under the conditions tested. When compared to the algal lipids, the oleic acid showed better sulphur rejection, despite having a higher ash recovery than the two bioreagents. This difference in selectivity is attributable to the chemical composition of the reagents. RALs and FAMEs contain a mixture of molecules, in different proportions, with carbon chain lengths ranging from 12 carbon atoms to 22, compared to oleic acid which is a pure reagent. The molecules with a lower number of carbon atoms are less hydrophobic and easily attach to hydrophilic pyrite particles. This is supported by Han (1983) who pointed out that lower molecular weight collectors are less specific than larger molecular weights.

Figure 4 shows the results of flotation experiments that were carried out at varying

biocollector dosages. The flotation efficiency index (FEI), which is the difference between combustibles and ash recovery, gives an indication of how efficient a reagent is at separating wanted material from unwanted material. It was observed that increasing the biocollector dosage increased the FEI. This is because increasing the concentration of the biocollector in solution increases the chances of hydrophobic interactions between the biocollector and the coal particles. This is supported by the collision theory presented by Demirbas and Balat (2004) where they described the flotation rate as a probability function of collector concentration, aeration rate and other parameters.

It was, however, noted that the increase in FEI with increase in collector dosage was coupled with a decrease in selectivity, with respect to sulphur recovery. For example, at a dosage of 1.20 kg RALs/t, there was about 24% combustibles recovery, 9.3% ash recovery and 12% sulphur recovery, while at a dosage of 3.70 kg RALs/t the coal recovered had a combustibles recovery of 53%, ash recovery of 25% and 34% sulphur recovery.

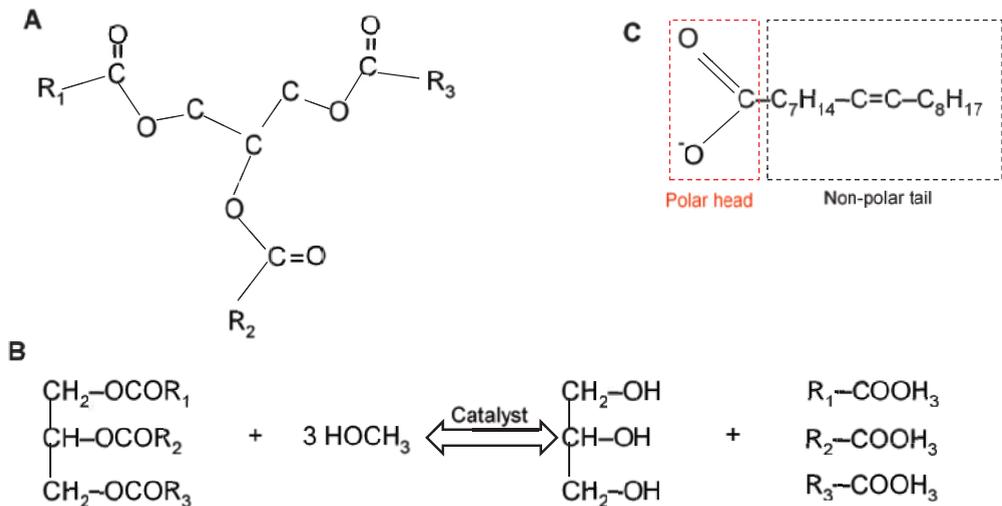


Figure 2 A - a triglyceride representing RALs, B - transesterification of a triglyceride to form a fatty acid methyl esters (FAMEs), C - An oleate ion, formed from the ionisation of oleic acid. The non-polar portions of RALs and FAMEs are represented by R_x where x is 1, 2 or 3. The R_x group can be either saturated (no double bonds in the chain length) or saturated.



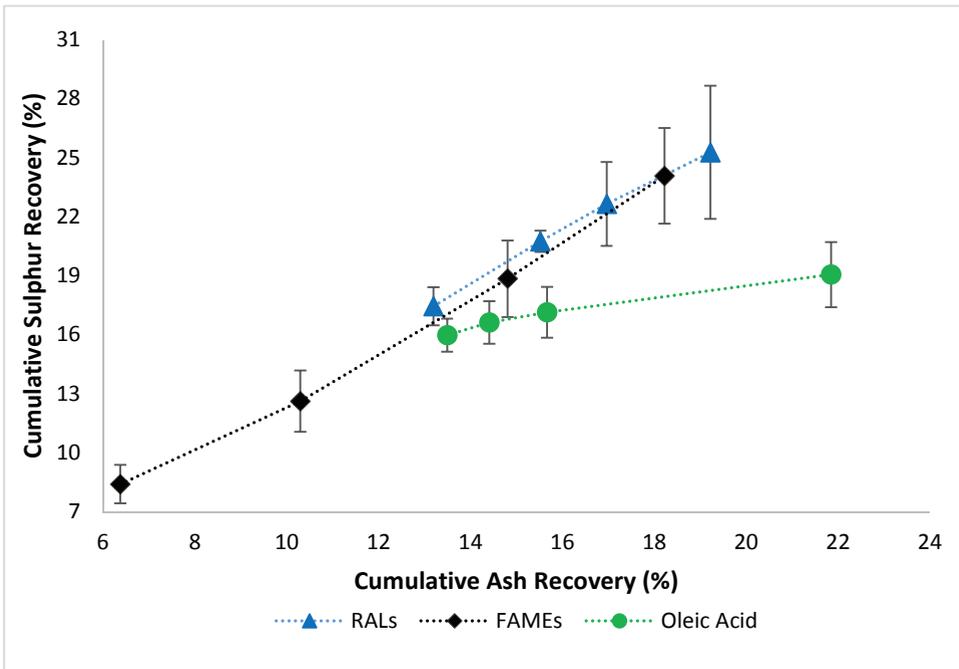


Figure 3 Ash recovery vs sulphur recovery to the concentrate for Waterberg discards flotation at a collector dosage of 2.79 kg/t and MIBC dosage of 0.28 kg/t.

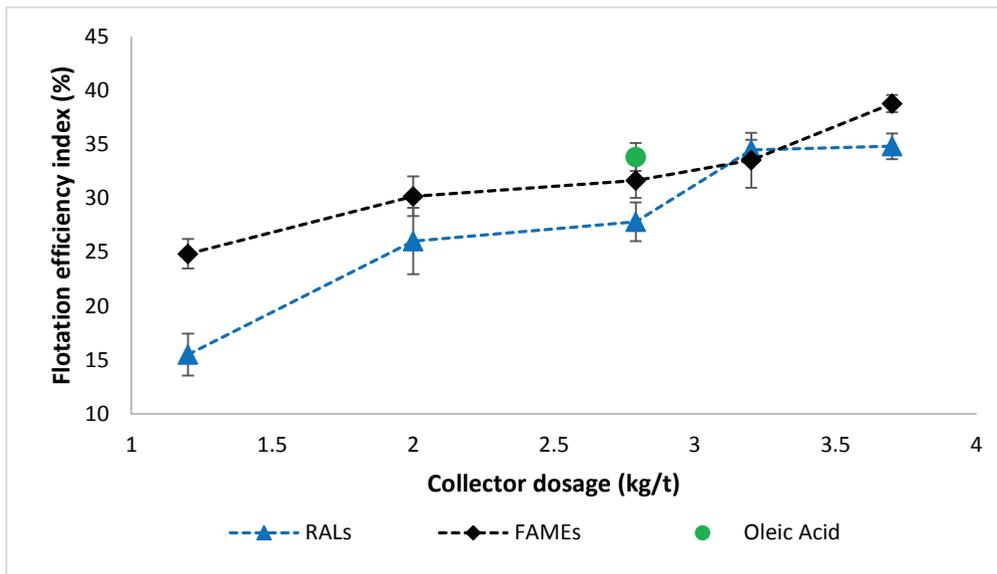


Figure 4 Flotation efficiency index results as a function of biocollector dosage for discards from the Waterberg area. RALs had a low FEI at low collector dosage (1.2 kg/t) compared to FAMEs.



Conclusions

The results proved that biologically derived products have the potential to replace chemically derived collectors for the desulphurisation of fine coal waste by froth flotation. The two bioflotation reagents successfully recovered a combustible coal fraction with reduced ash and sulphur content. The ash content was reduced by about 22.6%, from 49% in the feed to 26.4% in the product coal concentrate, and sulphur was reduced from 5.7% to below 3% in the product coal concentrate. The ash and sulphur were concentrated in the mineral tailings which would enter a second flotation stage for desulphurisation. Despite having the same coal recoveries as oleic acid, the two bioflotation reagents were not as selective as oleic acid with regards to sulphur. However, with further optimisation, the process may be improved to give even better yields, recoveries and selectivity.

A key benefit of biological reagents such as algal lipids is their environmental sustainability, whereas most of the collectors currently used have environmental risks associated with them. A preliminary economic evaluation on the production of the two bioreagents (not presented here) showed that they were about 20% cheaper to produce compared to oleic acid purchase (in 2011 costs), which makes them an economically viable option at the prevailing low coal prices.

Acknowledgements

The authors extend their gratitude to following for their generous financial support: the Water Research Commission (WRC) or their support of WRC K5/2389, Council for Scientific Industrial Research (CSIR) for postgraduate scholarship funding of KC and the Department of Science and Technology (DST) and National Research Foundation (NRF), South Africa for their support of the national SARChI research chair in bioprocess engineering (UID 64788). Further we are grateful to the Centre for Minerals Research (CMR), UCT for use of their laboratory and equipment and to Shireen Govender and Juarez Amaral Filho for technical advice.

References

- Axelsson, Martin, and Francesco Gentili. 2014. “A Single-Step Method for Rapid Extraction of Total Lipids from Green Microalgae.” *PLoS ONE* 9 (2):6. doi: doi:10.1371/journal.pone.0089643.
- Chamber of Mines Of South Africa. 2018. “Coal.” accessed 25 January. <http://www.chamberofmines.org.za/sa-mining/coal>.
- Demirbas, Ayhan, and Mustafa Balat. 2004. “Coal Desulfurization via Different Methods.” *Energy Sources* 26 (6):10. doi: 10.1080/00908310490429669.
- Department of Energy South Africa. 2018. “Coal Resources: Discards.” accessed 25 January. http://www.energy.gov.za/files/esources/coal/coal_discards.html.
- Griffiths, Melinda J., Robert P. van Hille, and Susan T. L. Harrison. 2010. “Selection of Direct Transesterification as the Preferred Method for Assay of Fatty Acid Content of Microalgae.” *Lipids* 45 (11):8. doi: 10.1007/s11745-010-3468-2.
- Han, Choon. 1983. “Coal Cleaning by Froth Flotation.” PhD, Chemical Engineering, Iowa State University (8476).
- Harrison, S. T. L., J. L. Broadhurst, R. P. van Hille, O. O. Oyekola, C. Bryan, A. Hesketh, and A. Opitz. 2010. A Systematic Approach to Sulphidic Waste Rock and Tailings Management to Minimise ARD Formation.
- Iroala, Onyinye Judith. 2014. “Combining Froth Flotation With Reflux Classification to Mitigate ARD Generating Potential of the Waterberg and Witbank Coal Ultrafines Via Sulfide Removal.” Master of Science in Engineering (Chemical Engineering), Chemical Engineering, University of Cape Town.
- Jera, Melody Kudzai. 2013. “An Economic Analysis Of Coal Desulphurisation By Froth Flotation To Prevent Acid Rock Drainage (ARD) And An Economic Review Of Capping Covers And Ard Treatment Processes.” Master of Science in Engineering (Chemical Engineering), Chemical Engineering, University of Cape Town.
- Kazadi Mbamba, Christian. 2011. “Using Froth Flotation To Mitigate Acid Rock Drainage Risks While Recovering Valuable Coal From Ultrafine Colliery Wastes.” Master of Science in Engineering (Chemical Engineering), Chemical Engineering, University of Cape Town.



- Kazadi Mbamba, Christian, J.-P. Franzidis, S.T.L. Harrison, and J.L. Broadhurst. 2013. “Flotation of Coal and Sulphur from South African ultra-fine colliery wastes.” *The Journal of the Southern African Institute of Mining and Metallurgy* 113 (2013):8.
- Kazadi Mbamba, Christian, S.T.L. Harrison, J.P. Franzidis, and J.L. Broadhurst. 2012. “Mitigating Acid Rock Drainage Risks While Recovering Low-sulfur Coal From Ultrafine Colliery Wastes Using Froth Flotation.” *Minerals Engineering* 29 (2012):9. doi: 10.1016/j.mineng.2012.02.001.
- Klassen, V. I., and N. S. Vlasova. 1967. “The Effect of Reagents in Coal Flotation.” *Fiziko-Tekhnicheskie Problemy Razrabotki Poleznykh Iskopaemykh* 1 (5):7.
- Langley, N, S. T. L. Harrison, and R. P van Hille. 2012. “The Effect of CO₂ Availability on the Growth of *Chlorella Vulgaris*.” *Biochemical Engineering Journal* 68:6.
- LECO Corporation. 2010. “Sulfur and Carbon in Coal, Coke, and Graphite.” Last Modified October 2010, accessed 2 May. http://www.leco.co.za/wp-content/uploads/2012/02/SC632_S-C_COAL_COKE_GRAPHITE_203-821-304.pdf.
- Mandal, Shovon, and Nirupama Mallick. 2009. “Microalga *Scenedesmus Obliquus* as a Potential Source for Biodiesel Production.” *Applied Microbiology and Biotechnology* 84 (2):11. doi: 10.1007/s00253-009-1935-6.

