Evaluating the Potential of Algal Pyrolysis Bio-Oil as a Low-Cost Biodiesel for use in Standby Generators for home Power Generation

Bothwell Nyoni^{*}, Shanganyane P. Hlangothi^{*‡}

*Department of Chemistry, Faculty of Sciences, Nelson Mandela University, Gqeberha, South Africa

(s215391977@mandela.ac.za, percy.hlangothi@mandela.ac.za)

[‡]Corresponding Author; Bothwell Nyoni, Department of Chemistry, Faculty of Sciences, Nelson Mandela University, Gqeberha, South Africa, Tel: +27 41 504 2574,

Fax: +27 41 504 3281, s215391977@mandela.ac.za

Received: 02.12.2022 Accepted: 30.12.2022

Abstract- Because of unpredicted weather patterns, households relying on power generation via solar systems are most often equipped with standby bio/diesel or gasoline generator systems. Electricity generation from solar systems is regarded as carbon neutral, however, the use of fossil fuels in standby generator systems used during solar outages compromises the carbon neutral-ness. In this study, an assessment of pyrolysis oils synthesized via a simple pyrolysis process is performed to determine the possibility of using the oil as a low-cost biodiesel fuel for standby generators used in home solar power systems. GCMS analysis revealed that the bio-oil was rich in fatty acids (6.3 - 10.7 %), alcohols (7.1 - 13.5 %) and fatty acid esters (11.3 - 23.7 %). The potential biodiesel content, i.e., the total amount of fatty acid esters and, alcohols and fatty acids that have a possibility of being further processed via transesterification reactions to generate more free fatty acid esters, is in the range 36.28 - 50.21 %.

Keywords Algae, biodiesel, biomass, fatty acid esters, pyrolysis.

1. Introduction

One of the main reasons why nations are investing in solar systems is the idea of moving away from energy sources that are associated with green-house gas (GHG) emissions. GHG emissions are known to be the major culprits that contribute to the damage of the atmosphere. Furthermore, due to the need to use energy in an efficient manner, modern homes are now equipped with smart-grid systems. However, the major drawback associated with smart-grid solar photo-voltaic (PV) systems is that the electricity generated most often depends on weather patterns. It is common knowledge that during overcast conditions, solar PV systems do not generate sufficient electricity. Considering this, it is now common practice in most households especially in developing countries to equip solar PV systems with standby diesel or gasoline generators. Other setups make use of wind turbine systems for standby power. However, the prolonged use of diesel or gasoline generators contributes to GHG emissions. Therefore, there is need to evaluate the use of other cleaner fuel sources such as biodiesel. It is now common knowledge that biodiesel is a type of a diesel derived from animal and plant matter consisting of long chain fatty acid esters; therefore, it is renewable. It can be

synthesized from a wide range of feedstocks like recycled cooking oil, plant matter and animal fats. Biodiesels have calorific value that almost equivalent to that of commercial diesel.

Coal-to-liquids (CTL) is a technology that is currently used in South Africa's Sasol plant to produce supplementary liquid fuels at commercial scale from locally mined coal [1]. Other institutions have performed assessments of CTL technology on other sources such as biomass in a bid to generate fuels in a carbon neutral and sustainable manner. The ultimate goal is the synthesis of fuels that have the potential of significantly reducing the net GHG emissions. Pyrolysis processes are arguably the simplest CTL technologies compared to liquefaction. The synthesis of liquid fuels via pyrolysis most often involves the thermal decomposition of a feedstock in an inert environment, the vapours evolved are condensed to form liquid phase. The liquid formed contains aqueous and oily phases which can be separated by decanting or solvent extraction techniques [1-3]. The use of biomass as a feedstock in pyrolysis technologies has gained huge research focus because of its sustainability. The so-called biomass-to-liquids (BTL) processes based on pyrolysis technology have been

INTERNATIONAL JOURNAL of SMART GRID B. Nyoni and S. Hlangothi, Vol.12, No.4, December, 2022

extensively studied; bio-oil yields of 30 - 60 % have been reported in literature [3-5]. Furthermore, there is ongoing research in evaluating the possibility of using the bio-oil or blending it with available petroleum-based fuels for use in internal combustion engines [6-7]. In terms of capital costs, pyrolysis systems are expected to have considerably low costs compared to other systems like gasification and liquefaction. This is because pyrolysis systems are easy to setup and operate [8]. They consist of a pyrolysis reactor, condensation train, gas cleaning and oil upgrading downstream processes. A block diagram of the perceived pyrolysis system is given in Fig. 1.

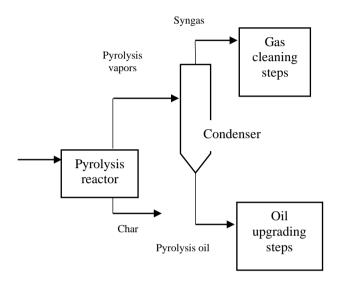


Fig. 1. Schematic of pyrolysis process

In this study, a chemical assessment of bio-oils obtained from two types of algae, i.e., Scenedesmus and Spirulina microalgae was performed with a view of using them as liquid fuels for standby generators in home power generating systems. There is a number of analyses that can be performed to a sample in order to ascertain its suitability as a fuel. Chemical analysis is the pre-requisite. Algae pyrolysis oil is fast becoming a fuel source of research focus. Because of fast growth rates associated with algae, it appears to be the only source of renewable fuels that can satisfy the current global demand [9]. Previous works have focused on replacing the current commercial diesel being used with biodiesel. However, this is a huge undertaking considering the amount of biomass that will need to be processed annually. In this study, a more realistic solution of replacing commercial diesel used in households is presented. As a result, household generators will be designed to take in biodiesel from biomass hence helping towards the achievement of clean energy for every household.

2. Experimental

2. 1. Materials and Methods

The bio-oils used in this study were obtained from experiments described in our previous studies [10-12]. The

main characterization of the bio-oil was performed via GCMS analysis. The GCMS instrument was an Agilent 7890A GC system coupled with an Agilent 5975C mass spectrometer (Agilent Technologies, USA) equipped with a fused silica capillary column SLB-5ms (Supelco, Sigma-Aldrich, USA). The capillary column was 30 m in length, with a diameter of 250 um and film thickness of 0.25 um. Helium injected at 250 °C was used as a carrier gas at a flow of 1.8 ml/min. During operation, the GC oven temperature was held for at 50 °C for 2 minutes and raised to 300 °C at a heating rate of 10 °C/min, the final temperature was then maintained for 4 min. A split ratio of 20:1 was used for all samples and the mass spectrometer was operated in full-scan mode; a of m/z range of 45 - 600 was scanned. Standard mass spectra with electron ionization voltage set at 70 eV were recorded. The eluted compounds were identified by matching with the in-built NIST library.

3. Results and Discussion

3. 1. Chemical Composition of Bio-Oil

The advantage of using GCMS instruments in characterization techniques is that depending on the methods and solvents used, almost all individual compounds in a sample can be detected and listed. GCMS analysis revealed that bio-oil is a complex mixture of a large number of organic compounds, however the complex mixture is dominated by three major compound groups, i.e., fatty acids, fatty acid esters and alcohol. The major compounds detected were palmitic acid, citronellyl iso-valerate and phytol. The compositions of the major compounds are given in Table 1. It is clear that the composition of algal bio-oil is dominated by citronellyl iso-valerate which is an indication that the bio-oil can be used in place of biodiesel. Commercially available biodiesels are composed of free fatty acid esters and have an advantage of low emissions compared to conventional petroleum diesel. Citronellyl iso-valerate is a fatty acid ester of molecular weight 240 g/mol and gross calorific value of approximately 39 MJ/kg [12]. The presence of palmitic acid and phytol within the bio-oil presents an opportunity of synthesizing more fatty acid esters via esterification processes. Palmitic acid is a saturated fatty acid which has the potential of being used in the synthesis of biodiesel whereby fatty acid methyl esters are synthesised by transesterification reactions. Phytol is a diterpene alcohol which is released when chlorophyl breaks down at high temperature. Previous studies have shown that catalytic cracking of phytol can produce gasoline with superior properties such as a high-octane number [13, 14].

Table 1. Composition of major compounds found in oil

	Palmitic acid	Citronellyl iso-valerate	Phytol
	(%)	(%)	(%)
Spirulina algae oil	10.7	11.3	7.07
Scenedesmus algae oil	6.35	23.7	13.5

3.2. Potential as biodiesel fuel

Biodiesel is composed of fatty acid (methyl) esters, which are normally synthesised via the transesterification reactions involving fats and alcohols. Therefore, it is important to evaluate the fatty acid, alcohols and fatty acid esters profile for algal oil in order to have an insight on the potential of algae oil as a biodiesel fuel. Table 2 presents a fatty acid, alcohols and esters profile of algal oil. It can be seen that the fatty acid ester content of algal oil that was used for this study varies in the range 11.26 – 23.71 %. Heterogeneous esters content is in the range 3.34 - 4.78 %. Alcohols and fatty acids which have the potential of undergoing esterification reactions to produce more fatty acids amount to 9.54 - 16.81 and 6.35 - 10.70 %, respectively. The total potential biodiesel content of algae oil samples is in the range 36.28 - 50.21 %. Previous studies that have managed to synthesise commercial grade biodiesel reported higher fatty acid content [15, 16]. In the works of Jambulingam et al. [15], the reported fatty acid concentration in biodiesel synthesized from waste animal fat was 93.2 %. Also, Sani et al. [16] synthesized biodiesel from water-melon seeds that had a fatty acid content of 88.8 %. The results presented in Table 2 suggest that algal oil can be further processed or upgraded to obtain commercial grade biodiesel that can be used in internal combustion engines that drive stand-by generators. There are several upgrading techniques that have been presented by researchers [17, 18]. Furthermore, there is ongoing research on the use of unprocessed pyrolysis oils in internal combustion engines [19, 20].

Table 2. Fatty acid, alcohol and ester profile for algal oil

Compounds	Molecular formula	Proportion (%)	
	Torrifura	Spirulina	Scenedesmus
Cyclopropane carboxylic acid-2- pentyl, ethyl(-2-butylthio) ester	$C_{15}H_{28}O_2S$	1.44	-
1,4-Benzenediol, 2,3,5-trimethyl-	$C_9H_{12}O_2$	1.22	1.64
Citronellyl iso-valerate	$C_{15}H_{28}O_2$	11.26	23.71
Citronellol	$C_{10}H_{20}O$	194	1.67
Phytol	$C_{20}H_{40}O$	7.07	13.49
L-Proline, N-valeryl-, hexadecyl ester	$C_{26}H_{49}NO_3$	3.34	2.26
Palmitic acid	$C_{16}H_{32}O_2$	10.70	6.35
Cyclohexane ethanol, 3-hydroxy- beta.,4-dimethyl-	$C_{10}H_{20}O_2$	1.25	1.09
Total pure ester content		11.26	23.71
Total heterogeneous ester content		4.78	3.34
Total alcohol content		9.54	16.81
Total fatty acid content		10.70	6.35
Total potential biodiesel content		36.28	50.21

Majority of other sources used in previous studies have a major disadvantage of low crop yields or biodiesel yields.

Table 3 shows a comparison of algae with different plant crops that have been evaluated in literature. It is clear that for algae, less amount of land is needed to produce the same amount of bio-oil compared with other types of biomass. Furthermore, majority of algal plants are not food sources for animals and human beings.

Table 3. Comparison of algae with other biomass types

Biomass	Bio-oil yield	Bio-oil yield ^[28]
	(L/kg)	(L/ha)
Algae	$40-60^{\ [10,\ 21]}$	1000000
Castor seeds	64.6 [22]	1413
Coconut shell	$38 - 44^{\ [23]}$	2689
Palm	$36 - 42^{\ \ \text{[24]}}$	5950
Safflower	27 - 35 [25]	779
Soybean cake	43 [26]	446
Sunflower	34 [27]	952

4. Conclusion

This work attempted to demonstrated that algae pyrolysis oil has a potential of being used as a low-cost fuel for household standby generators that are normally used during solar outage. The work focused on studying the chemical composition and comparing it with commercial grade biodiesel that was synthesized by other researchers. Results of chemical analysis suggest that there is a significant amount of biodiesel compounds in algal oil and upgrading techniques can be applied in order to obtain commercial grade biodiesel. A further comparison of the potential of algae against other biomass sources presented in various literature revealed that algae has the highest crop yield per hectare. Studies on the evaluation of some physico-chemical properties, that were beyond the scope of this work, need to be done in order to ascertain whether algal pyrolysis oil or any fuels derived from the oil are suitable for use in the internal combustion engines of the actual generators. Therefore, this study lays a foundation for future work on algal biomass derived biodiesel.

References

- M. Hook, and K. Aleklett, "A review of coal-to-liquids fuels and its coal consumption", *Int. J. Energy Res.*, vol. 34, pp. 848-864, 2009.
- [2] A. Bridgwater, *Fast pyrolysis of biomass for the production of liquids*, Birmingham: Woodhead, 2013, ch. 8.
- [3] V. Dhyani, and T. Bhaskar, "A comprehensive review on the pyrolysis of lignocellulosic biomass," *Renew. Energy*, vol. 129, pp. 695–716, 2018.
- [4] A.V. Bridgwater, and G.V.C. Peacock, "Fast pyrolysis processes for biomass", *Renew. Sustain. Energy Rev*, vol. 4, pp. 1–73, 2000.
- [5] A.V. Bridgwater, P. Carson, and M. Coulson, "A comparison of fast and slow pyrolysis liquids from mallee," *Int. J. Glob. Energy Issues*, vol. 27, pp. 204–216, 2007.

INTERNATIONAL JOURNAL of SMART GRID

B. Nyoni and S. Hlangothi, Vol.12, No.4, December, 2022

- [6] R.L. Graves, S.S. Lestz, S.S. Trevitz, and M.D. Garney, "Screening tests of coal pyrolysis liquids as diesel fuel extenders", SAE Transactions, vol. 93, pp. 665-675, 1984.
- [7] S.M. Auti, and W.S. Rathod, "Effect of hybrid blends of raw tyre pyrolysis oil, karanja biodiesel and diesel fuel on single cylinder four strokes diesel engine", *Energy Reports*, vol. 7, pp. 2214–2220.
- [8] N. Thibanyane, P. Agachi and G. Danha, "Effects of biomass/coal pyrolysis parameters on the product yield", *Procedia Manufacturing*, vol. 3, pp. 477–487, 2019.
- [9] A. Demirbas, "Use of algae as biofuel sources", *Energy Convers.* Manage, vol. 51, pp. 2738–2749.
- [10] B. Nyoni, and S. Hlangothi, "Intermediate pyrolysis of Scenedesmus microalgae in a rotary kiln pyrolyser: Effect of temperature on bio-oil yields and composition", *Biomass Convers. Bioref.*, vol. xx, pp. xxxx, 2022.
- [11] B. Nyoni, and S. Hlangothi, "Evaluation of the thermal decomposition behaviour of algal biomass in a rotary kiln pyrolyser", 9th International Renewable and Sustainable Energy Conference (IRSEC), Morocco, pp. 1–4, 23–27 November 2021.
- [12] B. Nyoni, B.M. Hlabano-Moyo, and S.P. Hlangothi, "Analysis of pyrolysis process for Spirulina and Scenedesmus microalga in a rotary kiln and the composition of their resultant bio-oils", *Int. J. Renew. Energy Res.*, vol. 12, pp. 1383–1392, 2022.
- [13] S. Kraub, and W. Vetter, "Phytol and phytyl fatty acid esters: Occurrence, concentrations and relevance", *European J. Lipid Sci. Technol*, vol. 120, pp. 1–14, 2018.
- [14] N.I. Tracy, D.W. Crunkleton, and G.L. Price, "Gasoline production from phytol", *Fuel*, vol. 89, pp. 3493–3497, 2010.
- [15] R. Jambulingam, V. Shankar, S. Palani, and G.R. Srinivasan, "Effect of dominant fatty acid esters on emission characteristics of waste animal fat biodiesel in CI engine", *Frontiers Energy Res*, vol. 7, pp. 1– 13, 2019.
- [16] S. Sani, M.U. Kaisan, D.M. Kulla, A.I. Obi, A. Jibrin, and B. Ashok, "Determination of physico chemical properties of diesel from *Citrullus lanatus* seeds oil and diesel blends", *Ind. Crops Products*, vol. 122, pp. 702–708, 2018.

- [17] T. Sundqvist, A. Oasmaa, and A. Koskinen, "Upgrading fast pyrolysis bio-oil quality by esterification and azeotropic water removal", *Energy Fuels*, vol. 29, pp. 2527–2534, 2015.
- [18] H. Yang, J. Yao, G. Chen, W. Ma, B. Yan, and Y. Di, "Overview of upgrading of pyrolysis oil of biomass", *Energy Procedia*, vol. 61, pp. 1306–1309, 2014.
- [19] C. Wongkhorsub, and N. Cindaprasert, "A comparison of the use of pyrolysis oils in diesel engine", *Energy Power Eng.*, vol 5, pp. 350– 355, 2013.
- [20] I. Kalargaris, G. Tian, and S. Gu, "Combustion, performance and emission analysis of a DI diesel engine using plastic pyrolysis oil", *Fuel Process. Technol.*, vol. 157, pp. 108–115, 2017.
- [21] Z. Hu, Y. Zheng, F. Yan, B. Xiao and S. Liu, "Bio-oil production through pyrolysis of blue-green algae blooms (BGAB): Product distribution and bio-oil characterisation", *Energy*, vol 52, pp. 119– 125, 2013.
- [22] R.K. Singh and K.P. Shadangi, "Liquid fuel from castor seeds by pyrolysis", *Fuel*, vol 90, pp. 2538–2544, 2011.
- [23] E.G. Sandaram and E. Natarajan, "Pyrolysis of coconut shell: An experimental investigation", *The J. Eng. Res.*, vol 6, pp. 33–39, 2009.
- [24] C.K. Ling, et al., "Yield and calorific value of bio-oil pyrolysed from oil palm biomass and its relation with solid residence time and process temperature", *Asian J. Sci. Res*, vol 8, pp. 351–358, 2015.
- [25] O. Onay, E. Bayram and O.M. Kockar, "Co-pyrolysis of Seyitomer-Lignite and Safflower seed: Influence of the blending ratio and pyrolysis temperature on product and oil characterisation", *Energy Fuels*, vol 21, pp. 3049–3056, 2007.
- [26] B.B. Uzun, A.E. Putun and E. Putun, "Fast pyrolysis of soybean cake: Product yields and compositions", *Bioresour. Technol.*, vol. 97, pp. 569–576, 2006.
- [27] A.I. Casoni, M. Bidegain, M.A. Cubitto, N. Curvetto and M.A. Volpe, "Pyrolysis of sunflower seed hulls for obtaining bio-oils", *Bioresour. Technol.*, vol. 177, pp. 406–409, 2015.
- [28] A. Demirbas M.F. Demirbas, "Importance of algae oil as a source of biodiesel", *Energy Convers. Manage*, vol. 52, pp. 163–170, 2011.