Chapter 11
Preparation and Characterization of Hydrotalcite-Derived Material from Mullite-Rich Tailings (I): Transesterification of Used Cooking Oil to Biodiesel

Daniel Ogochukwu Okanigbe and Shade Rouxzeta Van Der Merwe

11.1 Introduction

The interest in renewable fuels for internal combustion engines has significantly expanded due to environmental worries about climate change and global warming. Furthermore, finding alternative fuels is necessary to meet the current global energy demand because fossil fuels are running out day by day. As a result, biodiesel has emerged as a very desirable alternative fuel for diesel engines since it has less negative environmental consequences and has a smaller impact on acid rain and greenhouse gas emissions.

The usage of biodiesel is regarded as favorable in comparison with that of diesel fuel because of these features, as well as its biodegradability, largely sulfur-free nature, and aromatic nature [1]. In order to produce the necessary fatty acid methyl esters (FAME) and glycerol as a by-product, vegetable oils are transesterified with methanol in the presence of a catalyst to produce biodiesel, which is the most popular biofuel in Europe [2].

D. O. Okanigbe (✉)
Department of Chemical, Metallurgical and Materials Engineering, Faculty of Engineering and the Built Environment, Tshwane University of Technology, Pretoria, South Africa

Pantheon Virtual Engineering Solutions, Nigel, South Africa
e-mail: okanigbedo@tut.ac.za; okanigbeogochukwu@gmail.com

S. R. Van Der Merwe
Department of Mechanical and Mechatronics Engineering, Faculty of Engineering and the Built Environment, Tshwane University of Technology, Pretoria, South Africa
e-mail: vandermerweR1@tut.ac.za

D. O. Okanigbe, A. P. Popoola (eds.), *Resource Recovery and Recycling from Waste Metal Dust*, https://doi.org/10.1007/978-3-031-22492-8_11

The most widely used technology favors the employment of homogenous basic catalysts that have been dissolved in methanol, primarily NaOH or KOH [1]. Although a homogeneously catalyzed biodiesel synthesis can achieve high conversion rates and is reasonably quick, there are some significant limitations when the starting material has a high acidity [3]. At the conclusion of the reaction in this instance, the catalyst must be neutralized and removed from the methyl ester phase, resulting in the production of a sizable amount of waste water [4].

The formation of soaps as well as the separation and purification of biodiesel may be minimized by the use of heterogeneous catalysts [5, 6]. Furthermore, the application of heterogeneous catalysts could significantly lower the price of biodiesel while dramatically simplifying the process of product post-treatment. Different approaches have been suggested, including the use of solid catalysts for biodiesel generation, such as basic zeolites, alkaline earth metal oxides, and hydrotalcites (HT) among others [7–9], provided that the higher the raw material acidity, the lower the conversion efficiency [3]. Zeolites are superior to other heterogeneous catalysts in many ways; however, their catalytic activity in transesterification reactions using a pure mixture of fatty acids only reached 92% conversion, which is less than expected [10]. Owing to its promising performance, HT has been employed as a catalyst precursor [11].

Hydrotalcites (HT) are brucite-like octahedral-layered anionic materials with di and trivalent metal ions commonly referred to as layered double hydroxide (LDH) [12, 13]. Recently, HT are being investigated in the process of transesterification as catalyst in the production of biodiesel [14–16], although there is the existence of other types of catalyst, HT, as mentioned earlier has gained popularity because of their ease of separation, requirement of mild condition, ease of regeneration, reusability, hence affordable [17].

The most effective method for producing HT is co-precipitation, which involves mixing sodium carbonate solution with a mixed-metal solution that has been dissolved in deionized water. Sodium hydroxide solution is used to maintain a consistent pH. Nevertheless, it costs a lot of money to make HT from pure chemicals. A situation that has prompted research into developing cost-effective approaches for producing HT [13, 18], particularly from waste materials [19]. An example was presented in the work of Gil et al. [19], when they produced HT from saline slag wastes. Using a reflux system over a 2-hour period, saline slags were chemically treated with 2 mol/dm^3 aqueous solutions of NaOH. With the help of cobalt, magnesium, and nickel nitrates, as well as Na_2CO_3, aluminum aqueous solutions were employed as precursors to create HT materials with two different mole M^{2+}/Al^{3+} ratios, 2:1 and 4:1.

Despite efforts like the one mentioned in the paragraph before, costs associated with producing biodiesel are still being driven by raw materials [20]. The availability and price of the raw material have a major role in the choosing. Using edible oil to make biodiesel could potentially reduce the amount of oil available as food for both people and farm animals [2]. Hence, another laudable approach to minimizing the cost of biodiesel production will be the use of waste cooking oil/fat (which typically shows high acidity) which has been examined as a feedstock for biodiesel production [21].

To the best of my knowledge, not much research has described the usage of HT from metallurgical wastes to enhance the transesterification of WCO to biodiesel. In one similar study, Brito et al. [22] converted WCO into biodiesel using as-received HT and heat-treated HT. After, following an 8-hour reaction period, Hernandez et al. added up to 10% salt to heat-treated HT and observed a favorable response from the catalyst [23].

Premised on introduction leading to this point, the following subsequent aspects of this proposal report: problem statement, research objectives, research hypothesis, significance of study, literature review, and methodology, will elucidate the essence of this proposed research.

11.2 Problem Statement

Despite the potential of employing other sources, such as producing biodiesel from waste and biological sources [24–26], South Africa is still dealing with issues that prevent the biodiesel business from taking off. These include the following:

1. A lack of innovative activities that could assist in bringing down the cost of biodiesel to a reasonable level.
2. Choosing feedstocks that might potentially greatly reduce the overall cost of biodiesel manufacturing in South Africa is a difficult task.
3. It costs a lot of money to make HT from pure chemicals.

11.3 Research Objectives

11.3.1 Main Objective

Preparing and characterizing a hydrotalcite-derived material from mullite-rich tailings for the transesterification of waste cooking oil into biodiesel will be the main objective of this study.

11.3.2 Sub-objectives

The following sub-objectives will help to achieve the main objectives:

1. Preparation of edible cooking oil and WCO for transesterification
2. Characterization of edible cooking oil and WCO
3. Preparation and characterization of the waste copper dust (WCD)
4. Thermodynamic modeling of WCD oxidative roasting
5. Experimental oxidative roasting of the WCD
6. Density separation of WCD for production of MRT

7. Optimization of hydrotalcite production from MRT for the following:
    (i) Catalyst loading on catalyst activity.
    (ii) Molar ratio of methanol to oil on catalyst activity.
    (iii) Reaction time on the catalyst activity will be investigated to optimize transesterification conditions.
8. Characterization of the produced biodiesel for the following:
    (i) Thermal stability
    (ii) Physical properties
    (iii) Isoconversional models

11.4 Research Hypotheses

Premised on the proposed scientific idea, the following can be hypothesized:

1. That the use of WCO as feedstock will assist with the lowering of overall cost of biodiesel production in South Africa.
2. The use of WCO as feedstock for biodiesel production will eliminate the high cost of its disposal and associated environmental threats it poses.
3. Using WCO instead of edible cooking oil to make biodiesel will potentially increase the amount of edible cooking oil available as food for both people and farm animals.
4. Preparation and characterization of hydrotalcite-derived material from waste metal dust (i.e., MRT) for transesterification of WCO to biodiesel will assist with the cost reduction of biodiesel production in SA.
5. Since high basicity is one of the desired characteristics of heterogeneous catalyst used for transesterification, exploring the basicity of MRT to prepare and characterize a hydrotalcite-like material for transesterification will result in a much fast process than the existing one with existent catalysts.
6. The application of HT from MRT for the industrial production of biodiesel will contribute to addressing ecological and global stresses associated with environment.

11.5 Significance of Study

The information in this study will contribute to bridging the gap of knowledge that exist in the following studies:

1. The catalytic application of hydrotalcite-like materials:

    Among numerous applications of hydrotalcite-like material, its catalytical application as a heterogeneous catalyst in the process of transesterification at the industrial level of the production of biodiesel.

2. The catalytic effect of MRT elements in a HT:
   The choice of MRT and its availability, the role and contribution of the MRT element constituent for a HT structural feature, and their role in transesterification, leading to further feasibility studies on the preparation of a HDM from another material containing MRT-like elements.
3. Optimization of the preparation of a HDM from MRT:
   Paving ways on an optimal route of preparation of a HDM from MRT for future application and crystal structure studies.
4. Contribution of the HDM in the transesterification:
   Based on the results obtained, there will be clarity about the contribution of the HDM in the transesterification process.
5. Impact of the application of HDM as a catalyst on an industrial scale:
   Evaluate the economic possibility of using HDM from MRT as a catalyst in the transesterification process on an industrial scale.

11.6 Literature Review

11.6.1 Introduction

Interest in biofuels for transportation has been sparked by high energy prices, rising energy imports, supply concerns, and growing environmental awareness of the effects of fossil fuels [27]. As a result, the development of biofuels has multiplied enormously in response to the need for affordable, viable energy sources that do not harm the environment [28, 29]. Reiterating this, the pressure on petroleum-based fuels in the transportation sector has resulted in the development of vegetable oil-based fuels as the primary alternative fuel to non-renewable fossil fuel types [30, 31]. When using alternative sources, researchers can get the best outcomes by converting wastes and biological energy sources into goods, in this case, biodiesel [24–26].

11.6.2 Biodiesel Production in South Africa

Many nations are promoting the use and production of biodiesel because it reduces the need for foreign oil, increases domestic energy security, is safe for the environment by lowering greenhouse gas emissions, is renewable, and is both affordable and practical [31–34]. As at year 2010, it was estimated that 10% replacement of South Africa’s diesel usage will result in a 1 billion liters increase South Africa’s biodiesel market.

Table 11.1 Manufacturing costs of biodiesel for various feedstocks in SA [35]

SEBP plant		COBP plant	
Local feedstock	Manufacturing cost	Imported feedstock	Manufacturing cost
Canola	R4.81/liter	Palm oil	R6.62/liter
Sunflower seeds	R6.67/liter	Soybean oil	R6.89/liter
Soybeans	R6.70/liter	Sunflower oil	R7.48/liter
		Rapeseed oil	R9.28/liter

11.6.3 Manufacturing Cost of Biodiesel in South Africa

The ideal size of a biodiesel plant in South Africa (SA), according to Nolte [35], is between 1500 and 3000 kg/h [35]. A seed extraction biodiesel production plant (SEBP) uses locally produced oilseeds as feedstock, and a crude oil biodiesel production plant (COBP) uses imported crude vegetable oil as feedstock, according to the author's study. A COBP plant would require a capital expenditure of roughly R45 to R50 million (amounts inclusive of working capital of approximately R35), while a SEBP plant would require a capital investment of between R110 and R145 million. The calculated biodiesel manufacturing costs of the two types of plants for various feedstocks were computed on August 30, 2006, at the current prices, and this can be seen in Table 11.1.

11.6.4 The Choice of Feedstock and Its Impact on Biodiesel Production

The decision to use biodiesel as an alternative engine fuel is based on its characteristics, which are somewhat different from regular diesel and are frequently determined by the oil feedstock and alcohol utilized, although being otherwise extremely similar to diesel fuel [2, 36, 37]. According to Pratas et al. [38], Cao et al. [39], and Sajjadi et al. [40], it is made up of a lengthy organic chain of fatty acid methyl ester (FAME), also known as plant oil-based.

Plant oil-based (POB) fuels have long been successfully tested in diesel engines as an alternative engine fuel [32, 41, 42]. Short-chain alcohols, which are now combined with gasoline, and biodiesels, which are typically made from seed oils, are examples of POB fuels. Soybeans have established a reputation as the main source of biomass-derived diesel in the United States and Brazil because they produce the greatest oil by weight among the POB fuel feedstocks, up to 20% [43–45].

11.6.5 Soybean in South Africa

As a good substitute for biodiesel made from fossil fuels, soybean-derived biodiesel can be used to generate electricity [44]. According to the amount of land cultivated and the amount produced, soybeans are one of the most important grain crops in South Africa [38–40]. Since soybean has such a high socioeconomic value in South Africa, it is grown in all nine of the provinces there [46, 47]. The issue of waste management is a result of this, though.

11.6.6 Waste from Soybean Production

Tofu, soymilk, soymilk powder, beansprouts, dried tofu, soy sauce, soy flour, and soybean oil are only a few of the delicacies made from soybean in Asian nations. Every year, Japan disposes of around 800,000 tons of waste products from the manufacture of soybean oil. The annual disposal cost is roughly 2.1 million rand [48]. Currently, the garbage from this source is burned to create CO_2, disposed of in landfills, and other waste management techniques [49]. The environmental issues brought on by this source's large waste production have received a lot of attention [50]. According to Redondo-Cuenca, Villanueva-Suárez, and Mateos-Aparicio [51], waste from soybean oil is frequently high in moisture content (70–80%), making it difficult to manage and expensive to dry by conventional methods.

11.6.7 Proactive Measures for South Africa's Biodiesel Industry

While preparing for government assistance to help South Africa's biodiesel industry get off the ground, proactive steps are needed, especially in the field of creative initiatives that can help lower the price of biodiesel down to a respectable level. The selection of feedstock like those in Table 11.2 is an innovative strategy that has the potential to significantly lower the overall cost of biodiesel production in South Africa. Waste cooking oil (WCO) is an illustration of a plant-based oil waste product. WCO is a synthetic oil that has lost its ability to be used for cooking due to the presence of a significant number of contaminants and the loss of its original qualities. WCO is produced by a variety of sources, including residential, commercial, and industrial food manufacturers, which have an impact on the environment. One of the best methods to use the material effectively and affordably is to produce biodiesel from WCO.

WCO biodiesel has been regarded as a promising option, claims Demirbas [31]. For the production of biodiesel, WCO is inexpensive when compared to the price of fresh vegetable oil and, consequently, commercial diesel fuel (Table 11.3). Detailed

Table 11.2 Feedstock categories of biodiesel production [41]

Category	Classes		Feedstock	References
Oilseeds	Edible	C:	Soybean, rapeseed/canola, sunflower, palm, coconut, olive	[31, 52, 53]
		A:	False fax, safflower, sesame, marula, pumpkin, African peer seed, Sclerocarya birrea, Terminalia catappa L., yellow nut-sedge tuber, rice bran	[52, 54–60]
	Inedible	A:	Jatropha, karanja, mahua, linseed, rubber seed, cottonseed, neem, camelina, putranjiva, tobacco, polanga, cardoon, deccan hemp, castor, jojoba, moringa, poon, koroch seed, desert date, eruca sativa gars, see mango, pilu, crambe, syringa, milkweed, field pennycress, stillingia, radish Ethiopian mustard, tomato seed, kusum, cuphea, camellia, paradise, cuphea, terminalia, michelia champaca, garcinia indica, zanthoxylum bungeanum	[52, 61–70]
Animal fats		C:	Beef tallow, pork lard	[54]
		A:	Waste salmon, melon bug, sorghum bug, chicken fat	[54]
Waste materials		C:	Cooking oil, frying oil	[71, 72]
		A:	Vegetable oil soap stocks, acid oils, tall oil, dried distiller's grains (DDG), pomace oil	[73, 74]
Algae			Botryococcus braunii, Chlorella sp., Chlorella vulgaris, Crypthecodinium cohnii, Cylindrotheca sp., Dunaliella primolecta, Dunaliella salina, Isochrysis sp., Haematococcus pluvialis, Monallanthus salina, Muriellopsis sp. Nannochloris sp., Neochloris oleoabundans, Nitzschia sp., Phaeodactylum tricornutum, Porphyridium cruentum Schizochytrium sp., Spirulina, Arthrospira platensis, Tetraselmis suecica	[75–77]

Key: *A* alternative, *C* conventional

Table 11.3 Comparison of the qualities of commercial diesel fuel, waste cooking oil, and biodiesel from waste cooking oil [31]

Fuel property	WCO	Biodiesel (WCO)	Commercial diesel
Kinematic viscosity (mm^2/s, at 313 K)	36.4	5.3	1.9–4.1
Density (kg/L, at 288 K)	0.924	0.897	0.075–0.840
Flash point (K)	485	469	340–358
Pour point (K)	284	262	254–260
Cetane number	49	54	40–46
Ash content (%)	0.006	0.004	0.008–0.010
Sulfur content (%)	0.09	0.06	0.35–0.55
Carbon residue (%)	0.46	0.33	0.35–0.40
Water content (%)	0.42	0.04	0.02–0.05
Higher heating value (MJ/kg)	41.40	42.65	45.62–46.48
Free fatty acid (mg KOH/g oil)	1.32	0.10	–
Saponification value	188.2	–	–
Iodine value	141.5	–	–

analysis in Table 11.3 demonstrates that there are numerous similarities between the properties of biodiesel and diesel fuels in general. As a result, biodiesel is viewed as a suitable diesel substitute. The methyl esters made by transesterification of old cooking oil have a molecular weight that is nearly one-third lower, a viscosity that is about one-seventh lower, a flash point that is a little lower, a volatility that is a little higher, and a pour point that is a lot lower.

11.6.8 Transesterification of WCO to Biodiesel

Straight vegetable oil can be used as a fuel for diesel engines; however, there are a number of drawbacks, including high viscosity, injector coking, and engine deposits. By transforming the vegetable oils into their methyl esters, these issues can be somewhat resolved. This is accomplished by utilizing heterogeneous catalysts in the transesterification reaction. Fatty acid methyl ester (FAME), the end outcome, is also referred to as biodiesel.

Heterogeneous catalysts have been offering a sustainable and workable answer to issues occurring in various techno-economic limits of catalysis in recent years. The methods and technologies used to create these systems should serve as inspiration for addressing ecological and global environmental concerns. In recent years, intensive research has been conducted to produce these catalysts, and their prospective applications in a wide range of fields have been investigated. As previously mentioned, transesterification is one process where the use of these catalysts could soon have a significant impact on the manufacture of biodiesel at an industrial scale [14–16].

Although there are many different kinds of catalysts, including NaOH, KOH, HCl, and H_2SO_4 [78], heterogeneous catalysis has grown in popularity since it is simple to separate, only needs mild conditions, can be recycled, and can lower production costs [17]. Given their high surface area, basicity, and low production costs, zeolites made from bagasse and fly ash [79, 80], calcined cement waste [81], Li-modified rice husk [82], and CaO obtained from natural waste shells have all been investigated for their potential as heterogeneous catalysts like hydrotalcite in the production of biodiesel.

In the recent year, hydrotalcite has gained popularity in several fields and have been the topic of different studies due to their structural features and several applications [83]. Hydrotalcites are double-layered double showing a variety of stoichiometry due to the different arrangement of the stacking of the layers, ordering of the metal cations, as well as the arrangement of anions and water molecules, in the interlayer galleries, they are synthetic or natural occurring crystalline materials consisting of positively charged two-dimensional sheets with water and exchangeable charge compensating anions in the interlayer region as shown in Fig. 11.1.

The compounds of the hydrotalcite group show a wide range of the possible applications due to their specific properties, such as their large surface area, ion exchange ability, the insolubility in water and most of the organic sorbents, and others. Hydrotalcite-like compounds also referred to as anionic clays or layered double hydroxides (LDHs) are a valuable and commonly reported group of materials with a complex structure that is composed of positively charged brucite-like layers $[M^{2+}$ or $M^{3+}(OH)_2]^{x+}$. In which an isomorphous substitution of the divalent M^{2+} and the trivalent cation M^{3+} are distributed among octahedral positions, alternating with disordered and negatively charged interlayers $[A_{x/n}]^{n-}$ formed for instance by inorganic ions, heteropoly acids, organic acids, and others, which is represent by the formula of type $[M_{1-x2} + M_{x3} + (OH)_2]_x + [A_{x/n}]^{n-} \cdot mH_2O$.

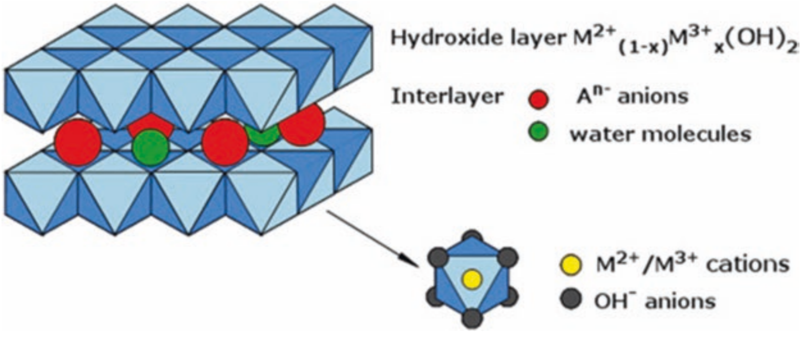

Fig. 11.1 Hydrotalcite structural representation. (Source: Google Image)

11.6.9 Production of Hydrotalcite from Natural Resources

11.6.9.1 Natural Dolomite

Dolomite is a naturally occurring double carbonate and a source of calcium and magnesium ions, according to Hosni and Srasra [84]. In their research, a straightforward process was used to create Mg-Al-CO_3 layered double hydroxide from dolomite feedstock. On their structure and textural qualities, the influence of synthesis parameters, including the M^{2+}/Al^{3+} ratio, reaction temperature, and pH, was investigated. X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA), and Brunauer, Emmett, and Teller (BET) measurements were used to determine the structural characteristics of the materials.

The authors came to the conclusion that dolomite can be processed into pure and well-crystalline phases of Mg-Al-CO3 LDH in an aqueous Na_2CO_3 solution. That a key consideration was the preparation's pH. Pure LDH was generated at a pH of 9.5. The LDH's crystallinity dropped below this threshold. Conditions that are quite alkaline do not seem to be favorable for the synthesis. The ideal dolomite/Al molar ratio was approximately 1. Above this ratio, brucite was generated. Low dolomite/Al ratios resulted in products with poor crystallinity. A factor that was thought to be crucial for regulating crystallinity and particle size was aging temperature. According to experimental research, hydrotalcite must be at a high temperature to form a well-crystalline phase.

11.6.9.2 Bittern

An assessment of the viability of employing Class C fly ash for the synthesis of faujasite (Type X) and tschernichite (Type A) type zeolite materials is shown in the study by Kunecki et al. [85]. Syntheses were performed to produce the well-formed zeolites. The variables were as follows: water, the filtrate (post-reaction solutions obtained during the hydrothermal synthesis of zeolites rich in Si), the ratio of fly ash to NaOH, and the quantity of aluminum foil added.

According to the analysis, three of the most efficient reactions (from which Samples 21–23 were formed) took place in the following circumstances: the amounts of H_2O, filtrate, and aluminum foil added were 100, 100, and 50 ml for each of the three reactions, respectively. The ratio of NaOH to fly ash was 1.6, 2.0, and 1.25, with fusion temperatures of 550 °C for each of the three reactions, fusion times of 1 hour, and reaction times of 4 hours. The reaction temperature was 80 °C for each of the three reactions (for each of the three reactions).

The three best zeolite materials (Samples 21–23) were submitted to mineralogical, chemical, and textural analytical characterization using X-ray powder diffraction (XRD), scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS), and X-ray fluorescence (XRF), Brunauer–Emmett–Teller (BET), to determine specific surface area and pore volume and size). The produced zeolites, according to studies, have a Type A (Samples 21–22) and Type X (Sample 23) structure, as well as well-formed grains with isometric and cubic properties. The obtained zeolites' computed unit cell characteristics point to a cubic crystal system and are quite similar to the reference values for the structures of X- and A-type zeolites.

The ratio of SiO_2/Al_2O_3 in each of the three tested zeolite materials was as follows: 2.16, 1.98, and 2.41. For samples 21–23, the specific surface area was 106, 104, and 256 m^2/g, respectively. The outcomes were comparable to the zeolite structures discovered in Class F fly ash. As a result, we can draw the conclusion that the Class C fly ash under analysis may also be a useful substrate for the synthesis of Type X and Type A zeolite materials.

11.6.9.3 Blast Furnace Steel Slag

The authors of this study by Kunecki et al. [86] reported the effect of time on the creation of the mineral structure of GIS Na-P1 zeolite. Aluminum and silica were obtained from thin microspheres. The material used in this project was created utilizing a prototype installation at a quarter-technical scale. X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy equipped with a system of chemical composition analysis based on energy dispersive X-ray (SEM-EDS), volumetric adsorption analyzer, Fourier transform infrared spectroscopy (FTIR), and particle size analyzer were used to determine the chemical, mineralogical, and textural properties of the material (PSA).

The interesting and in some cases remarkable phenomena of the lattice parameters ripening as a function of time is demonstrated by experimental calculations based on Miller indices. With longer synthesis times, both the number of zeolites present and the unit cell characteristics (a, b, c, and volume) rise. With the use of the XRD and FTIR techniques, this process may be seen clearly. The finished product's structural, morphological, and textural characteristics suggest that it might be beneficial as an adsorbent for several kinds of environmental pollution.

Muriithi et al. [87] reported the production of hydrotalcites (HT) from mineral waste (e.g., blast furnace slag), an area of research attracting growing attention. This paper describes a unique method for producing HT from fly ash, a common waste product of coal-fired power plants in South Africa. The optimization procedure, which highlights the boundary conditions for this mineral phase's crystallization, is the second area of originality.

The HCl content, aging duration and temperature, pH during the aging process, and crystallization time and temperature were the variables examined for the optimization of HT synthesis from fly ash. The best synthesis conditions were as follows: 3 M HCl concentration, 30 minutes of aging, 65 °C of aging, 11.5 pH during aging, 12 hours of crystallization, and 70 °C of crystallization temperature. The exterior surface area and microporosity of HT were both quite high.

The majority of the morphological components of synthesized HT were submicron, plate-like particles. Except for the presence of calcite, the structural features of HT made from fly ash were comparable to those of HT obtained from analytical grade chemicals. The waste Class F fly ash from SA was used in an innovative way to create high-quality HT under optimal processing conditions that reduced the production of secondary undesirable mineral phases like calcite or hydrogarnet.

11.6.9.4 Aluminum Slag

In this study by Wajima [88], hydrotalcite was created from bittern solution by adding $AlCl_3$ (the solution's Mg/Al molar ratio was 3), and its capacity to remove phosphate and nitrate from water was tested. Both bittern and seawater can be used to make hydrotalcite, although the product made from bittern has a higher hydrotalcite content than the one made from seawater. Higher than commercial hydrotalcite, the bittern product has phosphate and nitrate removal capabilities.

The experimental data are found to better fit the Langmuir than the Freundlich isotherm models when calculating the equilibrium adsorption capacity of the product for phosphate and nitrate ions. Because of the ion exchange process between chlorine and sulfate in the product, phosphate adsorption on the product reached saturation in 30 minutes and was essentially steady after that. Nitrate adsorption on the product increased in 15 minutes and then gradually decreased.

The main constituents of blast furnace slag (BFS) are CaO, SiO_2, Al_2O_3, MgO, and trace amounts of transition metals like Fe, Ti, and Mn, according to Kuwahara et al. [89] in their study titled "A novel conversion process for waste slag: synthesis of a hydrotalcite-like compound and zeolite from blast furnace slag and evaluation of adsorption capacities." We successfully used the chemical method of acid-leaching and precipitation to create a hydrotalcite-like molecule from BFS.

After undergoing HCl acid-leaching, BFS was separated into hydrated silica with 92 wt.% SiO_2 and leaching solution containing other components, which provided a hydrotalcite-like product after further NaOH addition in a high yield. The result generated at 100 °C was determined to be a Ca-Al hydrocalumite complex by XRD and chemical analysis. Its stoichiometric molar ratios are Ca: Al: Cl = 2: 1: 1, and it contains other metal cations in its structure.

The hydrotalcite-like compound had an elevated phosphate adsorption capacity of about 40 mg P/g, which was more than three times more than that of typical Mg-Al-based hydrotalcite. The phosphate adsorption capacity of the raw slag was 1.5 mg P/g. In addition, utilizing the remaining silica and a hydrothermal treatment lasting 6 hours at 100 °C, single-phase A- and X-type zeolites with high crystallinities and outstanding water adsorption capacities (247 and 333 mg g^{-1}, respectively) were effectively created. From the perspective of making efficient use of BFS, this conversion procedure, which enables us to create two distinct types of valuable materials from BFS at a cheap cost and with simple preparatory stages, is unquestionably advantageous.

According to Galindo et al. [90], due to environmental concerns, the powdered solid strapped in filter sleeves in the aluminum tertiary industry is currently disposed of in secure landfills. They are categorized as hazardous waste because they contain a lot of aluminum, either in the form of metallic aluminum or in compounds like aluminum nitride.

These substances have the ability to react with extremely little moisture, releasing toxic or dangerous gases like hydrogen and ammonia.

In three steps, the low-cost method described in this study allows for the complete recovery of this hazardous waste and the creation of two different added-value components. The trash is subjected to mild acid hydrolysis in the first step in order to produce an inert cake and a concentrated solution of aluminum. The subsequent steps involve synthesizing hydrotalcite from the resultant solution and using the cake to create transparent glasses based on the CaO-Al_2O_3-SiO_2 system. The products' characteristics show that the hydrotalcites can easily absorb anionic contaminants (molybdates), while the glasses offer better optical properties than those made by directly vitrifying the trash.

11.6.9.5 Oil Shale Ash

With the aid of ammonia and triethanolamine at pH 10, Galindo et al. [91] reported that hydrotalcite-like compounds were co-precipitated with dilute sodium hydroxide from an unconventional aluminum source: the aluminum waste produced by the tertiary aluminum industry. To compare results, these compounds were characterized using a variety of techniques (XRD, FT-IR, UV-vis-NIR, SEM, DTA-TG, and BET procedures).

Characterization of the products revealed considerable variations based on the choice of basic reagent. Products that co-precipitated with ammonia exhibited less crystal development, a higher internal surface area, and a structure that contained significantly more iron. Triethanolamine-derived products demonstrated how organic molecules entered the multilayer framework. These results were crucial for the development of waste treatment techniques that turned hazardous wastes made of aluminum into stacked double hydroxides, a product with additional value.

11.6.9.6 Coal Fly Ash

In the study conducted by Muriithi et al. [87], South African Class F coal fly ash, a generally available and inexpensive chemical feedstock, was used to successfully produce HT under optimal conditions. With the exception of the presence of calcite, the produced HT exhibited structural traits that were comparable to those of that made using analytical-grade chemicals. In the context of carbon capture and storage in South Africa, the production process might thus serve as a dual strategy for the re-exploitation of coal fly ash from power plants and for the reduction of CO_2. Additionally, authors recommend that future research should focus on stopping the co-precipitation of calcite, while showing how these HT may be suitable for both short- and long-term CO_2 collection. On the possibility for wet or dry ash dams to naturally collect carbon, very little information is currently known. This study compared a naturally occurring occurrence with accelerated ex-situ mineral carbonation of fresh fly ash to determine the degree of carbon capture in a wet-dumped ash dam and the mineralogical changes supporting CO_2 capture (FA). Sr, Ba, and Zr trace metals at significant concentrations were found in both fresh ash and weathered ash. However, it was discovered that weathered ash had more Nb, Y, Sr, Th, and Ba than fresh ash did.

Fresh ash is composed of quartz, mullite, hematite, magnetite, and lime from a mineral perspective; however, weathered and carbonated ashes also contained other phases like calcite and aragonite. The fresh FA was able to trap up to 6.5 wt% CO_2, and accelerated carbonation (done at 2 hours, 4 MPa, 90 °C, bulk ash, and a S/L ratio of 1) resulted in a 60% conversion of calcium to $CaCO_3$. On the other hand, it was discovered that over the course of 20 years of moist disposal of ash, 6.8 wt percent CO_2 was naturally carbonated.

Thus, the ash dumps' spontaneous carbonation is considerable and may be useful in extracting CO_2.

In their study, Gil et al. [19] described the co-precipitation method's use of aluminum recovered from saline slag wastes to synthesize hydrotalcite-like materials. Using a reflux system over a 2-hour period, saline slags were chemically treated with 2 mol/dm^3 aqueous solutions of NaOH. With the help of cobalt, magnesium, and nickel nitrates, as well as Na_2CO_3, aluminum aqueous solutions were employed as precursors to create hydrotalcite-like materials with two different mole M^{2+}/Al^{3+} ratios, 2:1 and 4:1.

X-ray diffraction, thermogravimetric studies, nitrogen adsorption at 196 °C, and scanning electron microscopy were used to analyze the resultant solids. The CO_2 adsorption at 50, 100, and 200 °C was assessed under dry conditions after thermal treatment at 200 °C. The Mg: Al-2: 1 sample had a remarkable sorption capacity of 5.26 mmol/g at 80 kPa and 50 °C, which was significantly greater than the sorption capacities previously reported in the literature for hydrotalcites under comparable conditions.

The values of the Henry's law constants, which range from 0.01 to 4.20 mmol/kPag, were directly deduced from the adsorption isotherms at low pressures. Using the Clausius-Clapeyron equation, the isosteric heats of CO_2 adsorption were discovered to be between 5.2 and 16.8 kJ/mol.

11.6.9.7 Mullite-Rich Tailings from Density-Separated Waste Copper Dust (WCD)

According to Linda et al. [92], the mullite-rich tailings (MRT) from WCD can serve as a secondary resource of mullite, because it contains 67.15% of aluminosilicates. It is therefore recommended that MRT be used to lower the cost of mullite refined powders in later engineering applications due to its size, potential, and possibilities, after several other studies.

Conclusion

The manufacture of biodiesel is acknowledged to lessen the demand for imported oil, boost domestic energy security, and be safe for the environment by reducing greenhouse gas emissions because it is a renewable resource. However, the effectiveness of biodiesel as an alternative engine fuel depends on its properties, which are usually influenced by the type of alcohol and oil used as feedstock. Diesel engines have long been successfully tested with plant oil base (POB) fuels as an alternative engine fuel. Among the POB fuel feedstocks, soybeans yield the most oil by weight, up to 20%, and have earned a reputation as the primary source of biomass-derived diesel in the United States and Brazil.

Despite initiatives like the one stated in the preceding paragraph, the cost of generating biodiesel is still largely determined by the cost of raw ingredients. The choice is heavily influenced by the raw material's availability and cost. Making biodiesel from edible oil can result in less oil being accessible for human and farm animal use. Therefore, the use of used cooking oil or fat, which normally exhibits high acidity, has been investigated as a feedstock for biodiesel synthesis, is another admirable strategy for reducing the cost of biodiesel manufacturing.

The second type of waste conversion to product will use the transesterification method to convert WCO to biodiesel using mullite-rich tailings (MRT) from density-separated waste copper dust.

To my knowledge, very little study has discussed the use of HT derived from metallurgical wastes to speed up the conversion of WCO to biodiesel. Therefore, the development of an affordable biodiesel production process in South Africa may be aided by research into an effective catalyst to convert a WCO into biodiesel.

11.7 Methodology

11.7.1 Introduction

The investigation on the preparation and characterization of hydrotalcites derived material from waste metal dust for transesterification of waste cooking oil to biodiesel will be carried out according to the methodology detailed as follows:

11.7.1.1 Materials

Waste Cooking Oil

The raw material that will be used for the production of biodiesel in this proposed study is a waste cooking oil.

Waste Metal Dusts

Two waste metal dust will serve as primary (i.e., mullite-rich tailings) and secondary (copper smelter dust) materials for synthesis of the heterogeneous catalyst (i.e., hydrotalcites derived material) that will be used to enhance the transesterification process of the waste cooking oil to biodiesel.

11.7.1.2 Methods

Preparation of WCO Feedstock for Transesterification

The contamination in the WCO will be filtered using a 5-μm filter cloth in a vacuum filtration unit. Seven WCO samples of 1000 ml each will be filtered in the machine.

The edible cooking oil (ECO) will be characterized for free fatty acid (FFA) content, relative density (RA), acid value (AV), saponification number (SN), and ester value (EV). These values will be compared with the properties evaluated from seven purified WCO samples as illustrated in Table 11.4. The best among these six samples will be used as feedstock for this study.

Density Separation of WCD

The WCD will be subjected to physical separation into using a centrifugal gravity separator. The parameters that will be optimized for the centrifugal gravity separation (CGS) will be the rotational bowl speed (RBS) and the fluidized water flow rate (FWFR) as detailed in Table 11.5.

The protocol for the CGS is detailed in Table 11.6, and it will involve 9 tests in total. These nine tests will be repeated 5 times as passes. The starting material for each new pass will be the tailings from the previous test. Based on this experimental plan, 45 test samples will be generated as shown in Table 11.7. These outputs from the CGS of WCD will be used as raw material for the production of the hydrotalcite-derived material (HDM).

Table 11.4 Characteristics of FSO and WCO

Characteristics	FSO	WCO1	WCO2	WCO3	WCO4	WCO5	WCO6	WCO7
FFA	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD
RA	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD
AV	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD
SN	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD
EV	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD	YTBD

Key: *YTBD* yet to be determined

Table 11.5 Parameters measured for density separation experiment

S/N	Parameters	Low (0)	Medium (1)	High (2)
X_1	RBS (m/s^2)	60	90	120
X_2	FWFR (l/min)	3.0	4.5	6.0

Table 11.6 Test protocol for density separation of WCD

Tests	RBS (G)	FWFR (l/min)	Treatment combination (TC)
1	A	A	AA
2	A	B	AB
3	A	C	AC
4	B	A	BA
5	B	B	BB
6	B	C	BC
7	C	A	CA
8	C	B	CB
9	C	C	CC

Table 11.7 Outputs from CGS of WCD

	MRT								
Passes	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	1(1)	1(2)	1(3)	1(4)	1(5)	1(6)	1(7)	1(8)	1(9)
2	2(1)	2(2)	2(3)	2(4)	2(5)	2(6)	2(7)	2(8)	2(9)
3	3(1)	3(2)	3(3)	3(4)	3(5)	3(6)	3(7)	3(8)	3(9)
4	4(1)	4(2)	4(3)	4(4)	4(5)	4(6)	4(7)	4(8)	4(9)
5	5(1)	5(2)	5(3)	5(4)	5(5)	5(6)	5(7)	5(8)	5(9)

Optimization of Hydrotalcite Production from MRT

Pregnant leach solutions (PLS) will be obtained from the 45 MRT samples following the procedure that has been reported in by Okanigbe [93] and Baktiari [94]. The different grades of PLS will be subjected to co-precipitation (Fig. 11.2). The parameters for the co-precipitation process will be optimized following Tables 11.8 and 11.9

Optimization of Catalytic Activity

The transesterification of filtered WCO will be carried out in a 500-ml three-necked round-bottom flask equipped with reflux condenser and a magnetic stirrer. Varied ratios of WCO: Alcohol (Table 11.10) will be mixed with varied concentrations of HT_{MRT} (Table 11.10) and stirred at a fixed temperature of 65.5 °C. This process will be optimized following the test protocol in Table 11.11. After carrying out the reaction, the mixture was cooled to room temperature, centrifuged at 6000 rpm for

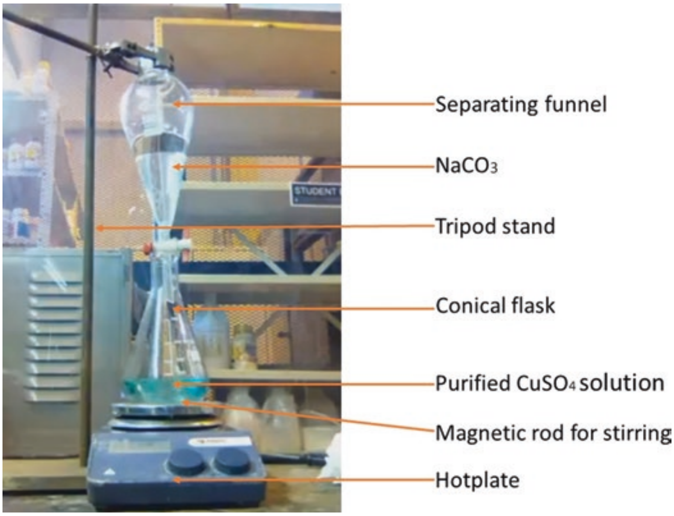

Fig. 11.2 Proposed experimental setup for production of HDM from waste copper dust

Table 11.8 Parameters considered for the production of hydrotalcite

	Levels		
Parameters	Low	Medium	High
Temperature (°C)	25	55	85
Rotational speed (rpm)	340	740	1480

Table 11.9 Design of experiment for the production of hydrotalcite

Tests	Temperature (°C)	Rotational speed (rpm)	Treatment Combination
1	25	340	25 °C–340 rpm
2	25	740	25 °C–740 rpm
3	25	1480	25 °C–1480 rpm
4	55	340	55 °C–340 rpm
5	55	740	55 °C–740 rpm
6	55	1480	55 °C–1480 rpm
7	85	340	85 °C–340 rpm
8	85	740	85 °C–740 rpm
9	85	1480	85 °C–1480 rpm

Table 11.10 Parameters measured for density separation experiment

S/N	Parameters	Low (0)	Medium (1)	High (2)
X_1	WCO: Alcohol	1:5	1:6	1:7
X_2	Catalyst concentration (wt %)	0.5	1.0	1.5

Table 11.11 Test protocol for optimization of HT_{MRT} activity

Tests	WCO: alcohol	Catalyst conc. (wt %)	Treatment combination (TC)
1	1:5	0.5	(1:5)(0.5)
2	1:5	1.0	(1:5)(1.0)
3	1:5	1.5	(1:5)(1.5)
4	1:6	0.5	(1:6)(0.5)
5	1:6	1.0	(1:6)(1.0)
6	1:6	1.5	(1:6)(1.5)
7	1:7	0.5	(1:7)(0.5)
8	1:7	1.0	(1:7)(1.0)
9	1:7	1.5	(1:7)(1.5)

10 minutes for catalyst separation, and the unreacted methanol was removed using rotary evaporator.

The biodiesel yield will be estimated using Eq. (11.1)

$$\text{yield\%} = \frac{\text{weight of methyl ester}\left(\text{g}\right)}{\text{weight of oil}\left(\text{g}\right)} \times 100 \tag{11.1}$$

Characterization of Biodiesel

The biodiesel produced will be characterized for physical and chemical properties. Specific gravities of all the samples will be measured using specific gravity bottle as per American society for testing and materials (ASTM) D 1298-85. The viscosities of the samples will be measured at 40 °C using rheometer (Rheostress RS 1) from Thermo Electron, according to ASTM D 445. Acidic value will be determined as per ASTM D664-89. Calorific values of the samples will be measured using bomb calorimeter according to ASTM D 240-92. 1H-NMR analysis will be performed at 25 °C.

11.7.2 Contribution to Knowledge

The information in this study will contribute to bridging the gap of knowledge that exist in the following studies:

- The catalytic application of hydrotalcite-like materials
- The catalytic effect of copper smelter dust in a hydrotalcite

- Optimization of the Preparation of a hydrotalcite-like material from copper smelter dust
- Contribution of the hydrotalcite-like materials in the transesterification
- Impact of the application of hydrotalcite-like materials as a catalyst on an industrial scale

11.7.3 Ethical Considerations

There are no ethical issues in this project.

11.7.4 Dissemination

The results will be presented at local and international conferences, while the full paper will be published in the corresponding conference proceedings. Other results will be published in Department of Higher Education and Training (DHET)-accredited journals like the following:

- Material Cycles and Waste Management—Journal —Springer
- Materials for Renewable and Sustainable Energy—Journal—Springer

11.7.5 Budget (Table 11.12)

Table 11.12 Estimated budget of the project

Items	**Cost**	**Source**
Literature sourcing and stationaries	X	TUT
Materials and supplies	X	TUT
Analytical equipment	X	TUT
Travelling expenses	X	TUT
Miscellaneous expenses	X	TUT
Total	X	TUT

Key: *TUT* **Tshwane University of Technology,** *R* **Rand**

11.7.6 Time Frame (Table 11.13)

Table 11.13 Estimated time frame of the project

S/N	Task name	Year	
		2020	2021
1	Proposal (compilation and presentation)	X	X
2	Literature review	X	X
3	Material sourcing	X	X
4	Sample preparation (sampling)	X	X
5	Fabrication of test samples optimization process	X	X
6	Fabrication of test samples	X	X
7	Thermal conductivity and wear resistance tests	X	X
8	Results, data, and analysis	X	X
9	Optimum predictive model development	X	X
10	3D print of brake rotor and validation of optimum prediction	X	X
11	Compilation and presentation of final report	X	X

References

1. M. Corral Bobadilla, R. Lostado Lorza, R. Escribano García, F. Somovilla Gómez, E.P. Vergara González, An improvement in biodiesel production from waste cooking oil by applying thought multi-response surface methodology using desirability functions. Energies **10**(1), 130 (2017)
2. S.G.I.L. Pinzi, I.L. Garcia, F.J. Lopez-Gimenez, M.D. Luque de Castro, G. Dorado, M.P. Dorado, The ideal vegetable oil-based biodiesel composition: A review of social, economical and technical implications. Energy Fuel **23**(5), 2325–2341 (2009)
3. M.P. Dorado, E. Ballesteros, J.A. De Almeida, C. Schellert, H.P. Löhrlein, R. Krause, An alkali–catalyzed transesterification process for high free fatty acid waste oils. Trans. ASAE **45**(3), 525 (2002)
4. M.P. Dorado, E. Ballesteros, F.J. López, M. Mittelbach, Optimization of alkali-catalyzed transesterification of Brassica Carinata oil for biodiesel production. Energy Fuel **18**(1), 77–83 (2004)
5. Y.C. Sharma, B. Singh, J. Korstad, Latest developments on application of heterogenous basic catalysts for an efficient and eco-friendly synthesis of biodiesel: A review. Fuel **90**(4), 1309–1324 (2011)
6. H.V. Lee, J.C. Juan, T.Y. Yun Hin, H.C. Ong, Environment-friendly heterogeneous alkaline-based mixed metal oxide catalysts for biodiesel production. Energies **9**(8), 611 (2016)
7. G. Arzamendi, I. Campo, E. Arguinarena, M. Sánchez, M. Montes, L.M. Gandia, Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: Comparison with homogeneous NaOH. Chem. Eng. J. **134**(1–3), 123–130 (2007)
8. I. Reyero, G. Arzamendi, L.M. Gandía, Heterogenization of the biodiesel synthesis catalysis: CaO and novel calcium compounds as transesterification catalysts. Chem. Eng. Res. Des. **92**(8), 1519–1530 (2014)
9. E. Santacesaria, G.M. Vicente, M. Di Serio, R. Tesser, Main technologies in biodiesel production: State of the art and future challenges. Catal. Today **195**(1), 2–13 (2012)
10. E.J.M. de Paiva, S. Sterchele, M.L. Corazza, D.Y. Murzin, F. Wypych, T. Salmi, Esterification of fatty acids with ethanol over layered zinc laurate and zinc stearate–kinetic modeling. Fuel **153**, 445–454 (2015)

11. A. Navajas, I. Campo, A. Moral, J. Echave, O. Sanz, M. Montes, J.A. Odriozola, G. Arzamendi, L.M. Gandía, Outstanding performance of rehydrated Mg-Al hydrotalcites as heterogeneous methanolysis catalysts for the synthesis of biodiesel. Fuel **211**, 173–181 (2018)
12. J.C. Villegas, Part I. Manganese oxide containing layered double hydroxides materials: Synthesis and characterization. Part II. Manganese oxide octahedral molecular sieves (OMS-2): Synthesis, particle size control, characterization, and catalytic applications, University of Connecticut, 2006
13. V. Volli, M.K. Purkait, Preparation and characterization of hydrotalcite-like materials from flyash for transesterification. Clean Techn. Environ. Policy **18**(2), 529–540 (2016)
14. L.L. Myint, M.M. El-Halwagi, Process analysis and optimization of biodiesel production from soybean oil. Clean Techn. Environ. Policy **11**(3), 263–276 (2009)
15. J.H. Ng, H.K. Ng, S. Gan, Advances in biodiesel fuel for application in compression ignition engines. Clean Techn. Environ. Policy **12**(5), 459–493 (2010)
16. J.H. Ng, H.K. Ng, S. Gan, Recent trends in policies, socioeconomy and future directions of the biodiesel industry. Clean Techn. Environ. Policy **12**(3), 213–238 (2010)
17. M.K. Lam, K.T. Lee, A.R. Mohamed, Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. Biotechnol. Adv. **28**(4), 500–518 (2010)
18. S.H. Wang, Y.B. Wang, Y.M. Dai, J.M. Jehng, Preparation and characterization of hydrotalcite-like compounds containing transition metal as a solid base catalyst for the transesterification. Appl. Catal. A Gen. **439**, 135–141 (2012)
19. A. Gil, E. Arrieta, M.A. Vicente, S.A. Korili, Synthesis and CO_2 adsorption properties of hydrotalcite-like compounds prepared from aluminum saline slag wastes. Chem. Eng. J. **334**, 1341–1350 (2018)
20. M.P. Dorado, F. Cruz, J.M. Palomar, F.J. Lopez, An approach to the economics of two vegetable oil-based biofuels in Spain. Renew. Energy **31**(8), 1231–1237 (2006)
21. A.B. Chhetri, K.C. Watts, M.R. Islam, Waste cooking oil as an alternate feedstock for biodiesel production. Energies **1**(1), 3–18 (2008)
22. A. Brito, M.E. Borges, M. Garín, A. Hernández, Biodiesel production from waste oil using Mg− Al layered double hydroxide catalysts. Energy Fuel **23**(6), 2952–2958 (2009)
23. M. del Remedio Hernandez, J.A. Reyes-Labarta, F.J. Valdes, New heterogeneous catalytic transesterification of vegetable and used frying oil. Ind. Eng. Chem. Res. **49**(19), 9068–9076 (2010)
24. A. Demirbas, Use of algae as biofuel sources. Energy Convers. Manag. **51**(12), 2738–2749 (2010)
25. L. Brennan, P. Owende, Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. Renew. Sust. Energ. Rev. **14**(2), 557–577 (2010)
26. T.K. Hari, Z. Yaakob, N.N. Binitha, Aviation biofuel from renewable resources: Routes, opportunities and challenges. Renew. Sust. Energ. Rev. **42**, 1234–1244 (2015)
27. J. Hill, E. Nelson, D. Tilman, S. Polasky, D. Tiffany, Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. Proc. Natl. Acad. Sci. **103**(30), 11206–11210 (2006)
28. A.L. Ahmad, N.M. Yasin, C.J.C. Derek, J.K. Lim, Microalgae as a sustainable energy source for biodiesel production: A review. Renew. Sust. Energ. Rev. **15**(1), 584–593 (2011)
29. M. Ayoub, A.Z. Abdullah, Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry. Renew. Sust. Energ. Rev. **16**(5), 2671–2686 (2012)
30. Y.Y. Tye, K.T. Lee, W.N.W. Abdullah, C.P. Leh, Second-generation bioethanol as a sustainable energy source in Malaysia transportation sector: Status, potential and future prospects. Renew. Sust. Energ. Rev. **15**(9), 4521–4536 (2011)
31. A. Demirbas, Progress and recent trends in biodiesel fuels. Energy Convers. Manag. **50**(1), 14–34 (2009)

32. J.M. Ogden, R.H. Williams, E.D. Larson, Societal lifecycle costs of cars with alternative fuels/engines. Energy Policy **32**(1), 7–27 (2004)
33. P.A. Owusu, S. Asumadu-Sarkodie, A review of renewable energy sources, sustainability issues and climate change mitigation. Cogent Eng. **3**(1), 1167990 (2016)
34. S. Mekhilef, S. Siga, R. Saidur, A review on palm oil biodiesel as a source of renewable fuel. Renew. Sust. Energ. Rev. **15**(4), 1937–1949 (2011)
35. M. Nolte, Commercial biodiesel production in South Africa: A preliminary economic feasibility study, Doctoral dissertation, University of Stellenbosch, Stellenbosch, 2007
36. A.K. Agarwal, Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Prog. Energy Combust. Sci. **33**(3), 233–271 (2007)
37. M.K. Yesilyurt, C. Cesur, V. Aslan, Z. Yilbasi, The production of biodiesel from safflower (Carthamus tinctorius L.) oil as a potential feedstock and its usage in compression ignition engine: A comprehensive review. Renew. Sustain. Energy Rev. **119**, 109574 (2020)
38. M.J. Pratas, S. Freitas, M.B. Oliveira, S.C. Monteiro, Á.S. Lima, J.A. Coutinho, Densities and viscosities of minority fatty acid methyl and ethyl esters present in biodiesel. J. Chem. Eng. Data **56**(5), 2175–2180 (2011)
39. P. Cao, M.A. Dubé, A.Y. Tremblay, High-purity fatty acid methyl ester production from canola, soybean, palm, and yellow grease lipids by means of a membrane reactor. Biomass Bioenergy **32**(11), 1028–1036 (2008)
40. B. Sajjadi, A.A.A. Raman, H. Arandiyan, A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. Renew. Sust. Energ. Rev. **63**, 62–92 (2016)
41. S.Y. No, Inedible vegetable oils and their derivatives for alternative diesel fuels in CI engines: A review. Renew. Sust. Energ. Rev. **15**(1), 131–149 (2011)
42. A.Z. Abdullah, B. Salamatinia, H. Mootabadi, S. Bhatia, Current status and policies on biodiesel industry in Malaysia as the world's leading producer of palm oil. Energy Policy **37**(12), 5440–5448 (2009)
43. A.S. Carlsson, Plant oils as feedstock alternatives to petroleum–a short survey of potential oil crop platforms. Biochimie **91**(6), 665–670 (2009)
44. H. Huo, M. Wang, C. Bloyd, V. Putsche, Life-cycle assessment of energy use and greenhouse gas emissions of soybean-derived biodiesel and renewable fuels. Environ. Sci. Technol. **43**(3), 750–756 (2009)
45. B.D. Solomon, Biofuels and sustainability. Ann. N. Y. Acad. Sci. **1185**(1), 119–134 (2010)
46. C.H. Foyer, K.H. Siddique, A.P. Tai, S. Anders, N. Fodor, F.L. Wong, N. Ludidi, M.A. Chapman, B.J. Ferguson, M.J. Considine, F. Zabel, Modelling predicts that soybean is poised to dominate crop production across Africa. Plant Cell Environ. **42**(1), 373–385 (2019)
47. G. Engelbrecht, S. Claassens, C. Mienie, H. Fourie, South Africa: An important soybean producer in sub-Saharan Africa and the quest for managing nematode pests of the crop. Agriculture **10**(6), 242 (2020)
48. K. Muroyama, R. Atsumi, A. Andoh, Effect of pretreatment on lactic acid fermentation of bean curd refuse with simultaneous saccharification, in *Studies in Surface Science and Catalysis*, (Elsevier, Amsterdam, 2006), pp. 133–136
49. K. Muroyama, T. Mochizuki, T. Wakamura, Methane fermentation of bean curd refuse. J. Biosci. Bioeng. **91**(2), 208–212 (2001)
50. F. Cuadros, F. López-Rodríguez, A. Ruiz-Celma, F. Rubiales, A. González-González, Recycling, reuse and energetic valuation of meat industry wastes in Extremadura (Spain). Resour. Conserv. Recycl. **55**(4), 393–399 (2011)
51. A. Redondo-Cuenca, M.J. Villanueva-Suárez, I. Mateos-Aparicio, Soybean seeds and its by-product okara as sources of dietary fibre. Measurement by AOAC and Englyst methods. Food Chem. **108**(3), 1099–1105 (2008)
52. S.P. Singh, D. Singh, Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. Renew. Sust. Energ. Rev. **14**(1), 200–216 (2010)

53. M. Balat, Fuel characteristics and the use of biodiesel as a transportation fuel. Energy Sources, Part A **28**(9), 855–864 (2006)
54. B.R. Moser, Biodiesel production, properties, and feedstocks, in *Biofuels*, (Springer, New York, 2011), pp. 285–347
55. U. Rashid, F. Anwar, Production of biodiesel through base-catalyzed transesterification of safflower oil using an optimized protocol. Energy Fuel **22**(2), 1306–1312 (2008)
56. V.I.E. Ajiwe, A.E. Obika, African pear seed oil: Potential alternative source to diesel oil. Energy Fuel **14**(1), 112–116 (2000)
57. H.Y. Zhang, M.A. Hanna, Y. Ali, L. Nan, Yellow nut-sedge (Cyperus esculentus L.) tuber oil as a fuel. Ind. Crop. Prod. **5**(3), 177–181 (1996)
58. P. Schinas, G. Karavalakis, C. Davaris, G. Anastopoulos, D. Karonis, F. Zannikos, S. Stournas, E. Lois, Pumpkin (Cucurbita pepo L.) seed oil as an alternative feedstock for the production of biodiesel in Greece. Biomass Bioenergy **33**(1), 44–49 (2009)
59. I.C.F. Dos Santos, S.H.V. De Carvalho, J.I. Solleti, W.F. de La Salles, K.T.D.S. de La, S.M.P. Meneghetti, Studies of Terminalia catappa L. oil: Characterization and biodiesel production. Bioresour. Technol. **99**(14), 6545–6549 (2008)
60. A. Mariod, S. Klupsch, I.H. Hussein, B. Ondruschka, Synthesis of alkyl esters from three unconventional Sudanese oils for their use as biodiesel. Energy Fuel **20**(5), 2249–2252 (2006)
61. M. Balat, H. Balat, Progress in biodiesel processing. Appl. Energy **87**(6), 1815–1835 (2010)
62. O.D. Hebbal, K.V. Reddy, K. Rajagopal, Performance characteristics of a diesel engine with deccan hemp oil. Fuel **85**(14–15), 2187–2194 (2006)
63. H. Shao, L. Chu, Resource evaluation of typical energy plants and possible functional zone planning in China. Biomass Bioenergy **32**(4), 283–288 (2008)
64. U. Rashid, F. Anwar, B.R. Moser, G. Knothe, Moringa oleifera oil: A possible source of biodiesel. Bioresour. Technol. **99**(17), 8175–8179 (2008)
65. J. Kansedo, K.T. Lee, S. Bhatia, Cerbera odollam (sea mango) oil as a promising non-edible feedstock for biodiesel production. Fuel **88**(6), 1148–1150 (2009)
66. Y.C. Sharma, B. Singh, An ideal feedstock, kusum (Schleichera trijuga) for preparation of biodiesel: Optimization of parameters. Fuel **89**(7), 1470–1474 (2010)
67. P.K. Devan, N.V. Mahalakshmi, Performance, emission and combustion characteristics of poon oil and its diesel blends in a DI diesel engine. Fuel **88**(5), 861–867 (2009)
68. G. Knothe, S.C. Cermak, R.L. Evangelista, Cuphea oil as source of biodiesel with improved fuel properties caused by high content of methyl decanoate. Energy Fuel **23**(3), 1743–1747 (2009)
69. B.P. Chapagain, Y. Yehoshua, Z. Wiesman, Desert date (Balanites aegyptiaca) as an arid lands sustainable bioresource for biodiesel. Bioresour. Technol. **100**(3), 1221–1226 (2009)
70. P.N. Giannelos, S. Sxizas, E. Lois, F. Zannikos, G. Anastopoulos, Physical, chemical and fuel related properties of tomato seed oil for evaluating its direct use in diesel engines. Ind. Crop. Prod. **22**(3), 193–199 (2005)
71. M.G. Kulkarni, A.K. Dalai, Waste cooking oil an economical source for biodiesel: A review. Ind. Eng. Chem. Res. **45**(9), 2901–2913 (2006)
72. C.C. Enweremadu, M.M. Mbarawa, Technical aspects of production and analysis of biodiesel from used cooking oil—A review. Renew. Sust. Energ. Rev. **13**(9), 2205–2224 (2009)
73. M.J. Haas, Improving the economics of biodiesel production through the use of low value lipids as feedstocks: Vegetable oil soapstock. Fuel Process. Technol. **86**(10), 1087–1096 (2005)
74. S. Çaynak, M. Gürü, A. Biçer, A. Keskin, Y. Içingür, Biodiesel production from pomace oil and improvement of its properties with synthetic manganese additive. Fuel **88**(3), 534–538 (2009)
75. Y. Chisti, Biodiesel from microalgae. Biotechnol. Adv. **25**(3), 294–306 (2007)
76. R. Harun, M. Singh, G.M. Forde, M.K. Danquah, Bioprocess engineering of microalgae to produce a variety of consumer products. Renew. Sust. Energ. Rev. **14**(3), 1037–1047 (2010)
77. G. Huang, F. Chen, D. Wei, X. Zhang, G. Chen, Biodiesel production by microalgal biotechnology. Appl. Energy **87**(1), 38–46 (2010)
78. F. Ma, M.A. Hanna, Biodiesel production: A review. Bioresour. Technol. **70**(1), 1–15 (1999)

79. C.W. Purnomo, C. Salim, H. Hinode, Synthesis of pure Na–X and Na–A zeolite from bagasse fly ash. Microporous Mesoporous Mater. **162**, 6 (2012)
80. M. Wdowin, M. Franus, R. Panek, L. Badura, W. Franus, The conversion technology of fly ash into zeolites. Clean Techn. Environ. Policy **16**(6), 1217–1223 (2014)
81. Q. Wang, D. O'Hare, Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets. Chem. Rev. **112**(7), 4124–4155 (2012)
82. K.T. Chen, J.X. Wang, Y.M. Dai, P.H. Wang, C.Y. Liou, C.W. Nien, J.S. Wu, C.C. Chen, Rice husk ash as a catalyst precursor for biodiesel production. J. Taiwan Inst. Chem. Eng. **44**(4), 622–629 (2013)
83. K. Yan, X. Xie, J. Li, X. Wang, Z. Wang, Preparation, characterization, and catalytical application of Mg coal hydrotalcite-like compounds. J. Nat. Gas Chem. **16**(4), 371–376 (2007)
84. K. Hosni, E. Srasra, Simplified synthesis of layered double hydroxide using a natural source of magnesium. Appl. Clay Sci. **43**(3–4), 415–419 (2009)
85. P. Kunecki, R. Panek, M. Wdowin, W. Franus, Synthesis of faujasite (FAU) and tschernichite (LTA) type zeolites as a potential direction of the development of lime Class C fly ash. Int. J. Miner. Process. **166**, 69–78 (2017)
86. P. Kunecki, R. Panek, A. Koteja, W. Franus, Influence of the reaction time on the crystal structure of Na-P1 zeolite obtained from coal fly ash microspheres. Microporous Mesoporous Mater. **266**, 102–108 (2018)
87. G.N. Muriithi, L.F. Petrik, W.M. Gitari, F.J. Doucet, Synthesis and characterization of hydrotalcite from South African Coal fly ash. Powder Technol. **312**, 299–309 (2017)
88. T. Wajima, Synthesis of hydrotalcite from bittern, and its removal abilities of phosphate and nitrate. Int. J. Chem. Eng. Appl. **6**(4), 228 (2015)
89. Y. Kuwahara, T. Ohmichi, T. Kamegawa, K. Mori, H. Yamashita, A novel conversion process for waste slag: Synthesis of a hydrotalcite-like compound and zeolite from blast furnace slag and evaluation of adsorption capacities. J. Mater. Chem. **20**(24), 5052–5062 (2010)
90. R. Galindo, A. López-Delgado, I. Padilla, M. Yates, Synthesis and characterisation of hydrotalcites produced by an aluminium hazardous waste: A comparison between the use of ammonia and the use of triethanolamine. Appl. Clay Sci. **115**, 115–123 (2015)
91. R. Galindo, I. Padilla, R. Sánchez-Hernández, J.I. Robla, G. Monrós, A. López-Delgado, Production of added-value materials from a hazardous waste in the aluminium tertiary industry: Synergistic effect between hydrotalcites and glasses. J. Environ. Chem. Eng. **3**(4), 2552–2559 (2015)
92. P.L. Linda, D.O. Okanigbe, A.P.I. Popoola, O.M. Popoola, Characterization of density separated mullite rich tailings from a secondary copper resource, a potential reinforcement material for development of an enhanced thermally conductive and wear resistant ti-6al-4v matrix composite, in *The proceedings of the 60th International Conference of Metallurgist*, Canada, 2021
93. D.O. Okanigbe, Production of copper and copper oxide nano-particles from leach solution of low grade copper smelter dust, 2019
94. F. Bakhtiari, Synthesis and characterization of tenorite (CuO) nanoparticles from smelting furnace dust (SFD). J. Min. Metall. Sect. B. **49**(1), 21–21 (2013)