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Biodiesel Production as a Renewable Resource for the Potential Displacement of the Petroleum Diesel

Ifeanyichukwu Edeh

Abstract

In the quest to comply with the Intergovernmental Panel on Climate Change (IPCC) on reducing the global temperature to 1.5–2.0°C as a measure to minimize the climate change caused by the emission of greenhouse gases from the combustion of fossil fuels, and the need for replacement of these fossil fuels, which are also generally believed to be depleting, biodiesel is being studied as a potential replacement for the conventional petroleum diesel. This fuel among other desired properties is renewable, biodegradable, sustainable, and emits less particles. It also contains no amount of sulfur, in addition to possessing most of the good characteristics of petroleum diesel. At the moment, more than 95% of biodiesel produced globally is obtained from vegetable oil feedstocks, which are usually very expensive and thus, without tax waiver and subsidy, makes biodiesel non-competitive with the petroleum diesel. Based on this, non-edible feedstocks are being investigated. Although, their oil yield is low, studies are carried out to ensure efficient extraction. The economics of the process is considered to determine the most economic variables that impact the profitability of biodiesel production. This chapter deals with the biodiesel classification, feedstocks, lipid/oil extraction, biodiesel production methods and the economic aspect of the process.

Keywords: biodiesel, renewable, feedstocks, extraction, properties, technologies, economics

1. Introduction

The need to substitute the conventional petroleum diesel with a renewable alternative, one that is sustainable and environmentally friendly, has driven various investigators over a decade now to research on the potentials of biodiesel [1]. This has risen due to depletion of fossil fuels and emission of greenhouse gases such as CO₂ and methane upon combustion, which causes climate change, the result of which is the rise in the global temperature above the nominal margin of 2°C with the potential to extinct over 1 million species [2, 3]. Other adverse effects of this global temperature rise also known as global warming include receding of glaciers, rise in sea level and loss of biodiversity [4]. However, biodiesel is a renewable fuel produced from the reaction between triacylglycerol or fatty acid with alcohol in the

Country	Biodiesel production/billion liters
USA	5.5
Brazil	3.8
Germany	3
Indonesia	3
Argentina	3
France	1.5
Thailand	1.4
Spain	1.1
Belgium	0.5
Colombia	0.5
Canada	0.4
China	0.3
India	0
Singapore	0

Table 1.
Countries with top biodiesel production in 2016.

presence of a catalyst [5]. The fuel exists as liquid and consists of mono-alkyl esters of long-chain fatty acids with similar characteristics as the conventional petroleum diesel, making it a potential substitute [6]. Biodiesel is biodegradable, sustainable, and nontoxic, and has less impact on the environment. The shortcomings of biodiesel include low energy density, relatively high production cost and poor cold flow [7]. The global production capacity of biodiesel is envisaged to reach 12 billion gallons by 2020 with Brazil, United States of America, Malaysia, Argentina, Netherlands, Spain, Philippines, Belgium, Indonesia and Germany meeting more than 80% of the world demand [8, 9]. In 2016, the biodiesel produced globally were contributed mostly by USA and Brazil (see **Table 1**). Larger proportions of which are consumed by countries such as USA, Brazil, Germany, Indonesia and France [2]. Countries like US, China and India are currently experiencing a great growth in the biodiesel market with their respective governments planning to replace about 15% of the conventional diesel with biodiesel by 2020.

2. Classification of biodiesel

Biodiesel can be classified into three types based on the kind of feedstocks used in its production [10]. These are first-, second- and third-generation biodiesels.

2.1 The first-generation biodiesel

This type of biodiesel is produced using edible vegetable oils. These oils are discussed in the next section. Biodiesel produced from these oils usually has the following disadvantages [11–14]:

- 1. Poor storage
- 2. Oxidation stability

- 3. High feedstock cost, up to 60–80% of biodiesel production cost
- 4. Low heating value
- 5. Higher NOx emission compared to the conventional diesel fuel
- 6. Loss of biodiversity

2.2 Second-generation biodiesel

In order to minimize the over dependency on the edible vegetable oils feed-stocks in biodiesel production, alternative sources from non-edible oils are explored. Biodiesel produced from this type of oils is known as second-generation biodiesel. The quality and yield obtained are similar to that from edible oils [15]. Lignocellulosic biomass (LCB) is also being considered as an alternative feedstock to edible oil in biodiesel production probably because it is suspected to promote faster production, less labour, more season and climate flexibility, easier scale-up, and potential economic advantage [16]. This biomass can be derived from food crops, non-food/energy crops, forest residue and industrial process residues (see **Table 2**). But, the most predominant is agricultural crop residues [17]. Although, some of the LCB resources might not be suitable for energy production, probably due to their wide dispersal or low bulk density, which makes energy recovery, transport and storage expensive [18]. Generally, the production of biodiesel from lignocellulosic biomass is hampered due to lack of economically feasible technologies [18].

Food crops	Non-food/energy crops	Forest residue	Industrial process residues
*Rice straw	*Cardoon (<i>Cynara cardunculus</i> , L.)	*Tree residue (twigs, leaves, bark, and roots)	*Rice husk
*Wheat straw	*Giant reed (<i>Arundo donax</i> L.)	*Wood processing residues (sawmill off-cuts and sawdust)	*Rice bran
*Sugarcane tops	*Salix	*Recycled wood (from demolition of buildings, pallets, and packing crates)	*Sugarcane bagasse
*Maize stalks millet	*Jute stalks		*Coconut husks
*Groundnut stalks	*Willow		*Maize husks
*Corn straw	*Poplar		*Groundnut husks
*Soybean residue	*Eucalyptus		
*Residue from vegetables	*Miscanthus		
*Residence from pulses	*Reed canary grass		
	*Switch grass		
	*Hemp		

Table 2.
Sources of lignocellulosic biomass for biodiesel production [17].

2.3 Third-generation biodiesel

This is produced from micro-and macro-species including algae [11]. Third-generation biodiesel is discussed further in Section 3.2.

2.4 Fourth-generation biodiesel and speculations

This can be produced from feedstocks that possess the capability of being genetically modified, accumulate large quantity of biomass, and can be utilized in photo-biological solar cells with the ability to convert solar energy directly to usable biodiesel. Example of such feedstocks is algal species. This concept focuses on producing biodiesel in addition to developing a means of trapping and storing CO₂. The method of producing this energy is similar to that of the second-generation biofuels, except that CO₂ is arrested at each stage of the production using techniques such as oxy-fuel combustion. The CO₂ trapped is stored in saline aquifers, gas fields or old oils through the method known as geo-sequestration. The process has the capacity to trap carbon inclusively making it ‘carbon negative’ as opposed to ‘carbon neutral’ [2, 19].

3. Feedstock for biodiesel production

These include edible and non-edible oils, and are presented below.

3.1 Edible oils for biodiesel production

At the moment, over 95% of biodiesel globally is produced from edible vegetable oils. The commonly used of these oils are palm oil, soybean, coconut oil, rapeseed and sunflower due to their availability [12–15, 19–20]. Rapeseed oil, sunflower oil, palm oil and soybean oil are used in Europe, Malaysia, Indonesia, Philippines and US, respectively to produce biodiesel [21]. There is no doubt that the use of these feedstocks for biodiesel production competes with their need for human consumption and some other applications, the disadvantage of which is insecurity, high cost of production and potential depletion of ecological resources due to some agricultural practices. Biodiesel produced from these oils usually has the disadvantages highlighted in Section 2.1 [12–14, 21]. The sources of edible oil and the respective yield of oil are presented in Table 3.

3.2 Non-edible oils for biodiesel production

Non-edible oils are cultivated on lands requiring minimum attention and as such are less expensive compared to edible oils [22]. These oils include jatropha, karanja, polanga, cotton seed, *Simmondsia chinensis* (jojoba), tobacco, neem, linseed, rice

S/N	Source	Yield
1.	Rapeseed (Brassica oilseed)	38–46
2.	Coconut	63–65
3.	Soybean	15–20
4.	Palm	30–60
5.	Sunflower	25–35

Table 3.
Sources of edible oil used in biodiesel production [11].

bran oil, microalgae, mahua, waste cooking oil, animal fats, activated sludge lipid and rubber seed oils, and are used for biodiesel production [5, 23–28], see **Figure 1**. The work done by Bankovic-Ili et al. revealed that jatropha, karanja, mahua and castor are the most commonly sourced non-edible oils for biodiesel production [22]. The methyl esters of these oils can be blended with edible oils such as palm oil to produce an alternative to the conventional diesel fuels, which conforms to the standards of US ASTM D 6751 and European EN 14214 [32].

3.2.1 Advantage of non-edible oils

These include

1. Could be a replacement for edible oils in biodiesel production [32–34]
2. Contain toxic materials, which make them unsuitable for human consumption [35]
3. Naturally available [33]
4. Inexpensive as they are planted in wastelands and no intensive care needed [22].

Figure 1.
Sources of non-edible oils used in biodiesel production [29–31].

3.2.2 Examples of non-edible oil used for biodiesel production

Some of these non-edible oils are discussed in more detail below:

3.2.2.1 Waste cooking oil (WCO)

This oil maybe yellow or brown grease obtained from palm, canola, corn, sunflower and other edible oils. Usually, it is ubiquitous and inexpensive, making it ideal for biodiesel production. In recent times, some researchers have demonstrated that biodiesel can be produced from WCO by pyrolysis and transesterification methods. The latter method is preferred due its low cost and simplicity [1]. The performance of the process is usually measured in terms of yield and it depends on factors such as catalyst, catalyst loading, temperature, time and methanol-to-oil molar ratio (see **Table 4**).

3.2.2.2 Algae

The use of algae in biofuel production is gaining traction globally, especially as it is considered to be safer, non-competitive and made up of microorganisms with precocious growth. These organisms are aquatic and may be unicellular or multicellular with over 300,000 species. The number is greater than plant species and the organisms exhibit varying compositions, but are faced with higher cost of production. Also, more complexity of processes and technology are required for cultivation compared to plants [51]. Algae grow naturally in open ponds and can be cultivated through tubular photobioreactors. The former is the oldest method involving a simple and inexpensive process, compared to the latter, which enjoys high productivity rate, less maturity time and the capacity to selectively produced high lipid content using desirable algae species. Algae contain lipids, carbohydrates and complex oil depending on their species [52–55]. The lipid content ranges from 20 to 80% depending on the various species. Some species such as *Tribonema*, *Ulothrix* and *Euglena* are considered to possess high lipid content and have great potential for biodiesel and kerosene production [56]. Efforts are being made to increase the lipid content of algae by modifying the algae genome in charge of nitrogen assimilation. This process could double the lipid content thereby increasing the potential of the commercial production of biodiesel. However, the production of algae is independent of season and it is characterized by an exponential growth rate with capacity to double their biomass in about 3.5h [51]. This ensures a relative abundance of algae on earth surface.

Algae are not edible and using them as a feedstock for biodiesel production poses no threat to food production. They have the capability to convert carbon dioxide to biofuels and oleochemical products [51]. The remaining biomass can be converted into useful chemicals to generate more revenue to ameliorate the high economic cost of the process.

3.2.2.3 Biodiesel production with algae as feedstock

Due to high lipid content and availability, several investigators have explored the potential of algae as a feedstock for biofuel production. This usually begins by selecting algae species with high lipid yield and very good fatty acid composition as shown in **Figure 2**. The desirable algae species for the production of biodiesel is usually selected based on growth rate, degree of survival and physicochemical properties and fatty acid composition.

S/N	Catalyst	Reaction condition	Biodiesel yield (%)	References
1.	Calcined chicken manure	Catalyst loading 7.5wt%, temperature 65°C and methanol-to-oil molar ratio 1:15	90	[36]
2.	Chicken manure biochar	Temperature 350°C	95	[37]
3.	CsPW-CB	Catalyst loading 2 wt%, methanol-to-oil molar ratio 11:1, temperature 70°C and time 2.5 h	95.1	[38]
4.	KOH	Catalyst loading 1 wt%, methanol-to-oil molar ratio 1:3, temperature 60°C and time 0.8 h	94	[39, 40]
5.	Titanium iso-propoxide (TiO ₂) + graphene oxide (GO)	Catalyst loading 1.5 wt%, methanol-to-oil molar ratio 1:12, temperature 65°C and time 3 h	98	[41]
6.	Calcium diglyceroxide	Catalyst loading 1.03 wt%, methanol-to-oil molar ratio 7.46:1, temperature 62°C and time 0.4 h	94.86	[40]
7.	KOH	Catalyst loading 1.5 wt%, methanol-to-oil molar ratio 7:1, temperature 60°C and time 1.5 h	92	[42]
8.	KOH	Catalyst loading 1.16 wt%, methanol-to-oil molar ratio 9.4:1, temperature 62.4°C and time 2 h	98.26	[43]
9.	CaO/MgO	Catalyst loading 6 wt%, methanol-to-oil molar ratio 1:15, temperature 90°C and time 2 h	96.47	[44]
10.	CaO	Catalyst loading 5 wt%, methanol-to-oil molar ratio 20:1, temperature 65°C and time 4 h	96.74	[45]
11.	BaSnO ₃	Catalyst loading 6 wt%, methanol-to-oil molar ratio 10:1, temperature 90°C and time 2 h	96	[46]
12.	Sulphamic acid	Catalyst loading 1 wt%, methanol-to-oil molar ratio 10:1, temperature 110°C and time 2 h	95.6	[47]
13.	Fusion waste chicken and fish bones	Catalyst loading 1.98 wt%, methanol-to-oil molar ratio 10:1, temperature 65°C and time 1.5 h	89.5	[48]
14.	Biomass fly ash	Catalyst loading 10 wt%, methanol-to-oil molar ratio 9:1, temperature 60°C and time 3 h	95	[49]
15.	Kettle limescale	Catalyst loading 8.87 wt%, methanol-to-oil molar ratio 1.7:3, temperature 61.7°C and time 0.25 h	93.41	[43]
16.	Calcium oxide (CaO) nano-catalyst	Catalyst loading 1 wt%, methanol-to-oil molar ratio 8:1, temperature 50°C, time 1.5 h and particle size 29 nm	96	[50]

Table 4.
Dependence of the yield of biodiesel from WCO on reaction parameters.

The typical properties of biodiesel algae oil compared with standards and biodiesel from other sources are presented in **Table 5**. Applying such biodiesel in an internal combustion engine usually consumes more fuel and has less thermal efficiency than petroleum diesel. This may be due to its physicochemical properties such as higher density and viscosity, lower calorific value and cetane number. The effect of this problem can be minimized by blending it with petroleum diesel (up to 30%) [57–65]. The presence of excess oxygen molecule in the algae biofuel ensures that complete combustion is attained, thereby eliminating the emission of undesirable substances such as hydrocarbons and carbon monoxide. But, NO_x emission like biodiesel from other sources is high and can be reduced by the addition of n-butanol to the blends [63].

Figure 2. Processes involved in applying algae as feedstock for the production of biodiesel at a small scale or experimental level [56].

S/N	Properties	ASTM 6751-12	EN 14,214	Diesel	Algae oil	Palm oil	Jatropha	Karanja
1	Calorific value (kJ/kg)	—	—	43,000	40,072	37,800	39,000	39,200
2	Density (kg/L)	086–0.90	0.86–0.90	0.84	0.912	0.850	0.940	0.874
3	Viscosity @ 40°C (mm ² /s)	1.9–6.0	3.5–5.0	2.64	5.06	4.32	4.8	5.21
4	Cetane number	>47	>51	53.3	46.5	55	50	50
5	Flash point (°C)	100–170	>120	71	145	167	135	100
6	Acid value (mg KOH/g)	<0.5	<0.5	0.0	0.14	0.24	0.4	0.43
7	Oxidation stability @ 110°C	3.0	>6.0	—	6.76	10.3	3.2	—
8	Oil yield (L/ha)	—	—	—	58,000	5950	1892	2590

S/N is serial number.

Table 5. Comparison between the fuel properties of algae oil and the petroleum diesel [51].

3.2.2.4 Tea seed oil

This is one of the cheapest vegetable oils with an average price of US \$514 per ton. It is composed of predominantly unsaturated fatty acids with lower pour point, making it suitable for biodiesel production [64]. The characteristics of biodiesel from tea seed oil share some resemblances with those from vegetable oil, but it has lower

pour point of -5°C and is less viscous than biodiesel from palm oil, cotton seed oil and peanut oil [1, 64, 66]. Like in algae biodiesel, the application of tea seed oil biodiesel in internal consumption engine requires more fuel consumption and causes high emissions of CO and CO_2 . To solve these problems, hydrogen is usually added to the petroleum diesel and biodiesel blends, thereby improving the performance characteristics of the engine. This gain is possible since there is absence of carbon atoms in the chemical structure. But, the disadvantage is increased NOx emission [65].

3.2.2.5 Activated sludge

This sludge is a residue from the secondary/biological section of wastewater treatment plant and composed predominantly of microorganisms [67]. It is being investigated as a feedstock for biodiesel production probably due to its availability, lipid content and possibility of obtaining it without any cost implication [5, 68–72]. The lipid/oil content is relatively low and various researchers have investigated the

S/N	Source	Characteristics	Yield (wt.%)	Fatty acid composition	References
1.	Karanja	Grown in Southeast Asia, flowers 3–4 years after planting while matures 4–7 years later, a single tree yields 9–90 kg of seeds	25–40	Oleic (44.5–71.3%), linoleic (10.8–18.3%) and stearic acids (2.4–8.9%)	[76–79]
2.	Mahua	Grown in Indian forest, produces 20–200 kg of seeds annually per tree depending on maturity, starts to bear seeds after 10 years of planting and continues up to 60 years	35–50	Oleic (41–51%), stearic (20.0–25.1%), palmitic acid (16.0–28.2%) and linoleic acids (8.9–18.3%)	[51, 80–82]
3.	Cotton	Grown for cotton fiber in China, United States and Europe, the seeds contain non-glycerides such as gossypol, phospholipids, sterols, resins, carbohydrates and related pigments	17–25	Linoleic (55.2–55.5%), palmitic (11.67–20.1%) and oleic acids (19.2–23.26%)	[83–85]
4.	Neem	Can grow in different kinds of soils such as saline, clay, dry, shallow, alkaline and stony in Asian countries including India, Malaysia and Indonesia. It matures after 15 years and has a life span of 150–200 years	20–30	Linoleic (6–16%), oleic (25–54%) and stearic (9–24%) acids	[17, 51, 85–87]
5.	Tobacco	Grown in countries such as Turkey, Macedonia and North America for leaf collection	35–49	Linoleic acid (69.49–75.58%)	[88–91]
6.	Rubber	Forest-based tree largely grown in Malaysia, India, Thailand and Indonesia	50–60	Linoleic (39.6–40.5%), oleic (17–24.6%) and linolenic acid (16.3–26%)	[20, 92–94]
7.	Jatropha	Grown in arid, semi-arid and tropical regions, such as United States, Brazil, Bolivia and Mexico. Produces seeds after 12 months of planting, attain optimum productivity by 5 years and has a life span of up to 30 years	20–60	Linoleic (31.4–43.2%), oleic acid (34.3–44.7%), stearic (7.1–7.4%) and palmitic (13.6–15.1%) acids	[95–98]

Table 6.
Non-edible oils from the seeds of their respective trees used for biodiesel production.

potential of increasing the yield using different methods to ensure its adaptability as a substrate for biodiesel production. Notable among them are Edeh et al., who using the combination of subcritical water technology and optimization increased the lipid yield from 7.4 (wt./wt.)% to 41.0 (wt./wt.)% [28]. The predominant fatty acid in activated sludge is palmitic acid [27]. Researchers have shown that activated sludge can be used as a feedstock for biodiesel production. But, due to low yield of 3–6 wt%, (dry cell weight), which is below the minimum of 10 wt.% (dry cell weight) required for biodiesel to have an economic advantage over the conventional petroleum diesel, this feedstock is still unattractive [60, 73–74]. Another problem is variation in the composition of fatty acids, which depends on the source and composition of wastewater and season of collection, which affect the quality and yield of the biodiesel [5, 75].

Other non-edible oils used in the production of biodiesel are presented in **Table 6**.

3.2.3 Fuel properties of biodiesel produced from various non-edible oils

These properties depend on the fatty acid and chemical composition of the non-edible oils. The fuel properties of biodiesel can be measured by using different standards including ASTM D6751 and EN 14214. The most essential properties used in assessing the suitability of biodiesel as fuel include density, flash point, cloud

Non-edible oil	Density at 40°C (kg/m ³)	Viscosity at 40°C (mm ² /s)	Flash point (°C)	Cloud point (°C)	Pour point (°C)	Cetane number	Calorific value (MJ/kg)	References
Karanja (<i>Pongamia pinnata</i> L.)	876–890	4.37–9.60	163–187	13–15	–3 to 5.1	52–58	36–38	[15, 77, 99–101]
Polanga (<i>Calophyllum inophyllum</i>)	888.6–910	4–5.34	151–170	13.2–14	4.3	57.3	39.25–41.3	[15, 102]
Mahua (<i>Madhuca indica</i>)	904–916	3.98–5.8	127–129	3–5	1–6	51–52	39.4–39.91	[15, 103–106]
Rubber seed oil (<i>Hevea brasiliensis</i>)	860–881	5.81–5.96	130–140	4–5	–8	37–49	36.5–41.07	[92, 107–109]
Cotton seed	874–911	4–4.9	210–243	1.7	–10 to –15	41.2–59.5	39.5–40.1	[110–112]
Joboba oil (<i>Simmondsia chinensis</i>)	863–866	19.2–25.4	61–75	6–16	–6 to 6	63.5	42.76–47.38	[113–116]
Tobacco oil (<i>Nicotiana tabacum</i>)	860–888.5	3.5–4.23	152–165.4	—	–12	49–51.6	38.43–39.81	[89, 90, 117]
Neem (<i>Azadirachta</i>)	912–965	20.5–48.5	34	—	—	51	33.7–39.5	[87, 110, 118, 119]
Linseed oil (<i>Linum usitatissimum</i>)	865–950	16.2–36.6	108	1.7	–4 to –18	28–35	37.7–39.8	[110, 120, 121]
Jatropha (<i>Jatropha curcas</i> L.)	864–880	3.7–5.8	163–238	—	5	46–55	38.5–42	[122, 123]
Diesel	816–840	2.5–5.7	50–98	–10 to –5	–20 to 5	45–55	42–45.9	[124–126]

Table 7.
Properties of diesel fuel and those of biodiesel produced from non-edible oils.

S/N	Property	Characteristics	Standard	References
1.	Density	Higher than the diesel	ASTM D1298 and EN ISO 3675	[127]
2.	Kinematic viscosity	High viscosity causes poor fuel flow resulting in delayed combustion	ASTM D445 and EN ISO 3104	[128]
3.	Flash point	Measures the flammability hazard of a substance. At flash point, if the source of ignition is removed, vapor ceases to burn	ASTM D93 and EN ISO 3697	[127]
4.	Cetane number (CN)	Measures the ignition quality of fuel in a power diesel engine. Higher CN causes shorter ignition delay. Biodiesel has higher CN due to its longer fatty acid carbon chains	ASTM D613 and EN ISO 5165	[127]
5.	Cloud point (CP)	Higher CP than diesel	ASTM D2500	[129, 130]
6.	Pour point (PP)	Higher PP than diesel	ASTM D97	[129, 130]
7.	Calorific value (HHV)*	Measures the heat content of a fuel. Biodiesel has lower calorific value than diesel due to its higher oxygen content	ASTM D2015	[107, 131, 132]

Table 8.
Standards for measuring properties of biodiesel [98].

point, pour point, calorific value and cetane point (see **Table 7**). The standards for measuring each property are presented in **Table 8** [99].

4. Lipid/oil extraction methods

In most cases oils are extracted from the oil-bearing biomass, for example oil seeds prior to use in biodiesel production. The methods used in oil extraction include solvent extraction, critical fluid extraction, mechanical extraction, enzymatic oil extraction, microwave-assisted extraction (MAE) and ultrasound-assisted extraction (UAE). They are discussed below:

4.1 Solvent extraction

This extraction method utilizes organic solvents extract lipid/oil from the oil-bearing biomass. The organic solvents used include: hexane, chloroform, ethyl ether, petroleum ether, toluene, methanol, ethanol and acetone [5]. The solvents can also be combined together depending on their polarity to achieve higher yield of oil, for instance, chloroform and methanol, hexane and ethanol, dichloromethane and methanol [23, 133]. The properties that influence the selection of a particular solvent for oil extraction are polarity, volatility, non-miscibility with water, safety, boiling point, environmental factors, absence of toxic or reactive impurities, ability to form two phases with for easy separation, capacity to extract a large range of lipid classes and cost of the solvent [134, 135].

The solvent extraction methods used in the laboratory include Soxhlet, Folch, and Bligh and Dyer methods. Soxhlet method is preferred due to the following advantages: it is easy to use, does not require filtration and inexpensive, and it

ensures higher oil extraction, supports simultaneous and parallel extraction. Despite these advantages, its demerits include requirement of high volume of solvents, health and environmental risks, long extraction time, potential to thermally degrade sample and difficulty to automate due to selectivity issues [136]. The Soxhlet extraction is influenced by the following factors: temperature, sample preparation, extraction time, high solvent-to-sample ratio, type and the volume of solvent [137].

Soxhlet extraction is carried out by heating the distillation/boiling flask containing the organic solvent to its boiling point (see **Figure 3**). The vapor produced passes through the tube to the condenser where it is condensed and the liquid formed trickles down to the thimble containing the sample. The soluble part of the sample is dissolved by this liquid and the process continues until the liquid marked is reached. The solubilized sample is aspirated to the distillation/boiling flask and the process continues until the predetermined number of cycle or extraction time is attained [138].

Figure 3.
Soxhlet apparatus.

4.2 Folch method

This method was developed by Folch et al. [139]. The method utilizes a combination of organic solvents: chloroform and methanol in a ratio of 2:1 (v/v) for lipid/oil extraction. It is usually used for extracting and quantifying total lipids [140].

4.3 Bligh and dyer method

This method has some similarities with the Folch method in terms of the solvent system and function. The method uses combined chloroform and methanol in a ratio of 1:2 (v/v) in converse to the Folch method to extract lipid/oil from samples. With this ratio, the Bligh and Dyer method is more economical than the Folch method [140].

4.4 Critical fluid extraction

This involves the use of supercritical or subcritical fluids in oil extraction. These are discussed below:

4.4.1 *Supercritical fluids (SCFs)*

These are fluids with critical temperature and pressure above their critical points. For example, above the critical point of CO₂ (31.1°C and 7.38 MPa) and that of water (374°C and 22.1 MPa), supercritical fluids exist [141, 142]. Supercritical fluids usually have high density, which increases their solubilization, and low viscosity, which enhances their mass transfer rate [143]. SCFs have the advantages of low operating cost; high product quality; ability to combine some operation units into one and to selectively extract certain lipids at different operating conditions of temperature, pressure, and time. The advantage of this is a reduction in cost and extraction time [143, 144]. The disadvantage of SCFs is that they required the use of high-pressure vessels which are usually expensive. A brief discussion on supercritical CO₂ and supercritical water is presented below.

4.4.1.1 *Supercritical CO₂ extraction*

This lipid extraction method uses CO₂ as the supercritical fluid probably because it is cheap, non-toxic, non-explosive and non-flammable and possesses high purity and low critical temperature [141, 143]. The low critical temperature makes it the most suitable method for the extraction of thermal labile substances such as lipid/oil as the original properties of the materials are protected [143]. Supercritical CO₂ is usually used to extract non-polar lipids but due to the introduction of co-solvents such as methanol, ethanol and water, it could recover polar lipids [143]. For instance, Hanif et al. increased the yield of phospholipid fatty acids (PLFAs) from 0.5 to 7.28 nmol/mg using methanol (10%, v/v) as a co-solvent [145].

4.4.1.2 *Supercritical water extraction*

Water is used as a supercritical fluid here. Supercritical water possesses liquid and gaseous properties including diffusivity, density and heat transfer, which can be manipulated through temperature and pressure to achieve an efficient extraction. For instance, a low-density supercritical water can be used to extract non-polar substances, and due to low dissolution it will not be effective in extracting ionic substances. At high temperature, it can dissolve organic substances, gases and salts

due to its decrease in dielectric constant [146]. Supercritical water extraction has been used by Gungoren et al. for oil recovery and products distribution from sewage sludge at temperatures between 350 and 450°C and pressures of between 21.5 and 30 MPa [147].

4.4.2 Subcritical water extraction

Subcritical water as shown in **Figure 4** is water at temperatures between its boiling point (T_b), 100°C and its critical point of 374°C with pressure sufficient to maintain water in the liquid state. Within this temperature range, water behaves like organic solvents due to decrease in its dielectric constant. At low temperature, subcritical water can extract both polar and ionic substances while at temperatures close to the critical temperature, extraction of non-polar substances is possible by the interaction with these substances and reduction in the binding forces [148–150]. Subcritical water has been demonstrated to be useful in decontaminating soil, removing polyhydroxyalkanoates (PAH), hydrocarbons and metals and extracting variety of natural products [151]. It has also been used to increase the lipid yield of activated sludge [34, 35].

4.5 Enzymatic oil extraction

This method uses the right enzymes in extracting oil from the oil-bearing biomass and it is environmentally friendly as there is no emission of volatile organic matter [2]. The disadvantages include: relatively high cost of enzyme production, prolonged incubation periods and requirement of de-emulsification during the downstream processing (DSP) [151, 152]. Some of these problems such as high cost of enzyme production can be minimized using enzyme immobilization, which helps to reduce enzyme losses, although, could reduce reaction rate due to steric hindrance. While others like de-emulsification during DSP can be made easier through the use of affinity chromatography and perfusion chromatography [2].

Figure 4.
Phase diagram.

4.6 Mechanical oil extraction

Oil is extracted using a manual ram press or an engine-driven screw press. With the manual ram press extracting up to 60–65% and engine-driven press recovering 68–80% of the oil content of the feedstocks, respectively. Usually, the oil extract undergoes filtration and degumming as a way of obtaining a more refined oil. Mechanical extraction is inefficient in extracting oil from seeds, which it was not designed for, although, this problem can be solved by using pretreatment methods such as cooking of the seeds and using at least double passes in the screw press. This could give rise to up to 91% yield of oil [2, 151].

4.7 Microwave-assisted extraction (MAE)

This extraction method uses microwave oven in the extraction process. It has been utilized in extracting values from plant materials [153]. The method requires transferring heat through direct contact to the polar solvent and/to the target substance. This can be controlled through ionic conduction and dipole rotation, which occurs simultaneously. Comparing MAE with the conventional extraction method, the latter requires longer time and resources while the former supports high yield of extraction with lesser volume of solvents and controllable heating process [154]. MAE also emits smaller amount of CO₂ and consumes lesser quantity of energy compared to the conventional extraction methods. The disadvantages are that the process is accompanied with the presence of solid residue, which limits heat and mass transfer, and the extraction using non-polar solvents or extracting non-polar substances is greatly affected [2, 151].

4.8 Ultrasound-assisted extraction (UAE)

This involves submerging the feedstocks usually of plant origin in a polar solvent (e.g. water) or non-polar solvent (e.g. ethanol) and subjecting the resulting mixture to an ultrasonic vibration. The vibration is made up of sound waves at the range of 18 kHz–100 MHz. This sound wave in the solvent enhances the biomass (flowers, seeds, leaves, etc.) solubilization resulting in the release of values such as oils entrapped within them, thereby increasing yield of the valuable materials. UAE has a very fast extraction rate and high efficiency, but could denature the structure of the extracted substance, for example, oil due to prolonged exposure to ultrasound. Also, it requires the use of large volume of solvent and repetition of the process in order to achieve an efficient extraction. This thus impacts on the operating cost of the entire process [155–157].

5. Biodiesel production

5.1 Methods of biodiesel production

According to Rezania et al., there are four commonly used methods for biodiesel production [1]. These are explained below:

5.1.1 Pyrolysis

This involves preheating of vegetable oil or animal fat at a temperature of 300–1300°C in the presence of catalyst and absence of oxygen [2]. This may result in product possessing desirable properties such as low viscosity, high cetane number, low amount of sulfur and water content, and standard corrosion values [158].

5.1.2 Microemulsions

These are clear, thermodynamically stable, isotropic liquid mixtures of oil, water, surfactant, mostly in combination of cosurfactant [159]. This method using ethanol has been used with soybean as feedstock to produce biodiesel with similar properties as No. 2 diesel. These properties include cetane number and viscosity [81, 151].

5.1.3 Blending

This is also known as dilution and it is simplest and oldest method used in biodiesel production. It involves the blending of preheated vegetable oil or animal fats with the conventional petroleum diesel in a ratio of 10–40% (w/w) [160].

5.1.4 Transesterification/esterification

This involves the reaction between triglyceride from vegetable oil or animal fat with alcohol usually methanol in the presence of catalyst such as acidic, basic or enzymatic catalyst [161]. When methanol is used, the reaction is called methanolysis while it is called ethanolysis if ethanol is used as the alcohol. The schematic diagram representing the processes involved in biodiesel production via transesterification is shown in **Figure 5**. Transesterification of triglyceride to bio-diesel (alkyl ester) and glycerol as the by-product is illustrated in **Figure 6**. The reaction mechanism involves the conversion of triglyceride (TG) to diglyceride

Figure 5. Flowchart of biodiesel (FAME) production through transesterification [156].

Figure 6. Production of biodiesel through a transesterification of triglyceride [162]. (Where R^I , R^{II} and R^{III} are carbon chain of fatty acids and R is the alkyl group of the alcohol, which could be methyl or ethyl when methanol or ethanol is used respectively).

(DG) followed by monoglyceride (MG) and then to a free glyceride. Each step is catalyzed by alkoxide, for instance methoxide when methanol is used as the alcohol [163]. The reaction mechanism is presented in **Figure 7**.

Similarly, esterification as a method of producing biodiesel involves a reaction between fatty acid and alcohol in the presence of catalyst (see **Figure 8**).

Both transesterification and esterification can occur simultaneously in the same process. This is most suitable for feedstocks with high free fatty acid and water content. The feedstock is firstly esterified using the acidic catalyst before transesterification by the alkali catalyst [2]. The performance of these reactions is measured in terms of yield.

Transesterification is the most commonly used method in biodiesel production probably due to its simplicity and low cost [165]. It can be carried out in situ using the oil-bearing biomass or ex situ directly with the oil extracted from the biomass-bearing oil. Some researchers have demonstrated the application of in situ transesterification of oil-bearing biomass to biodiesel. For instance, Mondala et al. investigated the production of biodiesel from municipal primary and secondary sludge (activated sludge) through in situ transesterification reaction [154]. On the other hand, numerous works have been conducted using lipid extracted from oil-bearing biomass (ex situ) to produce biodiesel. For example, Siddiquee and Rohani worked on the production of biodiesel via the methanolysis of lipids extracted from the primary and secondary sludge [133].

Figure 7. Reaction mechanism (chain reaction) of the transesterification of triglyceride to biodiesel (fatty acid methyl acid-FAME) [2].

Figure 8. Esterification of free fatty acid to methyl ester and water [164]. (Where R is the carbon chain of fatty acid and R₁ is the alkyl group of the alcohol, which could be methyl assuming that methanol is used as the alcohol).

5.2 Factors affecting the production of biodiesel

These include catalysts type, reactor type, temperature, agitation speed, solvent type, alcohol-to-oil ratio, residence time and nature of feedstock (water content, quantity of free fatty acid and esterifiable substances present in the feedstock) [133]. The catalyst type and nature of the feedstock are the most influential factors as they determine the cost of the production of biodiesel [11]. High free fatty acid and water content can cause low yield of biodiesel production due to soap formation via saponification reaction [166, 167].

6. Economic aspects

Researchers have posited that biodiesel is currently not competitive with the conventional petroleum diesel due to higher production cost despite numerous advantages [168]. This can be influenced by the type of raw materials, selling price of the by-product, labour and operation cost, catalyst and the reaction type [1]. The average production cost for biodiesel and diesel fuel is \$0.50 and \$0.35 per liter, respectively [169]. The price for producing biodiesel can be estimated using Eq. (1)

$$\text{Production price for biodiesel} = \frac{\text{Operating costs (\$/yr)} - \text{Byproduct credit (\$/yr)}}{\text{Product yr (kg/yr)}} \quad (1)$$

The cost of biodiesel production can be reduced by increasing yield using improved technologies, reducing capital investment cost and reducing the raw materials cost [168, 170–173].

6.1 Factors that influence the cost of biodiesel production

6.1.1 Alternative raw materials

This involves the use of cheaper feedstocks including wastes from oils, fats and non-edible crops in order to reduce the unit cost of producing biodiesel [28, 174]. The major drawbacks to using these feedstocks are high free fatty acid (FFA) and water content with the capacity to reduce the yield and quality of the biodiesel [9, 12, 22, 175]. The effect of this can be reduced by using multiple chemical processes with the tendency to increase the overall production cost [176]. For instance, using alkali to catalyze the transesterification reaction may require feedstock pretreatment, product separation and purification, thereby rendering the entire process uneconomical due to additional cost incurred [177]. However, acid catalysts are most suitable for the conversion of WCO with high FFA and water content to biodiesel. But, the disadvantages of this are that the reaction is very slow, requires more alcohol and large volume of reactor, and the acid used may corrode equipment, causing them to break down [178]. The use of acid catalyst may also increase the production cost. Some of these problems may be solved using supercritical fluid. The process does not need catalyst, it is faster and may require large volume of alcohol, high temperature and pressure giving rise to a considerable cost implication [179, 180].

The use of cheap and low-cost feedstock may affect the quality of the biodiesel, although, this can be improved. For example, poor cold properties can be improved using additives, although not without some cost implications. Despite the potential of cheap and low-cost feedstock to reduce the production cost of biodiesel, due to

high level of impurity, it may require pretreatment prior to use, product purification due to poor quality and, thus, have some cost implications.

6.1.2 Effects of technologies

Technologies used in biodiesel production to a large extent impact the cost of production. Some of these technologies require more unit operations than the other, which influences energy utilization and number of equipment [181]. For instance, the use of catalytic distillation (CD) process is more economical than conventional reactor as capital and production costs are reduced. This is possible due to reduction in the number of equipment, for example plug flow reactor and flash separation units, which are essential when using the conventional reactors are not needed [182].

Alkali catalyst technologies are preferred for producing biodiesel, especially heterogeneous catalyst technology using neat vegetable oil. The reason being that it requires less unit operation and number of equipment. It is also faster and cheaper and can easily be recovered. An example of such catalysts is calcium oxide [181, 183–185]. For use with high free fatty acid and water content feedstocks, alkali catalyst will cause such problems such as soap formation, which reduces the yield of biodiesel (**Figure 9**). The soap can gel at room temperature causing the production of semisolid mass instead of biodiesel and can cause difficulty in purifying glycerol [186]. Thus, when considering waste oils such as waste cooking oil with high free fatty acid and water content, acid catalyst technologies are the best option with the aim of reducing the overall production cost. The cost can be reduced because acid catalysts are less corrosive, easy to separate, can be reused and do not require additional washing steps. This will help to produce high-quality products in terms of biodiesel and glycerols [187, 188].

Alternatively, enzyme and supercritical technologies can be used to process feedstock with high free fatty acid and water content to biodiesel, although they are more expensive than acid-catalysed technologies [173, 189]. Enzyme-catalysed transesterification is a slow process and takes longer time, and the soluble enzymes are not reusable except if immobilized enzyme is used. These disadvantages impact negatively on the cost of production [190]. On the other hand, supercritical technologies do not require the use of catalyst and encourage the production of by-product glycerol with high purity [192].

Generally, technologies like feedstock and catalyst influence the overall cost of biodiesel production (**Table 9**).

Figure 9.
 Soap formation during the transesterification of triglyceride to produce biodiesel.

Production technology type	Capacity	Feedstock	Production cost \$/ton	References
KOH-catalyzed transesterification with methanol	8000 ton/yr	Waste cooking oil	868,60	[173]
H ₂ SO ₄ -catalyzed transesterification with methanol		Waste cooking oil	750,38	
Lipase (Novozym-435) -catalyzed transesterification		Waste cooking oil	1047,97	
Alkali catalyst process	Batch process with a production capacity of 1000 tons	Palm oil	1166,67	[191]
Soluble lipase catalyst process		Palm oil	7821,37	
Immobilized lipase catalyst process		Palm oil	2414,63	
Homogeneous H ₂ SO ₄ -catalyzed and using purchased feedstock	Continuous reactor operating at 30°C	Microalgae oil	620	[182]
Homogeneous H ₂ SO ₄ -catalyzed and using self-produced feedstock from recycled glycerol		Microalgae oil	580	
Homogeneous KOH catalyst and hot water purification process	Batch process with a production capacity of 1452	Waste cooking oil	921	[193]
Homogeneous KOH catalyst and vacuum FAME distillation process		Waste cooking oil	984	
Heterogeneous CaO catalyst and hot water purification process		Waste cooking oil	911	
Heterogeneous CaO catalyst and vacuum FAME distillation process	Batch mode with a production capacity of 7260 tons/year	Waste cooking oil	969	[193]
Homogeneous KOH catalyst and hot water purification process		Waste cooking oil	598	
Homogeneous KOH catalyst and vacuum FAME distillation process		Waste cooking oil	641	
Heterogeneous CaO catalyst and hot water purification process		Waste cooking oil	584	
Heterogeneous CaO catalyst and vacuum FAME distillation process		Waste cooking oil	622	

Table 9.
Dependence of biodiesel production cost on technologies [168].

6.1.3 Effect of alternative catalysts

The effect of alternative catalysts in the production of biodiesel can be seen in the reduction of production cost as supported by some of their characteristics such as being inexpensive, reusability and high catalytic potential. Examples of such catalysts are obtained from shells from egg, coconut, mussel, scallop and crustacean [183, 190, 194–196].

Generally, catalysts used in catalysing the transesterification reaction leading to the production of biodiesel may be either homogeneous or heterogeneous. The choice of which to use is dependent on the free fatty acid and water content composition of the feedstock. Usually, heterogeneous catalysts unlike homogeneous catalysts are used to catalyse reactions involving feedstock with high free fatty acid and water content as they can be reused, require less products separation and purification steps, and possess the capacity to enable the production of pure

by-products such as glycerol. Although, these advantages have some cost implications, heterogenous catalysts remain the best choice for biodiesel production unit cost reduction [168, 187, 197].

6.2 Profitability of biodiesel production

This is a measure of the amount of profit that can be obtained from an investment in biodiesel production. The profit is usually calculated from the difference between the income obtained from the sales of the products and the expenses incurred. Profitability of biodiesel can be determined using such economic parameters as net present value, break-even price of biodiesel, after-tax internal rate of return, gross margin [168].

6.2.1 Factors affecting the profitability of biodiesel production

6.2.1.1 Market variables

These include income variables such as biodiesel and glycerol and outcome variables, which are feedstock, catalyst, alcohol and washing water. Studies have shown that the major market variable that influences the profitability of biodiesel production is the cost of feedstock due to large quantity required, and others are selling price of biodiesel and glycerol, while outcome variables such as catalyst and washing water have less effect because less quantities are required [162, 198, 199].

6.2.1.2 Production scale

This is another factor affecting the profitability of biodiesel production. The higher the production scale, the lower the unit production cost of biodiesel, see **Figure 10**. This can be seen from the work of Van Kasteren et al. who compared three biodiesel production processes via supercritical method [201]. The results obtained show increase in profitability of biodiesel at high production scale compared to low production scale. The result was corroborated by the study conducted

Figure 10.
Effect of plant capacity/production scale on unit production cost [200].

by You et al. on the effect of production scales 8000, 30,000 and 100,000 annually on the feasibility of biodiesel production from food grade soybean oil using NaOH-catalyzed transesterification [202]. This conclusion was reached as production scale of 100,000 gave higher net annual profit after taxes (NNP) and after-tax of return (ARR), and lower biodiesel break-even price (BBP) compared to other production scales.

7. Conclusions

Commercial quantity of biodiesel is currently being produced from edible vegetable oils with the global production capacity envisaged to reach 12 billion gallons by 2020 and countries such as Brazil, United States of America, Malaysia, Argentina, Netherlands, Spain, Philippines, Belgium, Indonesia and Germany meeting more than 80% of the world demand. The problem with this type of biodiesel includes poor storage, oxidation stability, high feedstock cost, low heating value and higher NOx emission. The implication of these is that biodiesel is not competitive with the conventional petroleum diesel.

Researchers have suggested the utilization of non-edible oils as a way of minimizing cost since feedstocks consume up to 80% in biodiesel production. But, the problem with this is the presence of high free fatty acid (FFA) and water content, which reduces the yield and quality of the biodiesel. This can be reduced through the use of multiple chemical processes, although there is a tendency to increase the overall production cost.

Generally, the cost of biodiesel production is influenced by factors such as raw materials, technologies and catalyst. The raw material and catalyst cost can be reduced using alternatives to these factors while improved technologies could help to minimize the production cost.

The profitability of biodiesel can be determined using economic parameters such as net present value, break-even price of biodiesel, after tax internal rate of returns, and gross margin. These parameters are influenced by market variables and production scale.

Nomenclature

IPCC	Intergovernmental Panel on Climate Change
ASTM	American Society of Testing Materials
WCO	waste cooking oil
CN	cetane number
CP	cloud point
PP	pour point
HHV	high heating value
MAE	microwave-assisted extraction
UAE	ultrasound-assisted extraction
SCF	supercritical fluid
PLFA	phospholipid fatty acids
PAH	polyhydroxyalkanoate
Tb	boiling point
Tc	critical temperature
Pc	critical pressure
DSP	downstream processing
FAME	fatty acid methyl ester

TG	triglyceride
DG	diglyceride
MG	monoglyceride
FFA	free fatty acid
CD	catalytic distillation
NNP	net annual profit after taxes
ARR	after-tax of return
BBP	biodiesel break-even price
LCB	lignocellulosic biomass

Author details

Ifeanyichukwu Edeh
Chemical Engineering Department, Faculty of Engineering, University of Port
Harcourt, Port Harcourt, Nigeria

*Address all correspondence to: ifeanyichukwu.edeh@uniport.edu.ng

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