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Review Article

A Critical Review of *Croton* as a Multipurpose Nonedible Tree Plant for Biodiesel Production towards Feedstock Diversification for Sustainable Energy

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Oil demand has risen steadily due to the growing industrialization and modernization of the world. In addition to rising costs, the supply of fossil fuels is also declining. These and many other concerns couple with food shortages have drawn attention of scientists to a substitute fuel that is generated from feedstocks that can be renewed. Biodiesel as an alternative fuel with a lot of expectations is produced using edible grown conventional vegetable oils such as sunflower, rapeseed, palm, and soybean. The production of biodiesel from edible oils has, meanwhile, worsened the existing competitiveness of oil used for food and fuel. Emphasis on using nonedible feedstock is currently guided by research to discover more potential nonedible feedstock such as croton. Differences between perceptions and facts about these nonedible oils necessitate efforts to diversify feedstocks into sources that can warrant the production of energy without impacting on the security of food. Croton is a multipurpose evergreen plant that is nonedible and is commonly present and cultivated under environmental and socio-economic conditions, which are complex in nature. This plant, referred to as a golden tree, has various uses including fuels, medicinal, ornamentals, dyes, feed, enriching of soil, and afforestation. This research was therefore carried out to investigate the multipurpose use croton. Among the highlighted areas include croton (feedstock) used for biodiesel, the necessity for croton seed oil and its value chain, the process for the modifying croton oil to biodiesel, factors that influence the production of biodiesel, the application of croton biodiesel in engines for efficiency and emission characteristics, and prospects for croton biodiesel.

1. Introduction

Fossil fuels are not renewable sources of energy. Even though these fuels contribute mainly to the supply of energy globally, their production and usage has led to the rise in environmental issues and political discussions. Studies have established that 98% of the carbon emitted originated from the combustion of fossil fuels[1]. The demand for energy is continuously increasing as a result of rapid growth of industries and vehicles due to the surge in population. The major energy sources include nuclear, solar, wind, and hydrocarbons (natural gas, petroleum, and coal). The significant limitations in the application of petroleum-based fuels are pollution of the atmosphere due to the emission of greenhouse gases. Aside the greenhouse gases, petroleum diesel is the primary origin of these contaminants in the air, which include CO (black carbon), SO_X, NO_X, volatile organic compounds, and particulate matter [2]. Many substitute fuels have been identified as partial or full alternative to diesel fuel. Vegetable oils have been identified as feasible substitutes to diesel fuel since they share similar properties, and vegetables are mostly grown in rural areas. Vegetable production could also be a source of employment for many [3].

The process of converting vegetable oil to biofuel is not new. Vegetable oil, specifically, from peanut was initially used by Rudolph Diesel in a diesel engine in 1911. The use of biofuels (biodiesel) instead of conventional fuels slows down the advancement of global warming through the reduction of emission of carbon/sulphur oxides and hydrocarbon. Due

to economic importance and extra energy, biodiesel is usually blended with diesel fuel at ratio of 2, 5, and 20%. As biodiesel-to-diesel ratio is increased, the emission of carbon dioxide is reduced. The application of the mixture, which contains 20% biodiesel, lowers the emission of carbon dioxide by 15.66% [4]. Likewise, the application of pure biodiesel results in the nonemission of carbon dioxide [5].

Biodiesel is a mono-alkyl esters of long-chain fatty acids whose origin is natural plant oil and animal fats, and it is a substitute for fossil fuels. Biodiesel has gain full attraction globally because of its importance such as renewability, biodegradability, nontoxicity, and the benefits of being friendly to the environment [6]. Biodiesel possesses a relatively high flash point, thus making it have low volatility; hence, it is safe in terms of transportation and handling in comparison with petroleum diesel. Biodiesel also possesses good lubrication properties, which is an advantage to the engine since it reduces engine wear and lengthened the engine's life span [7–10].

Using edible vegetable oils and fats from animals for biodiesel production has, however, become a huge concern currently because of competition for food and fuel. Due to the tremendous rise in demand for vegetable oils for consumption in the current years, it is not possible to justify its use for other intentions like the production of biodiesel. Furthermore, using the edible oils for fuel can be more costly in comparison with the cost of producing biodiesel using nonedible oil sources [11, 12]. *Croton*, jatropha, jojoba, and waste cooking oil are some of the nonedible oil feedstocks that may be used to make biodiesel. Waste cooking oil is, however, the cheapest of these nonedible oil feedstocks. Waste cooking oil has the adequate potential of becoming fuel used in compression ignition engines. The kinematic viscosity of waste cooking oil (WCO) is almost ten times higher than that of diesel, while its density is almost 10% greater than the density of mineral diesel. These properties play crucial functions during the combustion in the ignition engine and thus make waste cooking oil necessary to undergo modification before use. As a result, several methods have been developed to minimize kinematic viscosity of waste cooking oil. Transesterification, pyrolysis, emulsification, and leaning are all processes for lowering the specific gravity of waste cooking oil and other plant oils. Transesterification is, however, the most commonly used technique [13]. Figure 1 shows the estimated cost of producing biodiesel.

Studies indicate that feedstock exclusively constitutes almost 75% of all the cost of producing biodiesel [14, 15] (Figure 1). The main goal of biodiesel is to reduce the cost of manufacturing it so that it can compete with petroleum-based fuel. This, henceforth, makes it critical to use low-cost and widely accessible feedstock to replace expensive refined oils for biodiesel [16–18]). Table 1 indicates some of the feedstocks for biodiesel production [19].

2. Oil as Feedstocks for Biodiesel

There are about 350 oil-bearing plants that are suitable for biodiesel production. These include peanut, soybean, hemp,

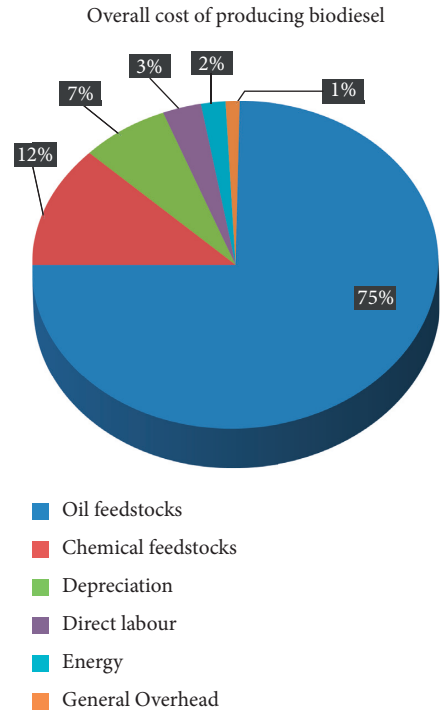

Figure 1: Estimated cost of producing biodiesel [14, 15].

sunflower, rapeseed oils, etc. [19] (Table 1). Emphasis on the choice of a feedstock is based on the availability and cost of the feedstock. European countries are self-sufficient in edible oil production with the export of leftovers. And hence, edible oils, for example, rapeseed, are widely used in the production of biodiesel in the European countries [18, 20].

Likewise, countries that are located in coastline areas, such as Indonesia, Thailand, and Malaysia, produce palm and coconut oil in excess and therefore used as feedstock for biodiesel production [21]. In Brazil, soya bean, castor, and palm kernel are the most widely used oils. In other countries, feedstocks such as canola oil, peanut oil, sunflower oil, cottonseed oil, and pomace oil are mostly used as feedstocks [22, 23].

3. The Need for Nonedible Feedstocks

Nonfood oils have been identified to be good resources for producing biodiesel due to the increase in the number of edible oils for food [24, 25]. Studies suggest that significant quantities of nonedible oil plants could be obtained [26]. However, the current situation of food security and the competitive value of edible oils for human consumption, using edible oils for producing biodiesel, are not viable. The conversion of edible oil to biodiesel (food shortages and rising energy prices) has an effect on the global stage. Oil from nonedible plants obviously is an alternative to oil from edible feedstocks and can be cultivated on a wide scale in nonfed marginal areas. The nonedible resources are comparatively cheap to grow as compared to edible feedstock [27, 28].

The cultivation of the nonedible feedstocks has various benefits, which include less consumption of water, pest, and

Table 1: Primary feedstocks for biodiesel production [19].

Edible oils	Nonedible oils	Animal's fats	Other sources
Barley	*Abutilon muticum*	Beef tallow	Cyanobacteria
Canola	*Aleurites moluccana*	Chicken fat	Bacteria
Coconut	Camelina (*Camelina sativa*)	Fish oil	Cooking oil
Corn	Coffee ground (*Coffea arabica*)	Pork lard	Fungi
Groundnut	Cottonseed (*Gossypium hirsutum*)	Poultry fat	Latexes
Palm and palm kernel (Elaeis guineensis)	*Croton megalocarpus*	Waste salmon	Microalgae (Chlorella vulgaris)
Peanut	*Cynara cardunculus*		Miscanthus
Pumpkin seed	*Jatropha curcas*		Pomace oil
Rice bran oil (*Oryza sativum*)	Jojoba (*Simmondsia chinensis*)		Poplar
Safflower (*Carthamus tinctorius*)	Karanja or honge (*Pongamia pinnata*)		Soapstocks
Sesame (*Sesamum indicum* L.)	Mahua (*Madhuca indica*)		Switchgrass
Sorghum	Moringa (*Moringa oleifera*)		Tall oil
Soybeans (*Glycine max*)	Nagchampa (*Calophyllum inophyllum)*		Terpenes
Sunflower (Helianthus annuus)	Neem (*Azadirachta indica*)		
	Pachira glabra		
	Passion seed (*Passiflora edulis*)		
Wheat	Pongamia (*Pongamia pinnata*)		
	Rubber seed tree (*Hevea brasiliensis)*		
	Terminalia bellirica		
	Tobacco seed		

Figure 2: Seeds of *C. megalocarpus* [36].

disease resistance, adapt easily to various climatic environments, high yields of seed and oil, fast spread, and being unpalatable to ruminants. In addition, unproductive land, degraded forests, farmland, irrigation canals, and road and field boundaries are useful for planting nonedible oil crops [3, 29–32].

4. Croton and Its Value Chain

4.1. Croton Plant. *Croton* tree is a member of the Euphorbiaceae family and is indigenous to India and the Malaysian archipelago. It is mostly cultivated in African nations, among them is Ghana. In East Africa, it grows readily in several parts of Kenya, Tanzania, and many other parts of the region and is found in homes, forests, and farms [33]. It commonly grows at an altitude ranging between 4,000 and 6700 feet above sea level. The croton tree is mostly used for shading, especially in the coffee plantation or even within various home environments. The tree may grow to the height of 120 feet and having a robust cylindrical trunk that is 40 to 60 feet long and 2 to 4 feet in diameter [34]. The *Croton* tree usually begins bearing fruit at three years and matures fully at around eleven years. Tanzania has a large-scale plantation of *Croton* spp. Privately owned companies are using croton plantation in Tanzania for the production of biofuel [35]. Figures 2–4 show *Croton megalocarpus* seeds, plant, and seeds processed into powder, respectively (Tables 2 and 3).

4.2. Croton Seeds. *Croton* begins to produce up to 25 kg of seeds per tree four years after planting. During the growing phase, the tree begins to produce flowers after 3 to 4 years, and this is followed by fruit ripening within five months of the stage of flowering. Maturation of the seeds usually occurs within the next six months in a cone, and each cone contains an estimate of 75 brown seeds, and collections of seed usually occur in the month of May and November [37]. According

Figure 3: *Croton megalocarpus* plant [36].

Figure 4: *C. megalocarpus* seeds processed into powder [36].

to an analysis by East Africa Tanning Extract Company (EATEC) Laboratory in Eldoret, Kenya, there was an average of 30 percent to 32 percent of the oil in terms of oil composition in nonedible seeds, while edible seeds contained 18 percent to 50 percent of the oil composition [35].

The annual yield of the seed per tree is 25 to 40 kg on average, and there is existence of significant variance in terms of weight of seeds from tree to tree [35]. Recently, oil derived from *Croton gratissimus* seeds has been revealed to be a promising feedstock of the second generation of large-scale biodiesel production [38].

4.3. Multiple Uses of Croton

4.3.1. Medicinal. Under traditional medicine, nearly the whole plant (from roots to leaves) is useful in the treatment of various ailments. It gives a variety of bioactivities that are crucial in the management of human health in most underdeveloped African regions [39]. Boiling the roots produces a liquor that is used as an aphrodisiac and to treat chest aches, coughing, weariness, and sexually transmitted infections (STDs). The bark is often used for the cure of abdominal problems, bleeding gums, earaches, and inflammation of the skin, including problems associated with the chest. Leaves and roots mixtures or roots and bark combinations are used for the treatment of respiratory disorders. *Croton gratissimus* bark and Amaryllidaceae root combined have now been deemed to be good when rubbed into incisions while treating swelling [38].

4.3.2. Reforestation and Agroforestry Utilization. *Croton megalocarpus* is a fast-growing natural tropical plant with a wide array of uses. It is an excellent choice for planting to reconstruct native forest or to establish forestry gardens. It is commonly used in hedges, live fences, shelter belts, and windbreaks since it is not grazed by animals. When the forest is removed, it is frequently left behind and utilized as a shade tree for coffee plantations. *Croton megalocarpus* plant has a

Table 2: Detailed properties of *C. megalocarpus* [36].

General information	Known hazards	Botanical references	Cultivation details
It is a deciduous tree with a dense, spreading, rather flat crown that grows up to 35 metres in height	Dry sawdust from the tree causes the irritation of the nose in addition to smoke from the wood, which also causes irritation of eyes	Range	Mainly found in region with average rainfall of 900–1,900 mm with dry season of about 3 to 4 months and average annual temperature of 11–26°c
Unbuttressed, cylindrical bole of up to 120 cm in diameter		East tropical Africa	Favours light, deep, and well-drained soils and the established croton plants are tolerant to the drought
It is a multipurpose tree useful to the native community in East Africa through provision of firewood, medicine, and timber		Eastern DR Congo, Uganda, Kenya, and southern Somalis, south to Zambia and Mozambique	In Kenya, the seedlings reach the height of 1.7 metres with in one year, while in Rwanda, it reaches 3 metres tall within 2 years
Currently, there is interest in the large-scale planting programme majorly in Kenya and Tanzania for biofuel production as well as commercial feeds for poultry from seeds		Habitat	*Croton* trees start flowering at age of 4 years
		Dominate upper-canopy tree of evergreen and semideciduous forest elevation from 700 to 2,400 metres	Management of tree is by lopping, pollarding, and coppicing
		Properties	There are no known edible uses
		It is a weed potential and has a fast growth rate	

Table 3: *Croton* agronomic parameters [33].

Agronomic parameters	Overall range	Optimal range
Annual temperature (℃)	11–26	16–22
Altitude	1200–2450	1200–1600
Annual rainfall (mm)	800–1900	1000–1400
Soil	Light deep and well-drained soils	

thick taproot. This makes the plant drought resistant and permits food crops to be cultivated beneath them. The foliage acts as a wonderful mulch. The fruit shells are utilized as mulch in vegetable gardens and in potting combinations [35].

4.3.3. Improvement of Environment. Research has found out that *Croton megalocarpus* trees have an impact that is beneficial to the environment owing to their potential to supply nesting materials, roosting locations, and resting spots due to the availability of shade. When animal carcasses are left below the trees, nutrients are produced in the soil, whereby there is two times increase in the sodium and nitrogen concentrations. Latest studies have established that *C. megalocarpus* trees is a potential outstanding prospect to be cultivated on large scale on degraded wastelands, which helps in the conservation of soil and mitigate the encroachment of the desert-like condition [40]. In several rural areas, the tree has been used to mark the boundaries of the land and act as windbreakers. All the benefits contributed by the *C. megalocarpus* tree are aimed at protecting the environment and restoring marginal lands to productive use [27, 41].

4.3.4. Sustainable Development. *Croton* cultivation becomes very important when it comes to sustainable development. Examples of the benefits of croton in sustainable development are nutrient management, animal feeds, and human health. The residual seed cake obtained after the oil has been extracted from the croton seed is used as the best biofertilizer as it contains more nutrient for plant growth than manure [42]. The residual seedcake is locally available for sale and is used for feeding poultry [43]. *Croton* seedcake also is an ingredient being sold for extending the value chain and benefit of *megalocarpus* in the poultry feeds. Seeds of croton have been subjected to testing in order to exploit its medicinal property, the same way the bark, leaves, and roots. Diabetes mellitus has been managed using medicine obtained from croton by the indigenous medical practitioners from Kenya's lower eastern region [43, 44].

4.3.5. Croton Oil Production. Having obtained the seeds, extraction of oil follows. Extraction of the oil involves the use of three major methods that have been identified. The methods include solvent extraction or chemical, mechanical extraction, and enzymatic extraction. Besides supercritical

fluid extraction (SFE), microwave-assisted extraction (MAE) as well as accelerated solvent extraction (ASE) methods are often used. Solvent extraction and mechanical pressing are mostly used in the commercial extraction of oil [19]. According to Atabani *et al* [3]; the major products obtained after the extraction of oil are cakes, which are useful by-products. Seed cakes are applied to farms as fertilizers enrichment to the soil, feeding poultry, fish, and swine, while certain oil cakes are useful in fermentation applications and biotechnological processes.

4.3.6. Composition and Properties of Croton Oil. *Croton* oil is principally made up of unsaturated fatty acids such as linoleic, linolenic, and oleic acids. Linolenic acid (C18 : 2), palmitic, oleic, and stearic acids are examples of saturated primary fatty acids often present in greatest percentage composition in croton oil for the three species of *Croton (megalocarpus, zambesicus, and gratissimus*). Comparatively, Jatropha *curcas* oil has highest percentage composition of linolenic acid (C18 : 2), palmitic, oleic, and stearic acids. However, the rest of the acids, which are lauric, myristic, palmitoleic, linolenic (C18 : 3), arachidic, and erucic, have lower percentage composition in three species of croton and similarly in Jatropha *curcas* oil. The oil contains the greatest percentage weight of linoleic acid (C18 : 2) of any raw plant oil for the three species of croton and jatropha might explain why it has a lower viscosity than other pure plant oils such as Moringa *oleifera,* which is grown at similar temperatures (Table 4) [43, 46–48].

Table 5 shows the physicochemical properties of raw and refined *C. megalocarpus* seed oil, as well as the corresponding limits (ASTMD6751 and EN14214) [50, 51]. The acid value describes the amount of potassium hydroxide required to neutralize the free fatty acids. A high acid number has an effect on the engine's fuel injection system and increases the corrosion of engine components [52]. The pH of the oil is another important factor in determining its quality. If the pH of the biodiesel is too high, more glycerine is formed at the end of the process, reducing yield, and quality [53].

Cloud point is a criterion for low-temperature fuel performance, and a higher cloud point can have a negative impact on engine performance and emissions in cold weather. Fuels with a high viscosity are more likely to cause engine problems. Fuel density is also an important factor in engine performance. The denser the fuel, the more difficult it is to pump. According to ASTM and EN14214, the density of biodiesel produced from *C. megalocarpus* seed oil is 890 kg/m^3, which is within the acceptable range. The density of biodiesel is determined by the raw materials used in its production as well as the methyl ester profile [54].

The saponification value (SV) of oil is used to calculate its average molecular weight. A high SV in oil indicates that the oil contains a higher proportion of low molecular weight fatty acids, or vice versa. The iodine value is a useful parameter in researching the oxidative rancidity and chemical stability properties of various oils. The iodine value of raw oil was higher than that the value of the specifications. The lower the iodine value, the better the biodiesel fuel [54, 55].

The refractive index (RI) of oil is a parameter that is related to its molecular weight, fatty acid chain length, and degree of unsaturation. It is an important parameter for determining the state of a biodiesel. This result is consistent with the findings of Ismail and Ali [56], Domingues [57], and Ullah et al [58] who reported that the refractive index of raw oil is 1.52 on average.

4.4. Oil-to-Biodiesel Conversion Methods. A variety of processes for transforming oil into biodiesel are available [59]. Crude oils are refined to reduce their viscosity to fit diesel engines. The four main methods, which are discussed in this study, are transesterification, blending, pyrolysis, and microemulsions [17].

4.4.1. The Blending of Crude Oils. Blending is the method that entails a reduction in the concentration of a solution, through the addition of more solvent to the mixture. To reduce viscosity, crude oils can be combined directly or blended with fossil diesel. The final solution is carefully balanced to ensuring that all characteristics of the combination are equal. Vegetable oils cannot be used in diesel engines directly due to its high viscosity. In the diesel engine, a mixture of 20 to 40% of this with fossil diesel has been tested to produce reasonable results. Research on blending in diesel engines using different nonedible oils with diesel fuel has been performed. They successfully recorded a combination consisting of 20% of vegetable oil and 80% of fossil diesel [25, 60].

Standard methods were used to measure some of the fuel properties of vegetable oils, biodiesels, and blends such as viscosity, density, and calorific value; the results are tabulated in Table 6. Vegetable oils have a lower gross calorific value, higher viscosity, and a slightly higher density than methyl esters and vegetable oil butanol-diesel blends. Methyl esters and blends have viscosity and density values that are comparable to diesel fuel, but methyl esters have a lower gross calorific value than diesel and blends [61].

Apart from the 45.54 MJ/kg of D2 fuel, the blend 10 percent CRO-10 percent BU-80 percent D2 had the highest gross calorific value of 44.09 MJ/kg. The energy content of oils varies depending on where they are grown, the season their composition, and other factors. Vegetable oils were found to have lower calorific values than biodiesels. The heat content of methyl esters increases as the length of the fatty acid chain increases. The presence of a significant amount of oxygen contributes to biodiesel fuels' low energy content [61].

Croton oil was found to have viscosity values that were approximately 6 times higher than the ASTM limits. The viscosity values of the croton methyl ester and butanol blend were found to be within the ASTM limits (Table 6) [61].

The density of vegetable oils varies according to their origin and composition. Their density, however, is generally higher than that of methyl esters and diesel fuel. Table 6 shows the density values of croton oil, methyl ester, butanol blend, diesel fuel, and 1-butanol alcohol; as can be seen from the results, croton methyl ester has the lowest density value

Table 4: Comparison of the fatty acid composition of the *Croton* plant oils (wt.%) [45].

Fatty acid	*C. megalocarpus* [43]	C. *megalocarpus* [46]	C. *zambesicus* [47]	C. *gratissimus* [48]	*Jatropha curcas* [43]
Lauric acid (C12 : 0)	0.11	—	1.10	—	0.14
Myristic acid (C14 : 0)	0.04	0.1	1.50	—	0.11
Palmitic acid (C16 : 0)	6.23	6.5	30.72	35.8	16.64
Palmitoleic acid (C16 : 1)	0.11	0.1	2.9	10.3	1.18
Heptadecenoic acid (C17 : 1)	—	0.1	—	—	—
Stearic acid C 18 : 0)	4.37	3.8	4.81	31.2	5.94
Oleic acid (C18 : 1)	9.95	11.6	33.28	8.7	37.25
Linolenic acid (C18 : 2)	74.31	72.7	21.47	15.9	38.03
Linolenic acid (C18 : 3)	3.62	3.5	2.93	5.9	0.25
Arachidic acid (C 20 : 0)	0.92	—	0.59	2.2	0.46
Erucic acid (C 22 : 1)	0.33	—	—	—	0

Table 5: Physicochemical properties of the C. *megalocarpus* seed crude oil.

Property	Oil	ASTM6751	EN14214	Reference
Viscosity at 40^0 C (mm^2/s)	27.23	1.9–6.0	3.5–5.0	[49]
Iodine value ($gI_2/100g$)	117	130 max	120 max	[49]
Density at 150C (kg/m^3)	920	850–900	860–900	[49]
pH	5.14	—	—	[49]
Moisture (%)	0.8	0.05max		[48]
				[49]
			—	
Ash (%)	2.4	<0.02		
Saponification value (SV) (mg/KOH/g)	188	—	—	[43]
Acid value (mg/KOH/g)	2.52	0.8 max	0.50 max	[49]
Refractive index at 25O C	1.54	—	—	[49]
Peroxide index (meq/Kg)	10.29	—	—	[48]
Cloud point ˚C		2 to −12	—	[49]
Flash point ˚C	—	>93	>101	[49]
Water sediment (%)	—	0.05 max	-	[49]
Specific gravity	0.918	—	—	[49]
Acid value (mg KOH/g)	3.343	—	—	[46]
Free fatty acid (FFA) (%)	1.68	—	—	[49]
SV	194.9	—	—	[49]

Table 6: Fuel properties of croton methyl ester and the butanol blend [61].

Test	Cetane number	Gross calorific value H_0 MJ kg-1	Viscosity mm^2 s-1 at 40˚C	Density kg m-3
Test methods	ASTM *D* 613	ASTM *D* 240	ASTM *D* 445	ASTM *D* 1298
Limits	47 <	—	1.9–6.0	—
CRO	40.7	39.65	33.38	920.00
CRME	46.6	39.95	4.78	865.00
10% CRO-10% BU-80% D2	52.8	44.09	3.82	831.76
D2	54.6	45.54	2.30	823.20
BU	17.0	36.94	2.63	811.95

of 865.00 kg/m^3. The density of the diesel fuel sample was found to be 823.20 kg/m^3, which is lower than the density of the croton oils, methyl ester, and butanol blend [61].

Croton oil-butanol-diesel blends achieve viscosity, density, and calorific values similar to diesel fuel; this may be due to the high proportion of diesel (80%) in the blends. The results of the experiments with vegetable oils and methyl esters are consistent with the values found in the literature [62, 63].

Methyl esters have a lower viscosity than vegetable oils, which influences their cetane number (CN). The CN of the tested methyl esters is consistent with the literature, as transesterification reduces the molecular mass of vegetable oils, improving volatility, and lowering viscosity. Viscosity

influences ignition delay; thus, improved volatility and viscosity explain why biodiesels have a higher CN than vegetable oils [64, 65].

4.4.2. Micro-Emulsification. Microemulsion is another way of modifying vegetable oils. Microemulsions are translucent, solid, three-component isotropic fluids (oil, aqueous phase, and a surfactant). During micro-emulsification, the aqueous phase contains salts or other components, whereas the oil phase is a complex combination of diverse hydrocarbons and olefins. This tertiary step can enhance the spray's characteristics by explosively vaporizing the micelles' low boiling elements. Microemulsions of butanol, octanol, and hexanol can achieve the total viscosity value for diesel engines. Microemulsion can be prepared with diesel fuel or without it. The method is known to be a successful solution for the viscosity of vegetable oils [66, 67].

In reciprocating engines, vegetable oils such as croton, jatropha, Karanja, and coconut oil have been investigated as alternatives to diesel. However, their use is fraught with difficulties, prompting researchers to investigate various methods for improving their performance. Among these, micro-emulsification with methanol has emerged as a key approach. However, it necessitates the use of additional materials and energy investments, raising the cost and decreasing suitability [68]. Micro-emulsification was used in a study to improve croton oil performance in a compression-ignition engine. Diesel, biodiesel, and three methanol emulsions were among the five fuels tested. At various engine load conditions, engine performance and emissions were evaluated for each fuel. The additional energy required for both approaches was also taken into account. When compared with petro-diesel, micro-emulsification improved combustion efficiency, but the additional energy requirement for biodiesel was higher. Micro-emulsification was found to be more energy efficient and produce lower emissions. The use of methanol in micro-emulsifications has a clear advantage over its use in transesterification for improving the performance of vegetable oil-powered engines [69, 70].

4.4.3. Pyrolysis. Pyrolysis is the process of converting crude oil from one form to another in the absence of air or oxygen using heat or a catalyst. The viscosity, pour point, flash point, and cetane number of pyrolysed products are greater than those of regular diesel [71, 72]. The sulphur concentration, copper corrosion, and water content of pyrolysed oil are acceptable, but the carbon residue, pour point, and ash content are unsatisfactory [26, 67]. Depending on the operating requirements, pyrolysis process is often split into three types: instant pyrolysis, rapid pyrolysis, and traditional pyrolysis. Several kinds of research have been conducted on the pyrolysis process for the production of biodiesel from edible and nonedible vegetable oils [73].

Osawa [74] conducted a study in which he extracted *Croton* oil from dry *Croton* megalocarpus seeds using a mechanical pressing machine and then filtered it. Changing parameters such as temperature oil: alcohol mole ratio and catalyst amount were used to determine the best conditions for producing biodiesel from oil in a two-stage chemical process in a reactor. Temperatures of 50 and 60°C were found to be optimal for esterification and transesterification, respectively, as were methanol-to-oil mole ratios of 3 : 1 and 6 : 1 for esterification and transesterification, respectively, and a base catalyst mass of 1 percent (w/w) of *Croton* oil for transesterification. The optimal reaction times for transesterification and esterification were determined to be 1 and 2 hours, respectively. At 40°C, a maximum yield of 88 percent biodiesel was obtained, with an acid value of 0.336 mg KOH/g, a density of 0.8858 g/cm^3, and a viscosity of 4.51 cs.

4.4.4. Transesterification. Transesterification, also known as alcoholysis, is a chemical process that involves triglyceride and alcohol in the presence of a catalyst to produce glycerol-formed esters as the main product. Catalysts are often employed to boost the reaction rate in order to complete the reaction in a comparably shorter reaction time [75]. Several catalysts for transesterification have been studied. Calcium oxides, magnesium, acid, and/or basic macroreticular organic resin carbonates, alkane alumina, sulphuric acids, phase transfer catalysts, p-toluene, sulphonic acid, and co-catalyst dehydrating agents are only a few examples [76, 77]. Acids, alkalis, nanocatalyst, and enzymes are the three types of catalysts [78, 79]. Because of their greater reactivity and better process conditions, alkaline catalysts are often preferred over acid catalysts, which require lower temperature. Transesterification creates ester and glycerol as a result of a forward process. Given the fact that esters are the end products of transesterification processes, glycerine recovery is equally crucial due to the wide range of everyday product uses [80].

Acidic and alkaline transesterification are the two primary kinds of transesterification [81]. Water, a by-product of esterification, must be eliminated since it reduces the process's efficiency. Sulphuric acid is the most common acid used as a catalyst. Enzyme catalysts are also gaining popularity in transesterification reactions [17].

Figure 5 shows the typical process of transesterification [11, 83, 84]. The figure indicates typical transesterification involving triglyceride and alcohol when a catalyst is present to form esters with glycerol as the backbone. Three consecutive reversible reactions are involved in the process: conversion of triglyceride to diglyceride followed by diglyceride to monoglyceride. Then, the triglyceride is converted into glycerol, giving one ester per step. Usually, catalyst is used to increase the reaction rate in order to complete the reaction within a relatively shorter reaction time [85].

4.4.5. Optimized Biodiesel Production. The study by Pugazhendhi et al [86] aimed to optimize four main factors that would influence the conversion of waste cooking oil to biodiesel: catalyst quantity, methanol: waste cooking oil molar ratio, mixing intensity, and reaction time. The optimal reaction parameters for maximum biodiesel yield (90 0.25

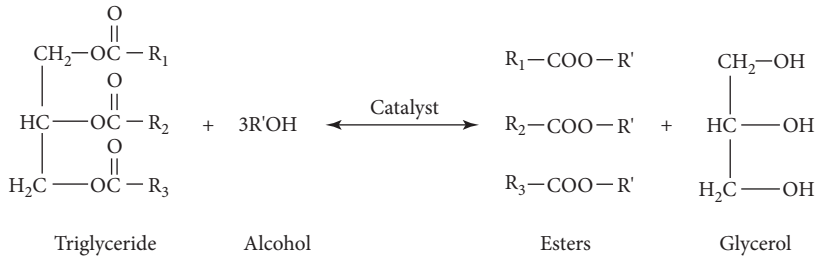

Figure 5: Typical process of transesterification [82].

percent) were determined to be 0.6 percent w/w catalyst loading a 10.6 : 1 methanol to waste cooking oil ratio, a mixing intensity of 559 rpm, and a reaction time of 63 minutes. The experimental data followed first-order reaction kinetics, and the energy required to activate the molecules to undergo chemical transformation was calculated to be 57.82 kJ/mol.

(1) Alkali-catalysed transesterification. Transesterification involving alkali catalysis is one of the most common processes. This is because the mechanism of reaction in alkaline transesterification occurs in three stages: the first step includes the interaction of the carbonyl carbon atom with the alcohol anion, which results in the formation of a tetrahedral intermediate from which the alkyl esters and matching diglyceride anions are formed [85]. Catalyst initiates a reaction of diglyceride with a second alcohol molecule through a new catalytic cycle. Diglycerides and monoglycerides are converted into alkyl esters and glycerol at this stage [87]. Alkali-catalysed transesterification of oils occurs more rapidly than transesterification using other catalysts (acids and enzymes). Jiyane and Musonge [85] investigated three-step reaction mechanism of croton oil transesterification. The ethyl group, according to them, can allow an ethoxide anion to form the breaking of the ethanol molecule, which is more difficult than for the methoxide anion. The quantity of free fatty acids (FFAs) often determines the catalyst's preference. A high FFA percentage of more than 1% w/w improves soap formation, but end product separation will be problematic, resulting in reduced biodiesel yields [88]. The mechanism of alkali catalytic transesterification is shown in Figure 6 [87].

The mechanism of reaction in alkaline transesterification is divided into three steps: the first is the reaction of the carbonyl carbon atom with the alcohol anion, which results in the formation of a tetrahedral intermediate from which the alkyl esters and corresponding diglyceride anions are formed. Once the catalyst reacts with a second alcohol molecule, a new catalytic cycle is initiated. At this point, the mono and diglycerides are transformed to alkyl esters and glycerol [85].

Kafuku and Mbarawa [46] conducted an experiment to optimize the biodiesel production process parameters using croton oil and potassium hydroxide as a catalyst. The amount of catalyst, alcohol, temperature, agitation speed, and reaction time were all factors in the optimization process. At the optimal conditions of 1.0 wt. percent potassium hydroxide catalyst, 30 wt. percent methanol, 60 ℃ reaction temperature, 400 rpm agitation rate, and 60-min reaction time, the optimum biodiesel conversion efficiency was 88 percent. *Croton* biodiesel's properties were determined to be within the recommended biodiesel standards.

Noreen et al (2022)conducted research aimed at optimizing reaction conditions for biodiesel production via alkali-catalysed transesterification of *Tamarindus indica* seed oil. To optimize performance parameters such as alcohol-to-oil molar ratio, catalyst amount, and reaction time, the Taguchi method was used. Gas chromatography was used to determine the fatty acid content of both oil and biodiesel. The optimized conditions of alcohol-to-oil molar ratio (6 : 1), catalyst (1.5 percent w/w), and reaction time 1 h resulted in 93.5 percent yield of biodiesel. The molar ratio of alcohol to oil (75.9 percent) made the greatest contribution, followed by the amount of catalyst (20.7 percent). In another case, an alcohol-to-oil molar ratio of 9 : 1, a catalyst (1.5 percent w/w), and a reaction time of 1.5 hours resulted in a biodiesel yield of 82.5 percent. *Tamarindus indica* methyl esters produced under ideal conditions had fuel properties that were within the ASTM D6751 biodiesel specified limits. The study's findings suggest that *Tamarindus indica* could be chosen as a prospective and viable option for large-scale biodiesel production, making it a viable substitute for petrodiesel.

(2) Acid-catalysed transesterification. The method of acid-catalysed transesterification is still relatively unknown compared with alkalize-catalysed transesterification. It is because of the slow reaction rate and high methanol-to-oil ratio characteristics. Main acid catalysts have decreased activities at a higher temperature during the transesterification process. To improve the performance of solid acid catalysts, higher pressures and temperatures are usually required [85]. Long reaction times, however, make the procedure inefficient and inexpensive. Biodiesel may be made directly from low-cost lipid feedstock having free fatty acids levels surpassing 6% using acid catalysts [90]. Sulphuric acid and other liquid acid catalysts are resistant to free fatty acids and may perform transesterification and esterification simultaneously with large yields of esters. The protonation of the ester carbonyl group in the acid catalyst process enhances carbon cation production following a nucleophilic alcohol attack and forms a tetrahedral intermediate. The intermediate removes glycerol and regenerates

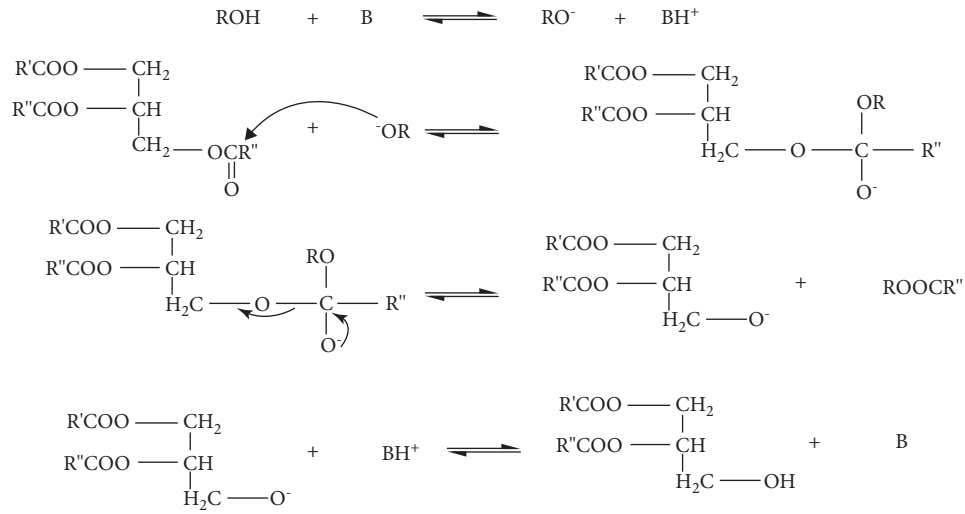

Figure 6: Transesterification process alkali-catalysed (B) base [77].

the solvent to form a new ester. Acid-catalysed transesterification can be carried out in the absence of water [87].

Schuchardt et al [91] suggested the correct conditions for acid catalyst by using powerful super acid catalysts made of sulphated tin and zirconium oxides as well as tung zirconia, for transesterification of soybean oil with methanol at 475 to 575 K. The use of concentrated sulphuric acid as a catalyst in transesterification operations to manufacture biodiesel from jatropha seeds generated 99.8% of jatropha methyl esters [92]. Figure 7 shows acid-catalysed transesterification process for vegetable oils [93].

The protonation of the ester carbonyl group in the acid-catalyst esterification process of vegetable oil enhances carbon cation production following a nucleophilic alcohol attack to form a tetrahedral intermediate. The intermediate removes glycerol and regenerates the solvent to form a new ester.

Acid-catalysed transesterification can be carried out in the absence of water [92]. The minimum amount of free fatty acids acceptable in an acid-catalysed transesterification is above 3 wt.% of FFA. Most *Croton* species, which is widespread in Africa, contain seed oil that possesses a free fatty acid value of less than 2 percent [94].

Dawodu et al [95] use biomass-derived acid catalysts to catalyse the conversion of nonedible seed oil, *Calophyllum inophyllum* with a free fatty acid content of 15% into biodiesel in a single step. The effective catalysts were created by incomplete carbonization of carbon materials in an inert atmosphere, followed by the introduction of SO_3H groups to produce catalysts with activities comparable to conventional acid catalysts. High conversion (99 percent) was achieved under optimal conditions Table 7.

(3) Enzyme-catalysed transesterification. Because of the speedy separation of the esters, little wastewater, faster recovery of glycerol, and no lateral reactions, enzymatic transesterification with a lipase catalyst is becoming increasingly popular [102]. Lipases are commonly known to function better than short-chain or long-chain alcohol. In the biochemical phase, moderate conditions of the reaction are performed.

Meanwhile, biocatalysts are more costly, and with a long operating time, their reusability and regeneration are limited. The enzyme-catalysed transesterification reaction yields are unfavourable when compared with the base-catalysed reactions and thus make the cycle unfavourable [87].

Immobilized *Candida* Antarctica lipase was used as a catalyst in the methanolic transesterification of *Croton megalocarpus* seed oil to produce biodiesel. The temperature, amount of methanol, and weight of lipase were all varied to optimize the reactions. At optimal conditions of 30% enzyme (m/m), 50°C reaction temperature, and a 1 : 4 oil-to-alcohol molar ratio, the transesterification process produced 98.71 percent biodiesel conversion. This process produced biodiesel with an unusually high acid value. All of the other fuel properties measured were within the ranges specified by the American Society for Testing and Materials (ASTM) and the International Standards Organization (ISO) [74, 103].

In a recent study [104], three different lipases (*Chromobacterium viscosum, Candida rugosa*, and Porcine pancreas) were screened for a transesterification reaction of jatropha oil in a solvent-free system to produce biodiesel; only lipase from *Chromobacterium viscosum* provided a significant yield.

(4) Noncatalytic supercritical alcohol transesterification. The aim of supercritical no-catalyst alcohol transesterification is to open up new possibilities of processing biodiesel. Research indicates that increasing the ratio of the reaction temperature to the supercritical temperature may have a beneficial effect on the conversion of triglyceride to an ester [87, 105, 106]. Because no catalyst is required during supercritical transesterification operations that avoid the creation of soap or saponification reactions, this strategy makes biodiesel purification considerably easier. During the

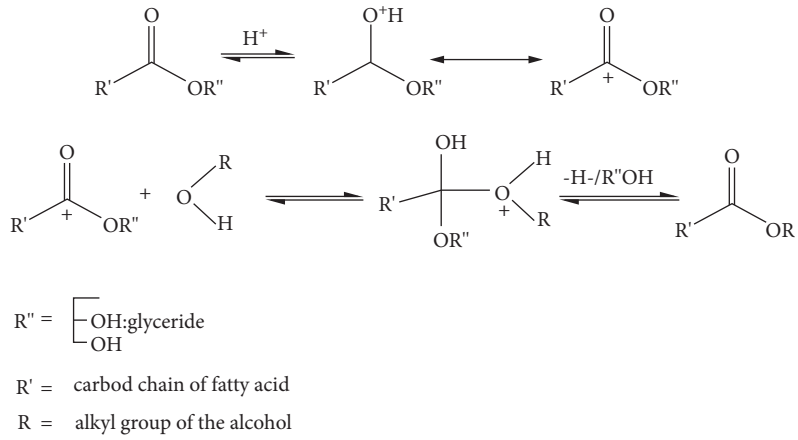

Figure 7: Acid-catalysed process for transesterification of vegetable oils [93].

Table 7: Catalysed transesterification of nonedible oils with optimized reaction variables.

Alcohol type	The molar ratio of alcohol to oil	Catalyst used	Catalyst amount (%)	Optimum reaction condition	Biodiesel yield (%)	References
Methanol	5 : 9:1	H_2SO_4	15	60°C 24h	99.8	[96]
Methanol	1 : 1	*Rhizopus oryzae*	4	30°C 60h	80	[97]
Ethanol	4 : 1	*Pseudomonas cepacia*	10	50°C 8h	98	[98]
Methanol	43 : 1	—		320°C 8.4 MPa 4h	100	[99]
Dimethyl carbonate	14 : 1	—		300°C 9 MPa 15h	97	[99]
Methanol	3 : 1	—		290°C 11 MPa 15h	99	[99]
Methanol	5 : 1	NaOH	1	60°C, 90 min	98	[100]
Methanol	4 : 2:1	NaOH	1.4	65°C, 120 min	90	[100]
Methanol	6 : 1	KOH	1	65°C, 60 min	99	[100]
Methanol	9 : 1	KOH	2	60°C, 120 min	95	[100]
Methanol	11 : 1	KOH	1.1	66°C, 120 min	93	[100]
Methanol	12 : 1	Alumina loaded with potassium nitrate	6	70°C, 360 min	84	[101]

synthesis of methyl esters in this method, the presence of water that has a detrimental effect during classical transesterification is no longer a concern [8, 26]. The drawbacks of this process, however, are related to the high temperature and pressure used, which results in a large equipment cost. To minimize the operating temperature and pressure as well as the quantity of alcohol required, co-solvents such CO_2, hexane, propane, calcium oxide, and subcritical alcohols are added to the reaction mixture. According to studies, utilizing supercritical methanol at a temperature of 593 K (320°C) at an oil pressure of 8.4 MPa and a molar ratio of 43 : 1 methanol to oil, a 100% biodiesel yield may be produced in 4 minutes [45, 84, 91].

4.5. Factors That Affect Croton Biodiesel Production

4.5.1. Reaction Temperature. The temperature of the reaction has a significant impact on the reaction rate. A high reaction temperature can reduce the viscosity of the oil, which helps speed up the process. To prevent the alcohol from evaporating, the heat of the reaction should be less than the boiling point of the alcohol (the boiling point of methanol is 60 to 70°C at atmospheric pressure). When the reaction temperature exceeds its optimal limit, the production of biodiesel decreases because a higher reaction temperature intensifies the saponification process, thereby lowering the yield [75, 107]. Depending on the kind of oil, the optimal yield is produced at a temperature of 60 to 80°C [17].

According to research carried out by Osawa [74], increasing the temperature of the reaction improved the percentage yield of biodiesel. After 1 hour at 60 ℃, the maximum biodiesel production was achieved. Although the maximum biodiesel yield increased with reaction time at 30, 40, and 50 ℃, no significant increase in biodiesel yield was observed after 1 hour at 60 ℃. The two-stage chemical process produced a high *Croton* biodiesel yield of 88 percent (v/v) under optimal conditions.

4.5.2. Effect of Alcohol-to-Oil Mass Ratio. One of the most important parameters influencing the transesterification process is the alcohol-to-oil mass ratio. A mass ratio of 0.2 was observed to give a higher yield of biodiesel [108]. Mass ratios of 0.5, however, give a slightly higher yield of *Croton* biodiesel [108].

A high alcohol-to-oil mass ratio on the one hand increases the polarity of the reactant mixture, accelerating the reaction to completion, whereas excess alcohol dilutes the concentration of the catalyst, resulting in a drop in oil conversion, which might explain why the esters level is so low. According to studies by Kuwornoo and Ahiekpor [108], increasing the alcohol-to-oil ratio efficiently enhances the output of alkyl esters. These results are consistent with those obtained by Alamu et al. [109] who found that as the alcohol-to-oil ratio rises, so does the biodiesel output. This clearly reveals that under the circumstances examined, the best percentage of alcohol (by weight of oil) required for the transesterification process was 20%.

Based on Osawa [74], *Croton* biodiesel yield increased as the amount of methanol used for transesterification increased. The highest biodiesel yield was obtained at methanol-to-oil mole ratio of approximately 6 : 1, with additional methanol addition having no discernible effect on biodiesel yield. In these reactions, the physiological temperature of 37 ℃ was used once more. Although the triglycerides in methanol stoichiometrically react with *Croton* oil in the ratio of 3 : 1, the higher ratio can be explained by the fact that the reaction is reversible, and thus, higher concentration of alcohol is one of the factors that favours the forward reaction [76].

Kipkoech [110] carried out research on the production of biodiesel from *Parkia biglobosa* oil using heterogeneous bifunctional clay catalyst. And from the results obtained show that at reaction conditions (temperature of 60 ℃, time 1 hour, and catalyst concentration 1 wt.%), the yield of *Parkia biglobosa* biodiesel increased from 78.9% to 85.07% and finally to 90.7%, which was an optimum yield, as the molar ratio of methanol to oil increased from 5 : 1 to 5.5 : 1 and to 6 : 1, respectively. As the molar ratio of methanol to oil was further increased to 6.5 : 1, it resulted into a reduction in the yield of biodiesel to 88.7% and this was attributed to the low separation of glycerol and biodiesel due to its high solubility.

4.5.3. Catalyst Concentration. The concentration of catalysts is a significant factor that determines the yield of transesterification. Base catalysts are often favoured over acid catalysts because of their increased reactivity at low process temperatures [111]. According to Reference [107], when sodium hydroxide is combined with methanol, sodium methoxide is superior to sodium hydroxide in terms of effectiveness. This decreases water quality, which is the by-product of the process. As the concentration of the catalyst rises, triglyceride conversion to biodiesel increases until optimum yield is reached.

The methyl ester conversion of neem oil was reported to be 90 to 98% at a NaOH concentration of 1.0–1.4% (w/w). KOH concentrations ranging from 0.55% to 2.0% (w/w) yielded 95 to 99% biodiesel. However, the yields were reduced beyond the optimum with the addition of the alkali catalysts [17].

The optimization of jatropha oil in the presence of a bio-based alcohol (butanol) for biodiesel production was investigated using a commercial enzyme (Eversa from Novozymes). The reaction temperature and amount of catalyst were varied, with a 6 : 1 butanol/oil molar ratio, and the reaction time was set to 60 minutes. The best results were obtained at the highest reaction temperature (42°C) and the highest catalyst concentration (9.79 percent), with an 83 percent biodiesel yield [112].

The oil extracted from *Ulva lactuca* marine microalgae was transesterified into biodiesel using silica doped with zinc oxide as a novel heterogeneous nanocatalyst, according to Kalavathy and Baskar [113]. The highest biodiesel yield of 97.43 percent was obtained at the optimized calcination temperature (1073.15 K), with an 8 percent catalyst concentration, a 9 : 1 methanol-to-oil ratio, 328.15 K reaction temperature, and a 50-minute reaction time. Ulva lactuca, a marine microalga, was discovered to be a potential source of biodiesel [113].

Guldhe et al [114] investigated the conversion of Scenedesmus obliquus lipids (microalgae) using a heterogeneous acid catalyst tungstate zirconia (WO_3/ZrO_2). The tungstate zirconia catalyst achieved 94.58 percent biodiesel conversion at 373.15 K with a methanol-to-oil molar ratio of 12 : 1 and a catalyst amount of 15% based on oil weight after 3 hours. Tungstate zirconia demonstrated comparable biodiesel conversion to homogeneous catalysts.

4.5.4. Reaction Time. With increasing reaction time, the rate of conversion of oil to esters increases. Generally, the reaction at the beginning is gradually slow due to the difficulties of combining and dispersing alcohol onto the oil. However, the reaction continues faster with time before achieving full yield [115]. For alkaline-catalysed transesterification, yields are best when the reaction duration is less than 120 minutes [116]. Furthermore, because alkaline catalysts are more reactive than acid catalysts, acid-catalysed transesterification takes even longer than alkaline-catalysed transesterification. The reaction time required to convert triglycerides to esters can go up to 18 to 24 hours. Due to the reverse transesterification process, an increase in reaction time will result in a drop in product yield, enabling more fatty acids to form soaps [17].

The duration of the reaction has been identified as a critical parameter for biodiesel production. However, it has been discovered that adding a cosolvent to the transesterification alcohol reduces the reaction time. Batches of 50 g of esterified oil were transesterified with a methanol/oil ratio of 3 : 1, catalyst (NaOH) concentration of 0.5 percent w/w of oil, 30°C reaction temperature, and methanol-to-cosolvent ratio of 1 : 1 percent v/v at a stirrer speed of 100 rpm to investigate the effect of time on the process. The reaction times were set at 10, 20, 30, 40, 50, and 60 minutes. The highest yield of 73.5 percent was obtained at the 50-minute reaction time under these conditions [117].

4.6. Fuel Quality and Properties of Croton Biodiesel. Table 8 summarizes the properties of *Croton megalocarpus* biodiesel as reported by various studies. The majority of them met the ASTM 6751 and EN 14214 biodiesel standards'

Table 8: Physical Properties of *Croton* biodiesel and petro-diesel.

Property	C. *megalocarpus* Biodiesel [118]	C. *megalocarpus* Biodiesel [52]	C. *megalocarpus* Biodiesel [119]	Petro-diesel [118]	ASTM recommended value	EN 14214 Recommended value
Density (40°C, g/cm^3)	0.886	0.883	0.886	0.823	0.860–0.900 g/cm^3	0.860–0.900 g/cm^3
Kinematic viscosity (40^{O}C, cs)	4.51	4.78	4.51	2.87	1.9–6.0	3.5–5.0
Calorific value (MJ/Kg)	39.18	37.24	39.18	44.65	Report	Report
Cloud point (°C)	−1.5	−6	−1.5	4.0	Report	Report
Pour point (°C)	−6.5	−11	−6.5	−2.0	Report	Report
Flashpoint	>200	192	>200	65	130 (Minimum)	120 min
Acid number (mg KOH/g)	0.336	0.20	0.336	—	0.8 (Maximum)	0.50 max
Cetane number	–	47.52		54.60	47 min	51 min
Oxidative stability (h)		2.88			3 min	6 min
Free glycerol % (m/m)	–	0.019	–	—	0.02 max	0.02 max
Total glycerol % (m/m)	–	0.22	–	—	0.24 max	0.25 max

minimum requirements. At 40°C, the kinematic viscosity was 4.51 and 4.78 mm^2/s, which were significantly higher than that of petro-diesel (2.87 mm^2/s). *Croton* biodiesel had a higher flash point than mineral diesel, which was above 100°C, making it safer to handle, transport, and store. *Croton* biodiesel had an acid value of 0.20 and 0.336 mg of KOH/g less than that specified in ASTM D6751 (0.8 max) and EN 14214 (0.5 max). The density of *Croton* biodiesel was 0.886 and 0.883 g/cm^3, which were higher than the density of petro-diesel (0.8321 g/cm^3) but within the EN 14214 standard range of 0.860–900 g/cm^3; thus, a higher density for biodiesel results in the delivery of a slightly greater mass of fuel in a CI engine. Biodiesels, on the other hand, have a lower energy content in both volume and mass. As a result, while the injection system delivers more biodiesel, the actual energy delivered is less than that of petro-diesel. *Croton* biodiesel had calorific value of 39.18 and 37.24 MJ/kg, which was lower than the heat value of petro-diesel, which was 44.65 MJ/kg. This was due to *Croton* biodiesel's higher oxygen content. *Croton* biodiesel had a cetane number (CN) of 47.52, which met the ASTM D6751 standard (47 min) and EN 14214 (51 min) but was lower than petro-diesel's 54.60. In general, biodiesel has a higher cetane number than conventional diesel, but the cetane number of the diesel fuel used in this study was higher than that of the *Croton* biodiesel, indicating that it contained a cetane number enhancing additive known as cetane improvers. *Croton* biodiesel's total glycerol (0.22 percent) was within ASTM (0.24 percent maximum) and EN (0.25 percent maximum) limits [52, 118, 119].

4.7. Engine Emission Characteristics Using Croton Biodiesel. According to Otta [74], as the quantity of croton biodiesel in the blends increases, the rate of exhaust emissions reduces due to enhanced combustion. At all engine loads, the engine performance characteristics of croton biodiesel blends were equal to those of petro-diesel with notable changes in performance parameters such as brake thermal efficiency, brake-specific energy consumption, and fuel flow rate. With an increase in the proportion of biodiesel in the blends, there was a considerable reduction in exhaust fume pollutants ranging from 10% to 41% but a minor rise in NOx emissions.

In the blends with a higher percentage of biodiesel, there was an overall increase in engine pressure and heat output. According to the findings of this study, high croton biodiesel blends of up to B50 had engine efficiency equivalent to petro-diesel and hence might efficiently serve as a replacement for petro-diesel [119]. High CO emissions from biodiesel blends can be minimized by employing low fuel mixes using exhaust gas catalytic reactors to complete the oxidation cycle or supplying more air to the cylinders. Lower combustion temperature or length of combustion can help to reduce NOx emissions from diesel engines [74].

4.8. Engine Performance. Biodiesel blends' performance was evaluated by comparing their effects on various engine parameters such as exhaust gas temperature, fuel flow rate, and brake thermal efficiency and to those of petro-diesel. The effects of load and biodiesel concentration in blends on engine performance parameters are discussed below [74].

4.8.1. Exhaust Gas Temperature. Because the temperature of exhaust emissions is directly proportional to engine temperature, they can be used to estimate the energy released during engine combustion. A general increase in exhaust gas temperature was observed with increased engine load due to increased fuel flow. A slight general temperature increase was also observed for each load as the concentration of biodiesel in the blends increased. This could be attributed to the presence of oxygen in the biodiesel molecules, which improves combustion. Figure 8(a) represents the temperature variation of

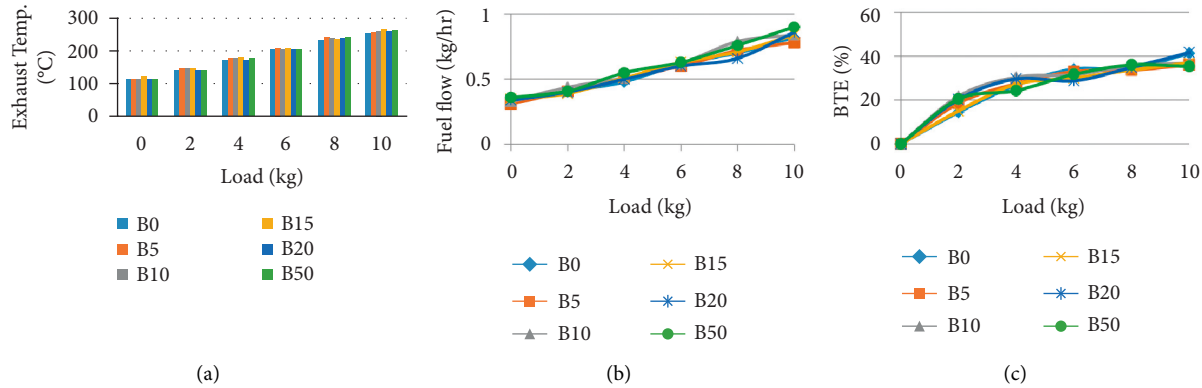

Figure 8: (a): Variation in engine exhaust emission temperature with load [74]. (b): Variation in engine fuel flow rate with load [74]. (c): Variation in brake thermal efficiency with load [74].

exhaust emissions with load for biodiesel blends and petro-diesel.

4.8.2. Fuel Flow Rate. Because of the extra energy required to overcome the increased load, the engine fuel flow rate for both petro-diesel and biodiesel blends increased steadily with increasing load [119]. At full load, the B50 blend had a 9.75 percent higher fuel flow rate than petro-diesel. Figure 8(b) depicts the variation in engine fuel flow rate as engine load increases [74].

4.8.3. Brake Thermal Efficiency. The brake thermal efficiency (BTE) of an engine indicates how well it converts heat energy from fuel to mechanical energy [120]. The BTE increased in general with increasing load for both petro-diesel and biodiesel blends. At an intermediate load of 4 Kg, all biodiesel blend BTE values were higher than petro-diesel. However, at maximum load, petro-diesel had the highest BTE, while blend B50 had the lowest. The maximum difference between the BTE of petro-diesel and the B50 blend was 4.93 percent. The lower BTE values for biodiesel blends could be attributed to their lower calorific values, which result in poor atomization and combustion. Figure 8(c) depicts the variation in BTE for biodiesel blends and petro-diesel as engine load increases [74].

4.9. Emission Characteristics. Exhaust gas and smoke analysers were used to determine the nature and levels of exhaust gases and smoke emissions for petro-diesel and biodiesel blends.

4.9.1. Carbon Monoxide (CO). CO exhaust emissions were highest at low engine loads and gradually decreased at moderate engine loads. At higher engine loads, the difference in CO exhaust emissions between petro-diesel and the corresponding biodiesel blends was smaller. The rich fuel/air mixture injected into the engine to overcome the extra loads could explain the slight increase in CO levels at higher engine loads. Figure 9(a) depicts how CO emissions change with engine load [74].

4.9.2. Nitrogen Oxides (NOx). Nitrogen oxides are produced during the combustion of fuel by the reaction of nitrogen and oxygen at high temperatures and pressures. The levels of NOx emissions increased steadily as the load applied to the engine increased. A gradual increase in the levels of NOx exhaust emissions was also observed for each engine load as the biodiesel concentration in the blends increased [118]. These findings could be explained by increased engine temperature and pressure which resulted in increased reaction time [121].

4.10. Combustion

4.10.1. Heat. The concentration of biodiesel in the blends increased the maximum heat released by the engine in general. The peaks for maximum heat released by engines fuelled with biodiesel blends occurred after those fuelled with petro-diesel, implying that the biodiesel blends ignited later than the petro-diesel. The delay in ignition of the biodiesel blends was most likely caused by poor fuel atomization [119]. The effects of biodiesel blend ignition delay could be reduced by adjusting the injection time (angle). Figure 10(a) and 10(b) show the variation in heat released against the crank angle around the ignition point for 0 and 10 kg engine loads, respectively [74].

5. Outlook for Croton and Its Biodiesels

5.1. Benefits of Croton and Biodiesel Production. The current food and fuel competition will be intensified if the food oils are used for production of biodiesel. There is a more significant benefit for growing croton as the nonedible oil tree, especially on abandoned lands which include medicinal, modification of the environment, and agroforestry as well as aesthetic value. Furthermore, it will encourage the promotion of organic farming as a result of the growth of these multipurpose trees. The use of biodiesel results in job creation, especially among the youths who are involved in

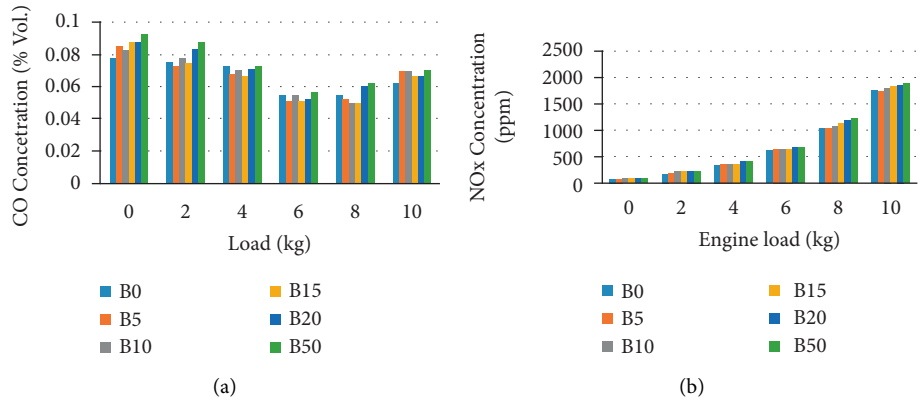

Figure 9: (a) Variation in exhaust CO emission with load [74]. (b) Variation in exhaust NOx emission with load [74].

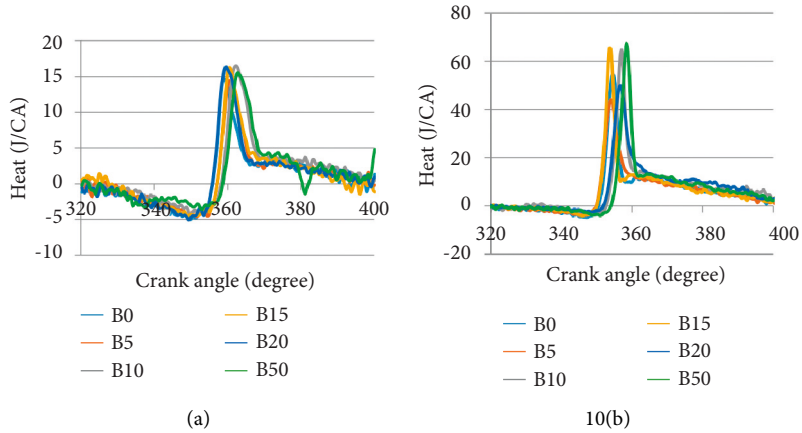

Figure 10: (a) Variation in heat released against crank angle at 0 Kg load [74]. (b) Variation in heat released against crank angle at 10 Kg load [74].

planting and marketing the seed for biodiesel [37]. High employment growth from integrated agriculture and biodiesel activities would provide competition for labour with other work opportunities, which would help to raise workers wage rates because more than one incentive will be offered at a time. *Croton* as a multipurpose nonedible tree will ensure that the seeds are harvested and available for a longer period of time since their lifespan is more than fifty years before they need to be replaced. Increasing the range of feedstocks for this multifunctional tree plant might also help countries who have been strategically located because of their total reliance on fossil fuels minimize their need on oil imports, which could be a huge economic advantage.

5.2. Economics of Large-Scale Biodiesel Production. According to the economic evaluation report of the biodiesel production plant in India dedicated to producing 39,208 metric tonnes of biodiesel per year, the capital investment charged for such a plant is approximately Rs. 1,615,133,000. One-third of this capital cost (Rs. 538,378,000) was for actual equipment purchase, and the other two-thirds (Rs. 1,076,755,000) were based on the assumption of a construction/installation cost roughly double the equipment costs. The biodiesel plant's annual operating costs are Rs. 2,075,333,000. It can be seen that raw material costs (80%) are the biggest component of overall production costs, followed by facility-dependent costs (11%), utilities (7%), and labour costs (2%). This analysis assumes that a new facility will be built for this process, with a 15-year project lifespan. The main source of revenue is the biodiesel selling price of Rs. 55.8/kg (Rs. 2,261,222,601/year). The sale of glycerol generates an additional revenue of Rs. 22.5/kg (Rs. 104, 373,027/year). This plant's total revenue is thus Rs. 2,365,586,252/year. The facility generates a gross profit of Rs. 290,253,000 per year [122].

5.3. Nano Biofuel and Barriers in Producing Biodiesel. Nano biofuel has sparked significant interest in the rationalization of biodiesel generation through the use of nanoparticles-based catalysts, resulting in the advancement of proficiency, financial strength, and nanocatalyst stability, with the potential to achieve higher product value and output [123].

Inadequate production facilities, vehicle access issues, a lack of storage space, poor quality, characteristics, a lack of processing technology, a lack of knowledge, and many other factors are among the barriers to biodiesel production. In several countries, the number of large-scale biodiesel production facilities to meet primary energy demands is still in its infancy. The distance between the collection points and the biodiesel production plant is primarily to blame for this issue. Space constraints frequently make large-scale biodiesel production prohibitively expensive. The presence of impurities such as high free fatty acid and water makes it difficult to use feedstocks such as used cooking oil as a biodiesel resource. This has a negative impact on the biodiesel production process. Because of economic reasons, biodiesel is typically produced through the transesterification reaction. However, in recent years, selecting an efficient method for biodiesel production has become critical. In some countries, biodiesel has a negative reputation as a result of one-sided media coverage on the food versus fuel conflict and a lack of understanding that biodiesel is energy for sustainable development [122].

6. Conclusions

With rising energy consumption and environmental issues affecting much of the fossil fuels' energy demands, energy conservation has become a top issue for most economic development. Biodiesel made from nonedible oils is gaining popularity as a sustainable energy source across the world. Vegetable oils and a few other nonedible oils were the focus of many of the biodiesel projects. Diversifying oil supplies will not only assure a steady and long-term supply of biodiesel feedstocks, it will also be beneficial in a variety of ways such as improving the ecosystem, reclaiming wastelands, degrading forest medicinal products, and many others. This is because these nonedible multipurpose trees attract attention to their various uses as better control of pests and nutrients, reforestation, and medicinal purposes apart from being used as a source of biodiesel. Given the prevalence of different nonedible biodiesel oils in many countries, a thorough research of these nonedible multifunctional trees is required to guarantee that they are produced entirely for sustainable agriculture and environment. *Croton* tree, therefore, has a lot of potential as nonedible biodiesel feedstocks and can help guarantee biodiesel manufacturing as sustainable [124–126].

Data Availability

All the data associated with the research are embedded within the article.

Conflicts of Interest

The author declares that there are no conflicts of interest.

Authors' Contributions

Mohammed Takase designed the research, contributed to literature search, prepared the draft and final manuscript, and addressed editor and reviewer queries during revision process.

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