

Review

# Kernel-Based Biodiesel Production from Non-Edible Oil Seeds: Techniques, Optimization, and Environmental Implications

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**Abstract:** Biodiesel represents a renewable alternative to conventional diesel, offering comparable potential. This paper delves into the production of biodiesel from non-edible oil seeds, emphasizing kernel-based feedstocks for their sustainable qualities. We discuss the critical stages of kernel separation and degumming, offering an in-depth examination of seed distribution, attributes, pretreatment, and oil extraction methodologies. Additionally, the paper considers the status of life cycle assessment (LCA) associated with biodiesel. Furthermore, it outlines the necessary steps toward sustainable biodiesel production and underscores the importance of integrating a sustainable circular bioeconomy in biodiesel synthesis.

**Keywords:** biodiesel production; LCA analysis; non-edible feedstock; oil cake; oil extraction; sustainability; transesterification



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## 1. Introduction

The depletion of fossil fuels and environmental concerns have led to the use of renewable energy as an alternative fuel source in recent years [1]. Biodiesel is an alternative fuel source that can substitute diesel fuel. Biodiesel is defined as mono-alkyl esters of long-chain fatty acids and is typically produced through the transesterification of oils and fats with methanol or ethanol in the presence of different acidic and alkaline catalysts [2–4]. The advantages of biodiesel as a fuel source are its renewable nature, non-toxicity, and mobility and the fact that it is readily obtainable and ecologically sound [5]. Biodiesel is obtained from fats and oils and has fewer hydrocarbons, reduced carbon monoxide emissions, and reduced smoke and particulates and provides engine lubrication and a higher cetane number compared with petro-diesel [6,7]. In addition to these benefits, biodiesel lacks sulfur and aromatic compounds, which are present in petroleum diesel. The minimization of air pollution is achieved by the reduction of carbon monoxide, hydrocarbons, and particulate matter through the replacement of petroleum diesel with biodiesel. Biodiesel usage not only provides a clean environment but can also decrease cancer-causing agents and air toxicity in a considerable range [5,8].

Over 350 oil crops have been identified for biodiesel production around the world [7,9,10]. The feedstocks used for biodiesel production are categorized into edible vegetable oils, non-edible oils, waste oils, and animal fats [7,9]. Biodiesel produced from edible oil sources that include palm and soybean serves as a first-generation fuel. Biodiesel derived from edible sources not only increases the price of food but also causes environmental issues.

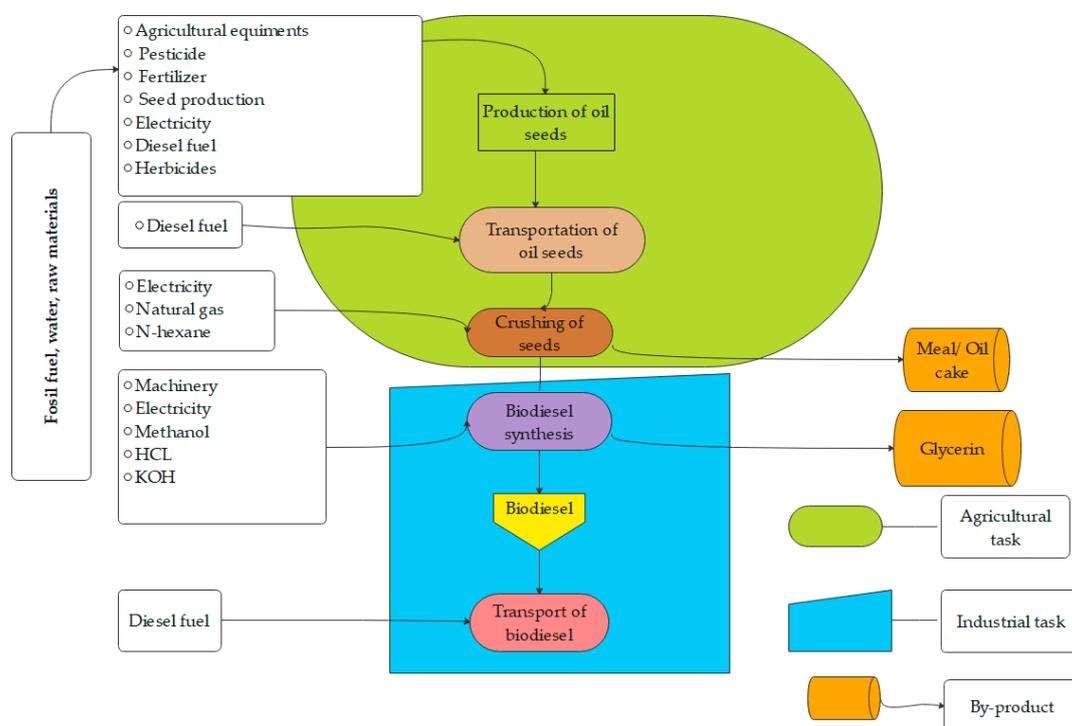
Biofuel production and use have drawbacks as well, including land and water resource requirements, as well as air and groundwater pollution [11]. Non-edible oil sources are found to be more beneficial than edible oil sources. Biodiesel obtained from these non-edible oil sources is considered a second-generation fuel [12]. Non-edible oil sources are preferred over edible oil sources due to the following reasons: adaptability in marginal land with a smaller moisture demand, development in arid zones, propagation through direct seeds or cuttings, the restoration of wasteland, the absorption of CO<sub>2</sub> emissions, increased rural employment, non-competition with agricultural resources, eco-friendliness, the ability to adapt intercropping systems, the production of other useful products along with fuel, resistance to pests, renewable sources, good availability, lower sulfur content, and lower aromatic content [1].

There are numerous methods available for the extraction of oil from vegetable sources. A screw press is commonly employed for oil extraction and it is one of the traditional methods used to extract oil from kernels [13]. The efficiency of the screw press depends mainly on the type of feedstock utilized [14]. Generally, dried and treated kernels are employed for this type of mechanical extraction [15,16]. Mechanical press extraction is a continuous process of extraction with a high yield. Castor seeds produce 36% of the oil, while *Jatropha* seeds produce up to 25% of the oil. A high oil yield was obtained at a temperature of 175 °C and 135 rpm speed for *Jatropha*, while, for castor seed, a 250 °C preheating temperature with a 35 rpm screw rotation speed was optimal. The hydraulic press produces less oil from *Jatropha* and castor compared to other mechanical methods because of oil absorption [17]. Another common method used for extraction is solvent extraction, where n-hexane is employed. The oil yield and oil quality are superior compared to mechanical extraction [18]. Numerous factors are involved in solvent extraction to obtain maximum yields, which include the solvent type, reaction temperature, stirring speed, feedstock size, time, solid-to-solvent ratio, and the moisture content of the feedstock [19]. To increase the oil yield, numerous pre-treatments of the feedstock are required, which comprise preparation, grating, drying, and moisture conditioning of the kernel required before oil extraction [20]. Seeds are processed by removing the shell or husk, followed by cracking, crushing, cooking, and kernel drying, which increase the oil yield during the pressing of oil seeds [21,22]. This pre-treatment of oil seeds has a substantial impact on the oil yield [23]. Unprocessed seeds with hulls decrease the yield considerably, due to the absorption of oil by the hull [23,24]. The harvesting and drying of oil seeds were also found to have a significant impact on the oil yield [25]. The particle size of the feedstock also plays a major role in the oil yield [6].

India has a huge land area for forestry. Many sources have been identified as possible sources for biodiesel production. Currently, the most common non-edible feedstocks analyzed for biodiesel production in India are karanja oil, *Jatropha* oil, mahua oil, Pongamia oil, rubber oil, palm oil, jojoba oil, cottonseed oil, and neem oil. These feedstocks have higher free fatty acid content, which are difficult to convert into biodiesel using alkaline catalysts because they undergo the saponification process, thereby reducing the biodiesel yield [26]. The use of an alkaline catalyst is possible when the free fatty acid levels are less than 0.3% to 3% [27]. Usually, two-step transesterification is performed for oils with higher free fatty acid content and the reduction of the free fatty acids in the oil is achieved using an acid catalysis technique followed by alkali transesterification [28,29]. The cost of biodiesel is dependent on parameters such as the type and availability of the source, the production process, and production costs and also includes the usage of additives while producing the biodiesel [30]. Among these parameters, feedstock acquisition plays a major role in the cost of biodiesel production [31]. Oilseeds are the major feedstock for biodiesel production; thus, focusing on the improvement of these feedstocks concerning their yields is key to the success of biofuel plants. The yield of oil content, free fatty acid content, fatty acid composition, and biodiesel yield through transesterification are all factors that play a major role in the maximum production of biodiesel. Most researchers focus on the type of oil extraction to improve the yield, transesterification methods, and the application of

green catalysts, but there are other factors that have to be considered, such as the quantity of seed yield, space between plants, propagation methods, fertilizer amount required, type of soil, water requirement, removal of weeds, pruning and harvesting techniques for seeds, processing of seeds, and seed storage.

Biodiesel assessment comprises three main parameters, which include the energy balance, a decline in greenhouse emissions, and the methyl ester yield [32]. Further investigations on the energy utilized in biodiesel synthesis and its life cycle assessment (LCA) are required [33]. The complete investigation of biodiesel production from soybeans was performed and the inputs used in lifecycle analysis had six phases: soybean production, transportation, crushing, biodiesel synthesis, distribution, and its application in the engine [34]. LCA is a technique used to assess the possible impacts created by the product on the environment, from the raw material to the end product. The standard method for LCA was developed by international organizations for standardization, namely ISO 14040:2006 and ISO 14044:2006. Most of the LCA studies have focused on single environmental concerns such as water usage, global warming, and the energy used to generate a single product. However, the impact on many parameters has to be studied [35]. The production of biodiesel has been categorized into two major stages, which are agricultural-based and industrial-based tasks, as shown in Figure 1. The production of oil seeds includes site processing, seed production, sowing, the usage of fertilizers, pesticide and herbicide application, watering, and harvesting [36]. The storage and processing of oilseeds, degumming, biodiesel production, the processing of oil cakes, and the purification of biodiesel and its by-product, glycerin, are considered industrial-based work. This paper aims to review the oil extraction techniques, biodiesel production, fatty acid composition, and physical and chemical properties of oil.



**Figure 1.** Agricultural- and industrial-based tasks in biodiesel production.

Biodiesel production from microalgae has vast advantages, and it is classified as a third-generation biofuel. Microalgae can use atmospheric carbon dioxide and different types of wastewater, accumulate lipids, and survive in extreme weather and offer a potential source for the extraction of valuable compounds [37]. Transesterification and thermo-pressure transformations are the two most common methods of producing microalgal biodiesel [38]. Transesterification converts only a small portion of the microalgal dry mass (between 7 and

40%) into biofuel [39]. Its economic yield can be increased further through gasification, pyrolysis as a catalyst in bio-refineries, and the production of valuable compounds such as polyunsaturated fatty acids or other by-products [40].

### *Objective of the Paper*

The most favorable condition for the selection of feedstocks for biodiesel production is based on the oil content of the source. Oil extraction from these feedstocks is done using either the seed or kernel. The direct usage of seeds for oil extraction is not applicable for a few feedstocks. This highlights the need for seed processing to obtain kernels. The foremost step in the production of biodiesel with high yields relies on the successful extraction of oil from seeds. The oil content of the seed is usually low compared to the kernel. The major constraint in oil extraction is the absorption of oil by the outer shell of the kernel. Proper separation of the kernel is an important step in maximizing the oil yield from the seed. Kernel-based oil extraction not only increases the oil yield but also enhances the quality of the oil cake. However, there is a lack of data on the processing of seeds to acquire kernels. The current work focuses on kernel-based biodiesel.

## **2. Kernel-Based Biomass Feedstock**

### *2.1. Jatropha curcas L.*

*Jatropha* belongs to the Euphorbiaceae family and tends to grow on abandoned agricultural land. It grows up to 5–7 m tall [41,42]. This species is native to India, Brazil, Central America, Argentina, Africa, Mexico, and Peru [10,43]. The tree can survive in soil that is moderately saline or degraded soil and adapts well in arid and semiarid areas. The oil content of *Jatropha* kernels varies from 43 to 59% [7]. The lifespan of this large shrub varies from 30 to 50 years, which mainly depends on the soil conditions, and the yield varies from  $0.1 \text{ t ha}^{-1} \text{ Y}^{-1}$  to  $8 \text{ t ha}^{-1} \text{ Y}^{-1}$  [44].

### *2.2. Pongamia pinnata*

*Pongamia pinnata* is a small tree belonging to the Leguminosae family that is native to India and Southeast Asia [45,46]. This tree is also found in tropical regions such as Australia, China, New Zealand, and the USA and has high tolerance to saline soil. The yield of seeds is around 9–90 kg per tree, which is roughly 900–9000 kg of seeds per ha [46]. This particular species not only produces oilseeds but also, in turn, fixes nitrogen in the soil [47]. The oil content of the seed varies from 30 to 40% and thus it could be a potential resource for the biofuel industry [44,45,48,49].

### *2.3. Calophyllum inophyllum*

*Calophyllum inophyllum*, also commonly called polang or honne, belongs to the Clusiaceae family, seen in East Africa, India, Australia, and Southeast Asia. It is a medium-sized tree that grows deep in the soil, is exposed to sea sands, and requires rainfall of 750 mm–5000 mm/year [48,50,51]. It grows up to 20 m long, and the color of the tree changes from pale green to dark green based on its growth condition [52]. The oil content of the seed varies from 65 to 75% [50,53].

### *2.4. Madhuca indica*

*Madhuca* belongs to the Sapotaceae family and grows to around 20 m in height. Its native country is India [54–56]. It adapts easily to arid regions [48,51]. This tree is usually seen in forest regions and can be a viable source of biofuel due to its availability in large quantities, around 60 million tons per year. The seed yield begins after 10 years of maturity and it has a lifespan of 70 years. Mahua tree yields can range from 20 to 200 kg annually, depending on the maturity of the tree [57]. The kernel constitutes 70% of the seed and yields oil of around 50% [56].

### 2.5. *Sapium sebiferum*

*Sapium sebiferum* is also known as the Chinese tallow or stillingia tree and belongs to the Euphorbiaceae family. It is a fast-growing tree and its lifespan is around 70–100 years. This tree can be grown on marginal land and it also adapts to alkaline, saline, drought, and acidic soils. Its native area is Eastern Asia, commonly seen in China and Japan. It is grown in the United States to control soil erosion [58–60]. The oil is used in soap production and candle making. It is popularly used as a biofuel [6].

### 2.6. *Azadirachta indica*

*Azadirachta indica* belongs to the Meliaceae family and grows to 12–18 m tall. It is an evergreen tree that grows well in saline, alkaline, dry, and shallow soil. It is native to India, Pakistan, Burma, Malaysia, Japan, Indonesia, Sri Lanka, and Australia [6,7,44]. It grows well in arid and semiarid regions and it can also adapt its growth to high temperatures and less rainfall of around 250 mm. The seed yields are optimal after 15 years and it has a life expectancy of 150–200 years. The neem seed yield varies from 2 to 4 t/ha/Year. The oil content of the seed is around 30%, whereas the kernel yields around 40–50% [61,62].

### 2.7. *Hevea brasiliensis*

*Hevea brasiliensis* is a rubber tree that belongs to the Euphorbiaceae family. This tree is native to Indonesia, Malaysia, India, Sri Lanka, and Thailand and is widely grown as an economic tree in Nigeria [63]. It grows up to a height of 34 m and requires heavy rainfall, and the seeds are considered waste and are not used in any industrial application [6,51]. The rubber seed contains between 40 and 50% oil [64].

### 2.8. *Sapindus mukorossi*

*Sapindus mukorossi* is also commonly known as soapnut and is found in tropical and subtropical regions around the world, which include, Asia, Himachal Pradesh, America, and Europe. It develops well in loamy and leached soil, which in turn helps to prevent soil erosion. The kernel has 39% oil and consists of 92% triglycerides, thus holding promise for biodiesel production [65–67].

### 2.9. *Prunus Sibirica*

Siberian apricot (*Prunus sibirica*) grows in mountainous and temperate regions. It is found in Mongolia, Russia, and the northern part of China. It belongs to the family Rosaceae. It is a shrub that yields about 192,500 tons of seed per year [68]. It grows well with abundant solar radiation, low temperatures, less rainfall, and poor soil. The kernel oil of Siberian apricot can be used as an edible oil, lubricant, cosmetic, and surfactant. It also lowers cholesterol levels and thus can treat cardiovascular diseases [69]. However, this tree is grown to enhance greenery and conserve water and soil. The presence of amygdalin in the seed kernel inhibits its usage for edible purposes because it breaks down into glucose, benzaldehyde, and hydrocyanic acid via the  $\beta$ -glucosidase enzyme. The lower concentration of hydrocyanic acid improves respiration and stimulates digestion, whereas a higher concentration leads to death [70].

### 2.10. *Sterculia foetida*

*Sterculia foetida*, usually known as jangali badam or poon tree in India, belongs to the family of Sterculiaceae under the order of Malvales [71,72]. It is an evergreen tropical tree and is native to Australia, Bangladesh, Djibouti, India, Eritrea, Ethiopia, Kenya, Malaysia, Myanmar, Indonesia, Pakistan, Sri Lanka, Thailand, the Philippines, Somalia, Tanzania, Zanzibar, Uganda, and Oman and is considered exotic in Ghana and Puerto Rico [73,74]. It grows to a height of 40 m and up to 3 m in girth [73,75]. The *Sterculia* fruit contains 10–15 seeds that appear red and have an almost smooth surface [1]. The seeds are white in the initial stages and turn black when they are ripe. The oil obtained from this seed is

commonly used as an illuminant and also in the surface coating industry, the soap making industry, and as a medicine for some skin diseases [72].

#### 2.11. *Prunus armeniaca*

The largest producer of stone fruit (*Prunus armeniaca*) in the world is Turkey, and other countries such as Iran and Uzbekistan are also leading in its production. The native stone fruit is found in India and Armenia. Most cultivation of stone fruit is performed in ice-free zones [76]. Currently, the stone fruit is cultivated in Australia, but the cultivation is limited to humid regions because of fungal attacks [77]. The fruit color of the stone fruit changes from yellow to orange, it has a diameter of 1.5–2.5 cm, and the seed is covered by a hard shell. The kernel yield from seeds is approximately 22 to 38% and the oil content is found to be 54.2% [78,79]. Most seeds are considered waste after fruit processing due to the presence of hydrocyanic acid [80].

#### 2.12. *Camelia sinensis*

*Camelia sinensis* is an evergreen shrub and belongs to the family Theaceae. Tea seed oil is extracted from tea seeds. The annual production of tea seeds is almost 3–4 tons [81]. It is indigenous to East Asia, India, and Southeast Asia but is currently grown all over the world in tropical and subtropical regions. The kernel content of tea seeds is 47% [82]. Tea seeds contain 29–34% of oil and the presence of saponins is around 11–15% [83]. Tea seed oil contains antioxidants and polyphenols, as well as vitamin E at around 200 mg/L. Thus, tea seeds can be a potent source of biodiesel and used for the extraction of saponins, and vitamin E can also be applied in fuel production [84].

#### 2.13. *Elaeis guineensis*

*Elaeis guineensis* is one of the highest oil-yielding crops, grown in tropical countries such as Malaysia and Indonesia [85]. Being a perennial crop, annual sowing is not required [86]. Palm fruit harvesting starts in the third year of plantation, whereas the maximum yield is achieved from the twelfth year until 25 years after plantation [87]. The palm tree's economic life is around 25 years [88]. Palm fruits usually grow in bunches, around 1000–3000 fruits per bunch. Every bunch weighs around 10–15 kg and the oil content of each bunch is 25% (*w/w*) [85]. Palm oil is extracted from the mesocarp, the fleshy part of the fruit, at around 49%, and about 50% of the oil is extracted from the palm kernel [85,89]. Palm kernel oil is utilized in soap manufacturing [90]. It has high productivity and a positive energy balance [32].

#### 2.14. *Thevetia peruviana*

*Thevetia peruviana* is native to Mexico, Brazil, America, and the West Indies and has adapted to tropical regions around the world. It is an evergreen shrub belonging to the Apocynaceae [91,92]. It is also known as yellow oleander and bush milk in India, Puerto Rico, and Nigeria. It grows up to 4.5–6 m, with green-colored leaves and white and yellow-colored flowers. The seed yield can vary from 400 to 800 fruits based on rainfall and the maturity of the plant. The oil content of the kernel is around 67% [48]. The feedstocks used for biodiesel production are shown in Table 1.

**Table 1.** Distribution, characteristics, and uses of kernel-based oil feedstocks.

S. No.	Common Name	Feedstock	Country	Oil Content (%)		Uses	Reference
				Seed (wt%)	Kernel (wt%)		
1	Physic nut	<i>Jatropha curcas</i>	Indonesia, Thailand, Malaysia, Philipines, India, Pakistan, Nepal	20–40	40–60	Lighting, lubricant, soap making and biodiesel	[5,6,44]
2	Mahuva tree	<i>Madhuca indica</i>	India	35–50	50	Biodiesel, illuminant	[6,7,44]
3	Pongam oil tree	<i>Pongamia pinnata</i>	Western Ghats in India, Northern Australia, Fiji, and some regions of Eastern Asia	25–50	30–50	Biodiesel, fodder, green manure	[5,6,44]
4	Neem seed	<i>Azardirachta indica</i>	Native to India, Burma, Bangladesh, Sri Lanka, Malaysia, Pakistan, and Cuba	20–30	25–45	Oil illuminant, timber, firewood, biodiesel	[5–7]
5	Rubber seed	<i>Hevea brasiliensis</i>	Nigeria, India, Brazil, Southeast Asia, West Africa	40–60	40–50	Surface coatings including paints, printing inks, rubber/plastic processing, pharmaceuticals, lubricants, cosmetics, chemical intermediates, and diesel fuel substitute/extender	[6,7,51]
6	Chinese tallow tree	<i>Sapium sebifeum</i>	China, France, India, Sudan, Martinique, Algeria, and the southern area of the United States	13–32	53–64	Candles, soap, wood varnish	[6,7,58,60]
7	Soapnut	<i>Sapindus mukorossi</i>	Asia (India, Nepal, Bangladesh, Pakistan), America, Europe	51.8	39	Rural building construction, oil and sugar presses	[66,93]
8	Stone kernel fruit	<i>Prunus armeniaca</i> L.	Turkey, Iran, Uzbekistan	-	54.2	Oil	[77]
9	Calophyllum	<i>Calophyllum inophyllum</i> L.	Tropical regions of India, Malaysia, Indonesia, and the Philippines	65	22	Cosmetics, oil, timber	[89]
10	Siberian apricot	<i>Prunus sibirica</i> L.	Eastern Siberia, Russia, Monogolia, and China	-	50.18	Lubricant, surfactant, cosmetics, and medicinal uses	[68]
11	Tea seed	<i>Camellia sinensis</i> L.	Turkey, India, and China	-	32.1	Vitamins, polyphenols, and saponins	[82]
12	Palm kernel oil	<i>Elaeis guineensis</i>	Malaysia, Indonesia, Nigeria, Colombia, Thailand, Zaire, and Equador	-	50	Soap, oleochemicals, cosmetics, soaps, toothpaste, lubricants	[94]
13	Java olive	<i>Sterculia foetida</i>	Australia, Bangladesh, Djibouti, India, Eritrea, Ethiopia, Kenya, Malaysia	-	50–60	Biodiesel, medicinal, illuminant	[95]
14	Yellow oleander	<i>Thevetia peruviana</i>	Mexico, Brazil, America, and West indies	-	67	Oil	[48]

### 3. Preliminary Steps for Oil Extraction

The preliminary steps include seed harvesting, cleaning, conditioning, and drying before extracting the kernel from the seed. Seeds for oil extraction are collected from the tree using long sticks. The collected seeds are cleaned to remove unwanted twigs, stones, and other impurities. The cleaning of seeds involves the removal of the outer skin and cover of the fruits. The initial step requires the separation of the pulp and seeds [79]. In a few species, the dewaxing of seeds is a preliminary step before oil extraction. In the industry, kernel oil from *S. sebiferum* L. is extracted by heating the seeds with saturated vapor, since the seeds are covered with wax. The seeds are centrifuged to remove the wax that has melted. The dewaxing of the kernel is important to ensure the properties of biodiesel, such as the cloud point and pour point, and also to provide better viscosity [96]. The process of oil extraction has numerous steps, as shown in Figure 2.



Figure 2. Oil extraction process.

#### 3.1. Kernel Processing

The seeds obtained are subjected to different processes, namely dehulling, kernel drying, oil extraction, and the purification of the extracted oil. The seeds are processed to separate the husk and kernels from the seeds. The husk obtained from seeds can be used to extract more biologically active compounds, and the kernel is employed for oil extraction. Thus, the oil is collected for further purification and processing, and the oil cake can be utilized for various applications, which include its use as a biogas or biofertilizer, enzyme production, animal feeding, and as briquettes for power generation, as shown in Figure 3.

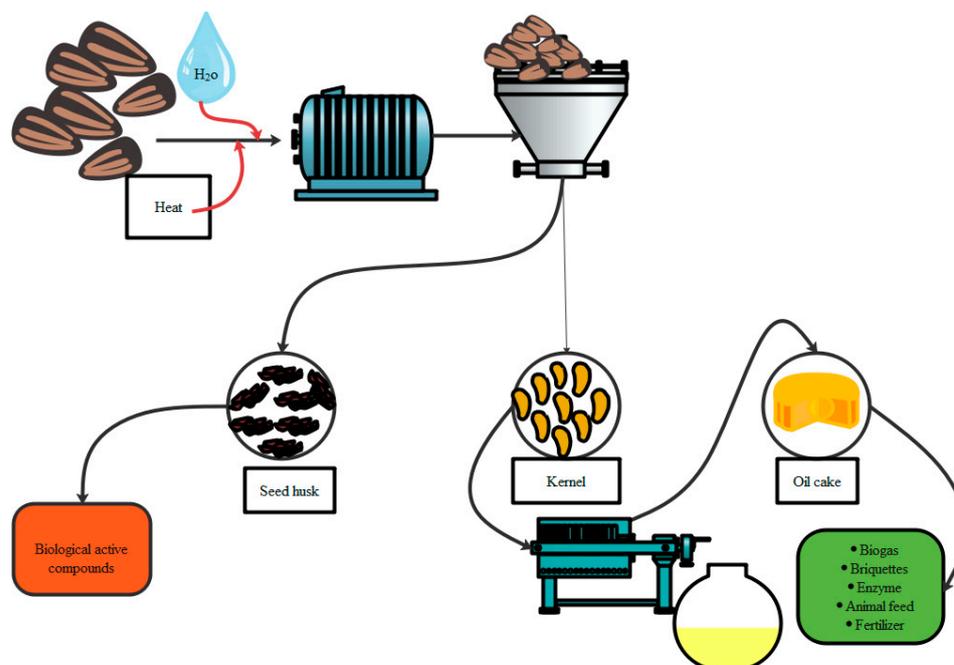


Figure 3. Oil extraction and by-products from oil cake and seed husk.

### 3.2. Decortication of Seeds

The dehulling of the seeds is an essential step in obtaining the kernel after the cleaning, conditioning, and drying of oilseeds. The removal of the hard seed coat results in the kernel and also increases the nutritional content and reduces the antinutritional constituents such as tannins, pigments, and insoluble dietary fiber (IDF). Kernel usage in the oil extraction process also reduces energy usage and equipment wear [97,98]. Usually, oil seeds are dehulled to enhance the oil yield and quality. The use of whole oil seeds leads to the accumulation of pigments and impurities in the oil. The protein content of the meal can be increased to 48.3% from 36% by dehulling [99]. Mostly, manual shelling is performed to separate the kernel from the seed, which requires high labor input and has low efficiency. Decorticated *Jatropha* seeds' oil content may vary from 40 to 60% based on their variety [100]. *Thevetia peruviana* shells are removed before the extraction of the oil, due to the presence of semi-oily material in the seed coat and also the presence of some hexane-soluble compounds. The typical methods utilized in the shelling process include cutting, rub-tearing, extrusion, and impacting [101]. However, the dehulling efficiency of oil seeds depends upon several factors, which include the size and shape of the seed, the kernel's adherence to the hull, the moisture content, and the capacity of the seed to bear mechanical loading [102]. Abrasive dehulling is employed to remove the outer coat of the seed layer, which has an abrasive surface, coated on the drum or rotor surfaces, which is also known as pearling [103,104].

### 3.3. Processing of Kernel

Oil extraction from the kernel is possible by removing the outer shell of the fruit and thus obtaining the kernel, which is dried to obtain the preferred moisture content [18]. The softening of the seed is done to recover the kernels from the hard shell. In some species, such as *Sterculia foetida*, the soaking of seeds is carried out to remove the powder layer in the seed and to obtain the kernel, so as to increase the oil extraction efficiency [95]. This particular step can avoid the absorption of the oil by the powdery layer. Hence, seed processing is an essential step for oil extraction. Seeds are manually cracked to open the kernel or by the application of stompers [105]. The manual processing of seeds is a time-consuming and laborious process. Apricot seeds are processed by immersing the seed in water for 10–20 min before breaking the shell [79]. The kernels are separated from the seeds, cleaned, and stored for oil extraction [6,105].

### 3.4. Kernel Drying

The moisture content is one of the main factors involved in achieving the maximum efficiency. The presence of moisture content of around 15% yields more oil in both mechanical and solvent extraction methods [20]. Seeds are dried at 50 to 70 °C until they reach the desired moisture content. Weighing the oilseeds constantly throughout the day facilitates the drying process [18,105,106]. The occasional stirring of the sample also ensures uniformity in drying [20]. The drying of the seed has a greater influence on the oil yield because the tissues are softened and the oil viscosity is greatly reduced [107]. Sufficient drying of the kernel not only softens the cellular structure but also increases the coagulation of proteins and collapses the oil cells, which increases the oil yield [108]. The high moisture content of the kernel increases its plasticity and reduces the compression strength [109,110]. A larger amount of water in the kernel generates an inhomogeneous layer between the lipids and water and thus the diffusivity of the lipids in the solvent is reduced, which in turn reduces the yield of oil [111–113].

### 3.5. Purification of Oil

The oil extracted by mechanical means may have several impurities, such as solids, dust particles, free fatty acids, water, phosphorous, and oxidative metals. The removal of these impurities is an essential step to avoid oil deterioration and prevent filter clogging in the engine when using crude oil. Impurities also have a negative impact on biodiesel

production [114]. Processes such as sedimentation, centrifugation, and filtration are applied for the removal of impurities [115]. Sedimentation is usually applied in small processing units. Filtration of the oil is carried out by gravity, band, or bag filters, or filter presses and leaf filters [114]. The FFA content is reduced by the esterification of the catalyst, steam distillation, and the extraction of alcohols [116].

### 3.6. Storage of Oil

The oil quality can deteriorate due to several reactions, such as hydrolysis, polymerization, and oxidation, when it is stored in improper conditions [117]. Many factors, such as temperature variations, exposure to light and air, the presence of volatile gaseous substances, and water condensation, will induce oxidation. The oil must be stored in a cool and dry room [114].

### 3.7. Seed Cake

The by-product obtained after oil extraction is the seed cake, which has leftover oil content, usually dependent on the extraction process. High oil content is present in the oil cake, which is subjected to mechanical extraction rather than chemical extraction, thus increasing its energy value [43]. The pressed cake has high levels of nutrients and protein and more calorific content after oil extraction [118]. Thus, the pressed cake can be utilized for fertilizer, fuel, and biogas production. The use of the *Jatropha* seed cake showed a significant increase in the yield of edible crops such as *Pennisetum glaucum*, *Brassica oleracea*, and *Oryza sativa* as well as an increase in the seed yield of *Jatropha curcas* [43]. The phorbol esters present in the seed cake are completely degradable in soil and have no impact on other microbial communities in the soil [119]. The seed cake can be directly burned as fuel due to its high calorific value [43]. The conversion of the seed cake into charcoal briquettes is beneficial compared to cake briquettes. The benefits of converting the pressed cake to charcoal briquettes include an increase in the energy content of the fuel, reduced weight, and a reduction in smoke while using it as a fuel [114]. The seed cake is also used as a resource for biogas production, and the yield varies depending on the type of extraction and the inoculum used in the biogas reactor [43]. The slurry from the biogas reactor can be diverted to fields as a nutrient for plants [120]. Solid-state fermentation of the oil cake is also possible to produce enzymes [121]. The use of seed cakes as animal feed is the best option to increase the nutritional content of the feed, but the presence of phorbol and other antinutritional compounds inhibits its usage as a feed. Further research on the detoxification of the seed cake is required for its application as an animal feed [119,122].

## 4. Current Status of Oil Extraction Techniques (Kernel Oil Extraction Techniques)

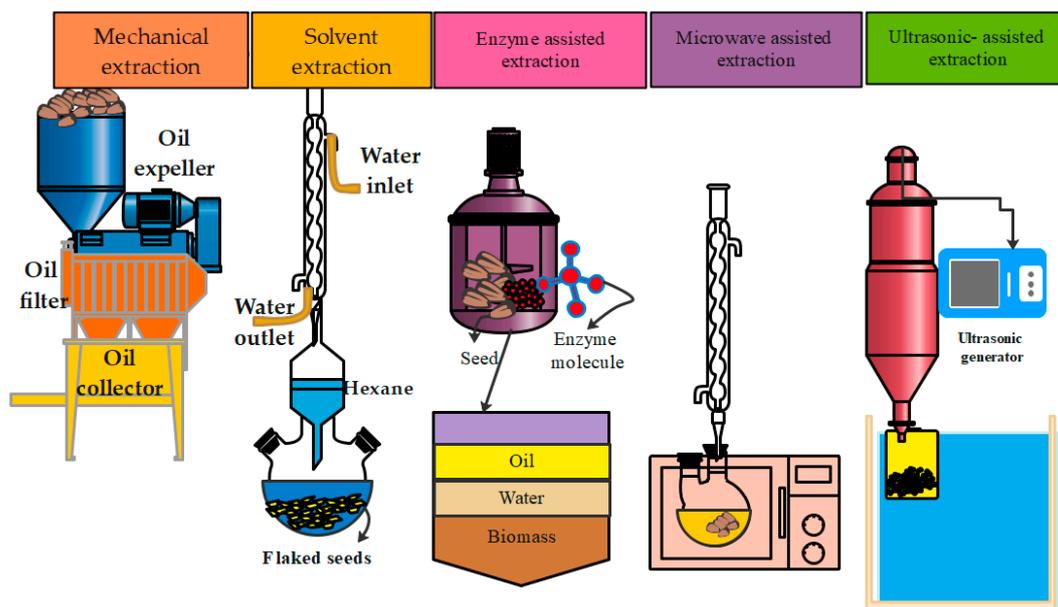
### 4.1. Oil Extraction Methods

Oil can be extracted from seeds using various techniques, which include mechanical extraction, solvent extraction, microwave-assisted extraction, ultrasonic-assisted extraction, and enzymatic extraction. On a commercial scale, only two methods of oil extraction are widely reported, which are mechanical extraction and solvent extraction. Both extraction methods require seed drying before oil extraction. The whole seeds are commonly used in mechanical extraction, whereas only kernels are used for solvent extraction [9,43]. The extraction of oil from oil seeds is a midstream process, whereas the growth of oil crops and the pre-treatment of seeds are upstream processes. The downstream process comprises biofuel production. The various methods of oil extraction are shown in Figure 4.

### 4.2. Mechanical Extraction Methods

Oil extraction can be achieved by mechanical extraction. Generally, expellers or screw presses are applied for the extraction of oil from seeds. The process is inefficient because the yield is lower compared to solvent extraction. Around 8–14% of the oil may be left in the oil cake [6]. Extraction through the ram process yields about 60–65%, whereas the application of an engine-driven screw press increases the yield compared to the ram press

to 68–80%. The equipment is designed for a particular seed, which reduces the oil yield for other seeds. The yield of oil can be enhanced by the application of heat and pressure [6]. In a screw press, the cooked seeds showed a high yield of oil ranging from 89 to 91% [9].



**Figure 4.** Various methods of oil extraction.

Mechanical extraction is divided into two methods, namely cold pressing and hot pressing [123]. Seed pre-treatment (cooking) is an essential step where thermal heat is used for hot pressing, whereas cold pressing is done without heat treatment [124]. Cold-pressed oil has its nutritional content preserved and is more valued by consumers [125]. Hot pressing yields more oil than cold pressing [126]. Hot pressing is the best option for the synthesis of biodiesel.

A screw-type press was used for the extraction of oil from *sterculia* seeds [95]. *Calophyllum* oil can be extracted from seeds by using either a hydraulic or screw press [6]. Different researchers have used various methods of mechanical extraction because the process is inexpensive [127]. However, mechanical means of oil extraction need further processing to improve the oil quality, such as filtering and degumming processes [6]. The density, free fatty acids, acid value, and viscosity were found to be higher than for solvent extraction [20].

#### 4.3. Solvent Extraction

Solvent extraction is a method of obtaining components from solids with the help of a solvent [128]. The selection of the solvent for oil extraction is based on its low viscosity to ease the free circulation of the solvent. Generally, oil is extracted from seeds using a Soxhlet apparatus, where contact between the solid and liquid is established to extract the oil from the seeds. The extraction of oil using a hexane solvent was found to yield a large amount of oil. The quality of the oil extracted using hexane was found to be high compared to mechanical extraction. The resulting biofuel had properties such as a high cetane number, calorific value, and oxidation stability [20]. There are many solvents used for oil extraction, which include hexane, chloroform, and methanol [129]. Commonly, n-hexane is used over other solvents such as petroleum ether, tetrahydrofuran, methanol, and chloroform based on the amount of unsaponifiable content in the extracted oil. *Sterculia* seeds yielded 57% of oil content when using n-hexane as a solvent, and *Jatropha* kernels yielded around 41% of oil [130,131]. Various parameters have an impact on the yield of oil, which include the sample size, solvent-to-seed ratio, extraction time, boiling temperature of solvents, particle size of seeds, solvent type, extraction temperature, and moisture content

of seeds [128]. Finally, the obtained hexane and oil mixture is exposed to evaporation to obtain the extracted oil. Solvent extraction is feasible for large-scale applications. This type of extraction takes more time than other methods and it harms the environment due to the generation of more wastewater and the evaporation of volatile compounds; there is also a risk to human health due to the use of flammable chemicals [6].

#### 4.4. Ultrasound-Assisted Extraction Method

In the ultrasound-assisted method, materials are immersed in a solvent and subjected to ultrasonic vibrations. The range of vibration created by ultrasound varies from 18 kHz to 100 MHz [132]. This technology is used currently to extract value-added compounds from different bio-sources and has been commercialized by various manufacturers [133]. Microscopic bubbles are formed and collapsed, emitting large amounts of energy, pressure, and mechanical shear. This technique targets particular compounds to extract from the intracellular to extracellular level [134]. The disruption of cell walls is seen, which releases oil into the solvent. The benefits of this method are the shorter time and lower solvent utilization, which in turn also have a positive impact on the environment [84]. The use of ultrasound on oil seeds reduced the number of cycles required in the Soxhlet process and also increased the oil yield to 75% [135]. There is no variation in fatty acid composition when applying the ultrasound technique [136]. This technique is a successful method for the extraction of essential oils and lipid molecules from oil seeds [137,138]. The advantages of this process include high extraction yields, less time, and less energy consumption [139,140]. This method is the best method for the extraction of oil and has been found to be a developing technology even in the food industry. The major drawback in the usage of ultrasound for oil extraction is in the development stage, because no report has been conducted on commercial oil seed pressing units. The grinding of seeds is required for ultrasound extraction. An economic analysis of the ultrasound extraction of oil seeds is required to utilize this technique on an industrial scale [136]. The kernel powder of an exotic fruit, *Canarium odontophyllum*, was investigated for maximum oil extraction using optimization techniques, and the optimal conditions were determined to be as follows: ultrasound amplitude level: 38.30%, n-hexane to kernel powder ratio: 50:1 in mL/g, extraction time: 45.79 min, and oil extraction yield: 63.48%. Thus, ultrasound-assisted oil extraction increases the maximum oil yield [141].

#### 4.5. Microwave-Assisted Extraction Method

This technique utilizes a micro-oven for extraction, through which various plant materials can be extracted successfully [142]. This method is a combination of conventional solvent extraction methods and microwave extraction methods [143]. An electromagnetic field is created by microwave irradiation, which enhances the oil extraction process. This technique is found to be an energy-efficient technique due to the lower energy requirement. Oil is extracted in less time and the consumption of the solvent is found to be minimal, and it gives a higher yield than expellers and solvent extraction methods [144]. Microwave extraction disrupts the cell wall and lipid fractions and releases the oil. The oil released from the cell forms a liquid phase, which is further separated [84]. Microwave-treated seeds show better storability as feedstocks. Microwave-treated seeds were stored for six months at 30 °C and found to have lesser acid values, small changes in peroxide values, and reduced water content [145]. This ensures the better storage capacity of seeds for further processing. Researchers have found that the treatment of seeds through microwave also enhances the oxidation stability of the oil, the nutraceutical content, and the oil yield [146]. Thus, the microwave technique can be used in the food industry, especially for the production of bioactive compounds from plant materials.

#### 4.6. Enzymatic Extraction

The aqueous enzymatic method is a promising technology utilized to extract oil from plant material [147,148]. The success of this technique mainly depends on the proper usage

of enzymes [149]. Enzymes can also be employed for oil extraction, and the yield is found to be high. The seed kernel cell wall is ruptured and the oil compounds are discharged into the extraction media. This technique is eco-friendly since solvents are not utilized in this process. The lower processing cost of the oil cake obtained after oil extraction is another advantage of this technique [84]. The primary location of lipid storage in oil seeds is found in cell organelles called oleosomes [29]. Cellulose, lignin, hemicellulose, and a small amount of pectin make up these walls [150]. The most crucial stage in the AEE process is breaking the cell wall. The application of the AEE technique utilizes hydrolytic enzymes such as cellulase, protease, pectinase, and hemicellulose. The optimum conditions for oil extraction have the greatest impact on the oil yield [151]. During enzyme treatment, the *Camelina oleifera* kernel yield ranged from 26 to 49%. This process is still not applied on a commercial scale due to the high enzyme costs [152]. This issue can be addressed by the production of enzymes from oil cakes through solid fermentation [84]. Although the use of immobilized enzymes lowers the overall cost, the reaction rate of the enzyme decreases due to steric hindrance [43]. The combined usage of enzymes and ultrasonication can increase the oil yield, as well as offering a lower acid value, higher iodine value, and similar fatty acid composition, regardless of the extraction process [153].

### 5. Fatty Acid Composition

A crucial characteristic of the yield of any biodiesel feedstock is the fatty acid composition. The oil composition varies in terms of the fatty acid proportion of any kernel oil based on the feedstock quality, the environment, and the geographic location [95]. Most of the non-edible oils, including Pongamia, have palmitic, stearic, oleic, and linoleic acids [154]. Biodiesel usually has a high percentage of unsaturated fatty acids, which generally undergo autoxidation. Additionally, oxidative deterioration negatively affects the acid value and kinematic viscosity. In contrast, biodiesel with a large number of unsaturated fatty acids has better flow characteristics than biodiesel containing only saturated fatty acids. In general, the use of biodiesel in cold areas is constrained by poor cold flow characteristics [52]. Therefore, the oil yield from seed kernels is a crucial characteristic in selecting any feedstock as a source of biodiesel. Table 1 displays the estimated results and oil content of various non-edible vegetable oil feedstocks. A higher biodiesel yield is based on the composition of fatty acids in the feedstock. Some non-edible oils have a distribution and composition of fatty acids that typically include aliphatic molecules with a carboxyl group at the end of a straight chain. Straight fatty acid chains are the major biodiesel components, and the most widely used ones are palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids [12]. However, some feedstocks have fatty acids other than the usual ones in substantial amounts. The fatty acid compositions have a negative impact on the fuel quality and attributes of biodiesel [12].

Furthermore, it has been suggested that biodiesel containing a high concentration of methyl oleate (a monounsaturated fatty acid) may exhibit outstanding ignition quality, fuel stability, and flow qualities at low temperatures [12,51]. On the other hand, the fatty acid content will influence the iodine value, and a lubricating oil will quickly deteriorate at greater iodine levels [155]. Saturated fatty acid alkyl ester enhanced the cloud point, cetane number, and stability of methyl ester, according to Sahoo and Das [156]. In general, non-edible oil contains a large proportion of double carbon chains (polyunsaturated acid), which suggests that it has more unsaturated fatty acids than saturated carbon chains [12]. As a result, this structural fatty acid composition will impact the physicochemical characteristics of biodiesel, such as its viscosity, heat of combustion, and cetane number [6,51]. Table 2 shows the fatty acid compositions of various feedstocks.

Table 2. Fatty acid compositions of various feedstocks.

Fatty Acids	<i>J. curcas</i> [157] (%)	<i>M. indica</i> [158] (%)	<i>P. pinnata</i> [51] (%)	<i>A. indica</i> [49] (%)	<i>H. brasiliensis</i> [63] (%)	<i>S. sebifeum</i> [59] (%)	<i>S. mukorossi</i> [153] (%)	<i>P. armeniaca</i> [77] (%)	<i>C. inophyllum</i> [20] (%)	<i>P. sibirica</i> [159] (%)	<i>C. sinensis</i> [82] (%)	<i>E. guineensis</i> [94] (%)	<i>S. foetida</i> [160] (%)	<i>T. peruviana</i> [157] (%)
Caprylic	-	-	-	-	-	-	-	-	-	-	-	3.3	-	-
Capric	-	-	-	-	-	-	-	-	-	-	-	3.4	-	-
Lauric	-	-	-	-	-	0.4	-	-	-	0.03	-	48.2	-	-
Myristic	1.4	1.0	-	0.26	2.2	0.1	-	-	-	0.03	-	16.2	-	-
Palmitic	12.7	17.8	3.7–7.9	14.9	10.2	7.5	4.75	5.85	13.60	3.79	11.4	8.4	22.4	15.6
Palmitoleic	0.7	-	-	0.1	-	3.71	0.35	-	0.2	0.67	-	-	-	-
Stearic	5.5	14.0	2.4–8.9	-	8.7	2	1.74	2.51	16.7	1.01	2.5	2.5	7.3	10.5
Oleic	39.1	46.3	44.5–71.3	43.9	24	16.7	60.95	63.8	40.1	65.23	62.3	15.3	16.4	60.9
Linoleic	40.4	17.9	10.8–18.3	17.9	38.6	27.5	4.50	25.3	26.3	28.92	20.0	2.3	45.6	5.2
Linolenic	0.2	-	-	0.4	16.3	41.5	2.45	0.51	0.3	0.12	2.2	-	-	7.4
Arachidic	-	3.0	4.1	1.6	-	-	4.47	-	0.7	0.09	-	-	6.46	0.3
Eicosenoic	-	-	2.4	-	-	0.59	18.84	-	0.3	0.11	0.8	-	-	-
Behenic	-	-	5.3	0.3	-	-	0.94	0.66	0.2	-	-	-	-	0.1
Lignoceric	-	-	1.–3.5	-	-	-	1.01	-	-	-	-	-	-	-
Total	100	100	74.2	79.36	100	100	100	98.63	98.4	100	99.2	99.6	-	-

## 6. Biodiesel Production Technologies

The direct usage of vegetable oil from diesel engines is impossible due to the viscosity of the oil, free fatty acid content, gum formation, and polymerization of the oil while storing it for further processing and also during combustion. The major problems that restrict the use of oil directly in the engine are carbon deposits and oil thickening [161]. To overcome these critical problems, the conversion of the oil into biodiesel is necessary. There are technologies available that can convert these oils into biodiesel, including micro-emulsification, dilution, transesterification, and pyrolysis. Among these methods, the most widely reported method is the transesterification process [162]. Fatty acids are converted into esters and glycerol as a by-product in the transesterification process. A large amount of methanol is required for the conversion of oil into methyl esters. Methanol is preferred over ethanol due to its low cost [163]. Acid or alkali catalysts can be utilized for the transesterification process, which are mostly chosen based on the free fatty acid content. Enzyme application in biodiesel production was also reported by previous researchers [164]. Numerous process variables are involved in biodiesel production, including the temperature, catalyst, molar ratio of oil to methanol, and agitation speed [165]. A few biodiesel production operating conditions are shown in Table 3.

Table 3. Biodiesel production through various methodologies.

Source	Catalyst Concentration (wt%)	Methanol to Oil Reaction (Ratio)	Reaction Temperature (°C)	Time (min)	Maximum Yield (%)	Ref.
<i>J. curcas</i>	KOH—2.09	7.5:1	60	60	80.5	[166]
<i>M. indica</i>	KOH—0.7	6:1	60	30	98	[167]
<i>P. pinnata</i>	H <sub>2</sub> SO <sub>4</sub> —1 mL	6:1	54.5–55.5	60	98.6	[168]
<i>A. indica</i>	Cu-ZnO 10%	10:1	55	60	97.18	[169]
<i>H. brasiliensis</i>	KOH 1%	6:1	55	67.5	96.8	[64]
<i>S. sebifeum</i>	Lipase 5%	5:1	40	125	55.22	[60]
<i>S. mukorossi</i>	H <sub>2</sub> SO <sub>4</sub> 1% and KOH 1%	6:1 and 8:1	60	30	92.5	[59]
<i>P. armeniaca</i> L.	KOH—0.5%	6:1	55	60	95.8	[77]
<i>C. inophyllum</i> L.	H <sub>2</sub> SO <sub>4</sub> 0.5 mL	8:1	45–65	30–150	89	[50]
<i>P. sibirica</i>	KOH-1	5.5:1	60	60	88.7	[94]
<i>C. sinensis</i>	NaOH—0.25	6:1	60	60	97.5	[170]
<i>E. guineensis</i>	NaOH	6:1	65	180	87	[171]
<i>S. foetida</i>	KOH 1.5	12:1	55	60	90.2	[95]
<i>T. peruviana</i>	KOH 1	6:1	55	35	97.5	[172]

### 6.1. Homogenous Catalyst

Most catalysts are used in liquid form for both alkali- and acid-based transesterification processes. The reaction between alcohol and fatty acids is known as transesterification and also called alcoholysis. Triglycerides are converted into biodiesel via three steps. In the initial step, the formation of tetrahedral occurs, followed by the conversion of intermediate tetrahedral into diglycerides, and the last step is catalyst recovery through proton transfer [173]. These steps are repeated for each fatty acid molecule to form biodiesel and glycerol [174]. Homogenous catalysts are usually employed in industry, but researchers are still focusing on the usage of heterogenous catalysts to maximize the yield.

### 6.2. Alkali-Catalyzed Transesterification

The most common method used in laboratories at the pilot-scale level and also on a commercial scale is the utilization of alkali catalysts in biodiesel production [175,176]. The catalysts employed for fuel production include sodium hydroxide, potassium hydroxide, alkaline metal hydroxides, potassium carbonate, sodium carbonate, and alkoxides [177]. High yields in less time and also the low cost of the catalyst characterize this method of biodiesel production [161,177]. The use of alkali catalysts is favored when the feedstock has low free fatty acid content in the oil, preferably less than 3% [178]. However, it has a few disadvantages: it is energy-intensive, the recovery of glycerol is challenging, the separation of the catalyst from biodiesel is difficult, and wastewater is generated during separation [176,179]. Potassium hydroxide has been used as a catalyst for biodiesel production from stone fruit kernel oil and palm kernel oil, yielding around 95.8 and 96% [77,94]. The average transesterification yield was 95.8% when utilizing 100 g PKO, 20.0% ethanol (wt% PKO), 1.0% NaOH, a 60 °C reaction temperature, and 90 min of reaction time [172]. The optimum methanol-to-oil molar ratio of 7.5:1, a catalyst-to-oil ratio of 2.09% *w/w* of oil, and a reaction temperature of 60 °C resulted in the highest yield of 80.5% biodiesel from *Jatropha curcas* [166]. Thus, the usage of low-cost alkali catalysts is favorable for biodiesel production for maximum yields.

### 6.3. Acid Catalysts

Usually, when the feedstock has high free fatty acid content, low quality, and a low price, acid catalysts are used for biodiesel production [161,179]. Pongamia kernel oil and Calophyllum kernel oil are high in FFA content, thus requiring an acid catalyst for transesterification [50,168]. The acid catalysts used for biodiesel production are phosphoric acid, hydrochloric acid, and sulfuric acid. Biodiesel fuel properties are mainly dependent on the feedstock fatty acid composition and the methyl esters formed during transesterification [50]. Biodiesel production through this method usually employs a larger amount of methanol than required. This method is slow compared to the alkali-based catalyst method, and the use of high concentrations of acids is required [163,180]. The water content present in the oil also has a significant impact on the biodiesel yield. The purification of biodiesel is tedious and capital-intensive.

### 6.4. Two-Stage Transesterification

In this technique, both acid-based and alkali-based transesterification are performed, because of the high FFA content of oil and the reaction mechanism, as shown in the literature [178]. If the FFA content is above 3%, a high biodiesel yield cannot be achieved in single-stage transesterification; hence, to optimize the yield, double esterification is employed [181]. Initially, the oil is subjected to acid transesterification, where FFA is converted into FAME [182–184]. After acid transesterification, alkali transesterification is performed to maximize the yield [185–187]. Biodiesel fuels from Karanja, mahua, and a mixture of both Karanja and mahua at a ratio of 50:50 were studied and produced yields of around 98.6, 95.71 and 94% through two-stage transesterification [171]. Mahua biodiesel synthesis was optimized using a central composite rotatable design to identify the optimum concentration of acid usage in the esterification reaction. The acid value was reduced to less than 1% after treating the oil with 1.24% *v/v* H<sub>2</sub>SO<sub>4</sub>, a 0.32 *v/v* methanol-to-oil ratio, and 1.26 h reaction time at 60 °C [167]. Few studies report the usage of two-stage transesterification using alkali catalysts to increase the yield. Double-step transesterification using an alkali catalyst for both times increased the production to 10% [188].

*Sterculia* oil was taken into a three-necked flask and kept above a hot plate magnetic stirrer. The oil was mixed with a methanol-to-oil ratio of 12:1 and 1% anhydrous sulfuric acid was added. The oil was continuously stirred using a magnetic stirrer at 1200 rpm for around 3 h. After three hours, the sample was transferred into a separating funnel to remove the excess methanol, and the lower layer had free fatty acid content, which was washed with distilled water. Then, the oil was dried using anhydrous CaCl<sub>2</sub> for one day.

The oil was filtered using filter paper and again anhydrous  $\text{Na}_2\text{SO}_4$  was used for drying for around three hours. Finally, the sample was filtered using filter paper. The oil obtained from the lower layer of the separating funnel was further transesterified. Then, the oil was poured into the separating funnel for the separation of the biodiesel and glycerol. The biodiesel obtained was washed with distilled water, dried using 100 g of anhydrous  $\text{CaCl}_2$  for one day, and filtered [1].

### 6.5. Heterogeneous Catalysts

The major obstacle in commercializing biodiesel production is the price of feedstocks and the processing costs of feedstocks. The use of heterogeneous catalysts in biodiesel production overcomes the difficulties related to homogenous catalysts. The benefits of heterogeneous catalysts include catalyst recycling, reducing the feedstock level involved in processing, and minimizing the processing costs. They can also be utilized on a commercial scale without any need for further purification steps [189,190]. Heterogeneous catalysts including acidic and basic catalysts are vital in biodiesel production [189,191]. The solid catalysts are categorized based on the temperature as high-temperature and low-temperature catalysts. The generation of wastewater during the production of alkali catalysts is avoided during the use of heterogeneous catalysts. Thus, the requirement of a wastewater treatment unit is eliminated in a biofuel plant that utilizes heterogeneous catalysts. The need for the removal of the spent catalyst from the biodiesel is also avoided by the use of heterogeneous catalysts [178]. The biodiesel purity is also almost 99% and it can decrease the water content in the medium [192]. It is cheap compared to homogenous catalysts [178]. The reaction mechanism of a heterogeneous catalyst is similar to that of a homogenous catalyst, irrespective of the type of catalyst (acid or alkali). Acid transesterification by heterogeneous catalysts will be beneficial when using low-quality feedstocks [179]. This type of catalyst creates fewer environmental problems than the conventional catalysts [192]. Feedstocks that are acidic in nature can be treated with this type of catalyst [190]. A heterogeneous alkali catalyst in biodiesel production is much preferred due to the ease of production and the refining process of the fuel. It reduces the amount of water required for purification and also reduces the cost by downsizing the equipment required for the separation or purification process [193]. A copper-doped zinc oxide nanocatalyst was shown to be an effective catalyst for biodiesel production and to achieve a greater yield. It could also be recycled five times [169].

### 6.6. Solid Acid Catalysts

Solid acid catalysts are an eco-friendly alternative to liquid acids. The use of a solid acid catalyst allows the product to be separated solely by filtration [194]. The primary characteristics of solid acid catalysts can be modified in an economical and environmentally friendly manner to reduce the overall cost of fuel products on an industrial scale [195]. Researchers have used metal oxides as a support for the development of solid acid catalysts [196]. The majority of these oxides, such as zinc oxides, zirconium oxides, iron oxides, tungsten oxides, tin oxides, and titanium oxides, are of transition metal group origin and are of interest to industry and research groups. Sulfonated zirconia, tungstened zirconia, and  $\text{CaO}$  zirconia are promising solid acid catalysts for the conversion of triglycerides to fatty acid alkyl esters [197]. A cobalt-doped zinc oxide nanocatalyst was used for biodiesel production from *Mesua ferrea* oil, which achieved maximum biodiesel conversion of 98.03% after 3 h at 333.15 K with 2.5 wt% catalyst loading and a 1:9 oil-to-methanol molar ratio under optimal reaction conditions [198].  $\text{TiO}_2$ - $\text{Cu}_2\text{O}$  nanoparticles were effective for biodiesel production, with a 60% conversion rate of triglycerides from thumba oil [199].

### 6.7. Natural Heterogeneous Catalysts

The application of biomass to produce heterogeneous catalysts is possible and it can be also utilized for biodiesel production [200,201]. The production of catalysts from natural sources will have an impact on the cost of the process and at the same time will

be eco-friendly. Catalyst recycling is also possible after the separation of biodiesel and glycerol [202]. Solid catalyst production is complicated and requires trained personnel and also a time-consuming process [201]. Calcium-based natural sources are also used in biodiesel synthesis, including eggshell, dolomite, limestone, calcite, hydroxyapatite, and cuttlebone [203]. Researchers studied the effect of eggshell and dolomite, which yielded biodiesel at around 95 and 98% [201,203]. During calcination, calcium oxide is formed, which acts as a catalyst [202].

#### 6.8. Enzyme-Based Transesterification

Enzyme-based catalysts alleviate the problems caused by the usage of conventional acid or alkali catalysts, which are wastewater generation, catalyst removal, energy-intensive processes, and feedstock pre-treatment. Lipase is an enzyme used for the transesterification process, produced by various microbes, plants, and animals [204,205]. Enzymes are quite high in price, but this can be addressed by immobilizing the enzyme. The utilization of enzymes can increase the efficiency of the process, thereby increasing the yield of biodiesel [206,207]. Glycerol separation from biodiesel was found to be superior to the alkaline process [161]. The major advantage of utilizing enzymes as catalysts is that the feedstock has high FFA content and also can be used without any pre-treatment [204,208]. The temperature required for transesterification is 30–40 °C. Methyl ester reduction is visualized in alkaline catalysts for high FFA oils [161,205]. In enzyme transesterification, triglycerides are transformed to partial glycerides and partial glycerides to FFA, which is further converted into methyl esters while reacting with methanol [209]. Thus it favors the production of methyl esters from oil with high FFA content. Methanol and ethanol usage in enzyme transesterification hinder the production process because of the inhibitory effect on enzymes [210]. This inhibitory effect is created by the alcohol in the lipase, and this can be overcome by the batch-wise addition of alcohol [211]. The usage of solvents and alcohol has an impact on the enzyme activity [212]. The use of enzyme catalysts in production for biofuel plants is hampered by the high production costs and long processing times [161,213]. The transesterification of oil through enzymes and its maximum production rate depend on the process parameters and catalytic activity. Lipase extract powder obtained from *Leonotis nepetifolia* seed was used for enzyme-catalyzed biodiesel production using *Leonotis nepetifolia* oil, commercial olive oil, and waste cooking oil as substrates, and the yields were around 70 to 75% [214].

#### 6.9. Transesterification Using Ultrasound

The usage of ultrasound for transesterification increases the mixing of reactants and maximizes the yield [115]. It increases the mixing of the alcohol and oil phases and also increases the reaction rate [215]. There is less energy usage than mechanical stirring in conventional systems [216]. Higher conversion rates are achieved as the ultrasonic power is increased. Furthermore, raising the ultrasonic frequency from 1 MHz to 3 MHz results in higher conversion rates (48.7 to 79.5%) for the same reaction time [217]. A few studies revealed that the combination of ultrasound and microwave irradiation was efficient and the yield of methyl esters from rice bran oil was around 97.74% [218].

#### 6.10. Microwave Transesterification

Microwave transesterification is another technique used for biodiesel production. The microwave-assisted method has many advantages, including high yields, reduced time, and an eco-friendly method [219,220]. The microwave method increases the collision of molecules of reactant molecules [219,221,222]. The heat increases in the feedstock, which creates uniform heat transfer. The disadvantage of the microwave method is the safety issues on a commercial scale [221,223]. Biodiesel production from *Camellia* using microwave energy was investigated. The parameters, namely the reaction time, catalyst load, and molar ratio of methanol to oil, were investigated to maximize the yield using an RSM-BBD design. The highest biodiesel yield of 95.31% (desirability of 95%) was obtained

at the reaction time of 5.85 min, a catalyst concentration of 1.26 wt%, and a molar ratio of 6.91 [224].

#### 6.11. Direct Transesterification

Direct transesterification eliminates the need for the processing of seeds and thus avoids the pre-treatment of seeds and other related processing steps. The direct conversion of fatty acids to esters is achieved through this technique [225]. Oil extraction and transesterification reactions progress in a single step in the presence of alcohols, catalysts, and co-solvents [226–228]. The cell wall breakage of oil-bearing seeds is the major challenge in direct transesterification, which inhibits solvent diffusion; thereby, optimizing the process parameters is essential to achieve maximum yield [229]. The process can be enhanced by the utilization of ultrasound- and microwave-assisted direct transesterification [230,231]. The usage of sulfuric acid in direct transesterification to degrade the cell wall and increase the yield was studied [232]. *Jatropha* was subjected to direct transesterification, with a 95% yield at 60 °C for 30 min in the presence of alkali catalyst NaOH 0.15 N [233]. Sulfuric acid was used as a catalyst at 0.87 M at a reaction time of 240 min at 56 °C, with a yield of 93% of biodiesel from rubber seeds [234]. Therefore, the usage of reactive transesterification yields more biodiesel and also eliminates the preliminary step of seed processing.

### 7. Properties and Characteristics of Non-Edible Biodiesel

Numerous non-edible feedstock properties have been analyzed for the development of biofuel [7]. The determination of the properties of various feedstocks has become demanding due to the increased usage of alternative fuels. The physical and chemical properties of various feedstocks of kernel oil are shown in Table 4.

#### 7.1. Kinematic Viscosity and Density

The viscosity and density of biodiesel are the foremost fuel properties in ensuring the quality of biodiesel [235]. Kinematic viscosity is defined as the resistance of a liquid to flow. This value is an indication of the thickness of the oil. This has been evaluated by considering the total time taken for a specified amount of fuel to flow through the orifice at a specified size [128]. It has a major impact on the working of the fuel injection system, especially at lower temperatures, when the fuel has higher viscosity [236]. Soot formation engine deposits were the main problem found with a higher-viscosity fuel. The kinematic viscosity of *Sterculia* oil was found to be 4.92 mm<sup>2</sup>/s [72], 6.0 mm<sup>2</sup>/s [160], 3.96 mm<sup>2</sup>/s [1], and 4.72 mm<sup>2</sup>/s [237]. The values are within the limit specified in the ASTM D445 standard. The viscosity of stone fruit kernel oil was found to be 34.82 mm<sup>2</sup>/s, whereas that of the biodiesel was 4.26 mm<sup>2</sup>/s. Thus, the biodiesel produced met the ASTM and EN standards. The density must be tested at a temperature of 15 °C [128]. The density of the fuel directly affects its properties, such as the cetane number, viscosity, and heating value [238]. The density also has a direct impact on the engine output. The combustion quality of fuel is greatly influenced by the biofuel density. Most of the biodiesels produced from kernel oils are within the range of the ASTM standards' limit for density, which is within 860–900 kg/m<sup>3</sup> [52].

#### 7.2. Flash Point

The flash point is one of the key parameters that determines the safety of a fuel. The flash point of a biofuel is determined by exposing the fuel to heat. The fuel ignites at a specific temperature and creates a spark, known as the flash point. Usually, biodiesel has a high flash point compared to diesel. The flash point of biodiesel usually lies above 150 °C, while diesel has a range of 55–66 °C. The flash point of *Pongamia* is 180 °C, which is higher than that of kernel oils [239], followed by tea seed oil at 165 °C [240], and palm kernel oil has the lowest flash point at 100 °C.

### 7.3. Cloud and Pour Point

The cloud and pour points are important fuel properties that ensure their usage in low-temperature regions. Biodiesel usually forms wax-like crystals when the fuel is cooled. The pour point is the temperature at which the fuel forms a gel. Usually, the cloud and pour points are higher in biodiesel than diesel. The cloud and pour points are mainly dependent on the fatty acid composition and also vary depending on the type of feedstock. The pour point of biodiesel produced from tea seed oil is one of the lowest ever reported for a biodiesel fuel at  $-5\text{ }^{\circ}\text{C}$  [170].

### 7.4. Cetane Number

The cetane number is a significant parameter that measures the ignition quality of a fuel [241]. The cetane number also provides data on the ignition delay of the fuel. The higher the cetane number, the lower the ignition delay. A low cetane number leads to incomplete combustion and raises the particulate exhaust emissions. The cetane number of biodiesel is higher than that of diesel fuel [163]. *Pongamia pinnata* has a high cetane number of 58 compared to other kernel oils [239].

### 7.5. Acid Number

The acid number of a feedstock is measured by the extent of carboxylic acid present in the fatty acids [241]. The acid value is also a measure of the mg KOH necessary to counteract the free fatty acids [242]. A high acid value can cause more corrosion in the fuel system [77]. Siberian apricot (0.25), stone fruit kernel (0.25), and *Sterculia* biodiesel (0.14) have the lowest acid numbers compared to other kernel oils [73,77,159].

### 7.6. Calorific Value

Calorific value is an essential parameter for the selection of feedstocks. The calorific value of biodiesel is usually lower than that of diesel due to the oxygen content of biodiesel [243]. Table 5 shows that the calorific value of *Jatropha* is higher (41.17 MJ/Kg) and *Pongamia* has the lowest calorific value (35.56 MJ/Kg) [239,244].

### 7.7. Iodine Number

The iodine number is an indicator of double bonds, which influence the unsaturation degree of biodiesel. This property has an influence on the oxidation stability, and it is related to other fuel properties such as the viscosity, cold flow, and cetane number. Rubber seed biodiesel has a high iodine number of 144, and mahua seed has a lower iodine number of 74.2 [158,245].

Table 4. Physicochemical properties of various kernel oils.

Property	Unit	<i>J. curcas</i> [162]	<i>M. indica</i> [57]	<i>P. pinnata</i> [147]	<i>A. indica</i> [56]	<i>H. brasiliensis</i> [7]	<i>S. sebifeum</i> [8]	<i>S. mukorossi</i> oil [3]	<i>P. armeniaca</i> [1]	<i>C. inophyllum</i> [4]	<i>P. sibirica</i> [6]	<i>C. sinensis</i> [2]	<i>E. guineensis</i> [5]	<i>S. foetida</i> [9]	<i>T. peruviana</i> [86]
Density at 15 °C	(kg/m <sup>3</sup> )	918	920	931	912	0.920	-	-	-	943	879.7	907	874	955	890
Kinematic viscosity at 40 °C	mm <sup>2</sup> s <sup>-1</sup>	37	24.58	46	20.5	38.10	46.92	-	34.82	26.642	4.34	27	4.03	42	36
Free fatty acids (%)	%	-	-	-	-	23.47	-	-	-	-	-	2.7	-	3.10	-
Saponification number	mg KOH g <sup>-1</sup>	-	-	-	-	-	206.35	191.83	173	204.3	-	195.2	-	-	-
Iodine value	$\frac{g\ I}{100\ g^{-1}}$	82	71	-	-	-	137.52	113.15	103	77	-	106.8	59	-	-
Acid value	mg KOH g <sup>-1</sup>	-	-	30	-	42.2	-	4.12	1.65	40.4	-	0.206	0.2	6.171	-
Calorific value	$\frac{MJ}{kg^{-1}}$	37.5	36	39.122	32	39.72	-	-	38.69	37.81	-	37.14	41.3	36.446	39.8
Flash point	°C	238	232	226	214	-	-	-	-	238	175	-	119	-	190
Pour point	°C	4	10	-2	10	-	-	-	-	6	-	-8	-6	-3	-
Cloud point	°C	9	15	1	19	-	-	-	-	9	-	-	2	1	-
Cetane number	-	39	57	-	31	49.73	-	-	-	-	49.2	43.8	57.8	-	-
Oxidation stability	hour	-	-	-	12.4	-	-	-	-	-	2.7	-	-	-	6

**Table 5.** Physicochemical properties of kernel biodiesel.

Property	Unit	<i>J. curcas</i> [6]	<i>M. indica</i> [5]	<i>P. pinnata</i> [7]	<i>A. indica</i> [62]	<i>H. brasiliensis</i> [4]	<i>S. sebifeum</i> [8]	<i>S. mukororsi</i> [67]	<i>P. armeniaca</i> [1]	<i>C. inophyllum</i> [53]	<i>P. sibirica</i> [2]	<i>C. sinensis</i> [10]	<i>E. guineensis</i> [3]	<i>S. foetida</i> [9]	<i>T. peruviana</i> [91]
Density at 15 °C	(kg/m <sup>3</sup> )	880	916	890	820	860	900	876	-	868.6	878.2	884		875	875
Kinematic viscosity at 40 °C	mm <sup>2</sup> s <sup>-1</sup>	4.4	3.98	4.85	3.2	5.81	4.81	4.63	4.26	4.7	4.341	4.95	3.36	6	4.33
Iodine value	%		74.2	89		144			104.70		-		-	98	69.9
Acid value	mg KOH g <sup>-1</sup>	0.48		0.42		0.9	0.7	0.14	0.25		0.25		-	0.14	0.057
Calorific value	MJ kg <sup>-1</sup>	41.17	39.4	35.56	39.6			40.02	39.04	39.38	-	37.5	-		42.279
Flash point	°C	163	129	180	120	130	137	140	105	141.5	173	165	100	162	75
Pour point	°C		6		2	-8	0	-4	-8	8		-5	-3		+3
Cloud point	°C	4	5		9	4		-1	-4	10	-		3	-13	+12
Cetane number	-	57.1	51	58	48	36.5	50	56	50.45		48.8	51.1	-	54	61.5
Oxidation stability	h	6		6	7.1		0.6	1.20	7.15	6.01	2.7		-		

## 8. LCA of Biodiesel Production

Biodiesel produced from non-edible oil sources is considered environmentally friendly since the carbon emissions during combustion are absorbed by crops. Apart from these advantages, numerous benefits of biodiesel synthesis are reported compared to fossil fuels. However, the large plantation of energy crops may lead to deforestation and thus eradicate the available natural carbon sink. The GHG emissions are high due to the cultivation and fertilization of non-edible plants, energy spent on oil extraction and biodiesel synthesis, and use of chemicals in oil extraction and biodiesel synthesis. Thus, a life cycle impact assessment (LCA) for biodiesel using various feedstocks has to be performed to understand the complete impact of biodiesel synthesis. The LCA of biodiesel production from substandard resources such as sewage sludge and used vegetable oil was investigated. The biodiesel synthesis from sewage sludge and vegetable oil decreased greenhouse gas (GHG) emissions by 79.7 and 24.5%, respectively, compared to sulfur diesel [246]. *Sapindus mukorossi* plantations showed a higher impact due to the fertilizers used and contributed the most to the global warming potential, primary energy demand, acidification potential, eutrophication ozone depletion, and abiotic depletion potential. Thus, the cultivation of these plants needs to be improved from an environmental perspective [247]. Biodiesel from rubber seed oil showed lower carbon mitigation potential than fossil fuel-based diesel and conformed with global sustainability standards [248]. Compared to rapeseed biodiesel, palm biodiesel has a higher energy ratio; thus, palm oil would be a more sustainable feedstock for the manufacturing of biodiesel. A GHG assessment of palm and rapeseed biodiesel showed no adverse effects on the environment because the amount of CO<sub>2</sub> released into the atmosphere was significantly lower than the amount of CO<sub>2</sub> absorbed. However, this study emphasizes the utilization of existing plantations rather than deforestation to promote biodiesel and valuable by-product synthesis from the seed cake, to enhance the economy of the process. The usage of scrubland to grow energy crops is strongly recommended for higher CO<sub>2</sub> assimilation [248]. The agricultural and industrial tasks of biodiesel production are shown in Figure 5.

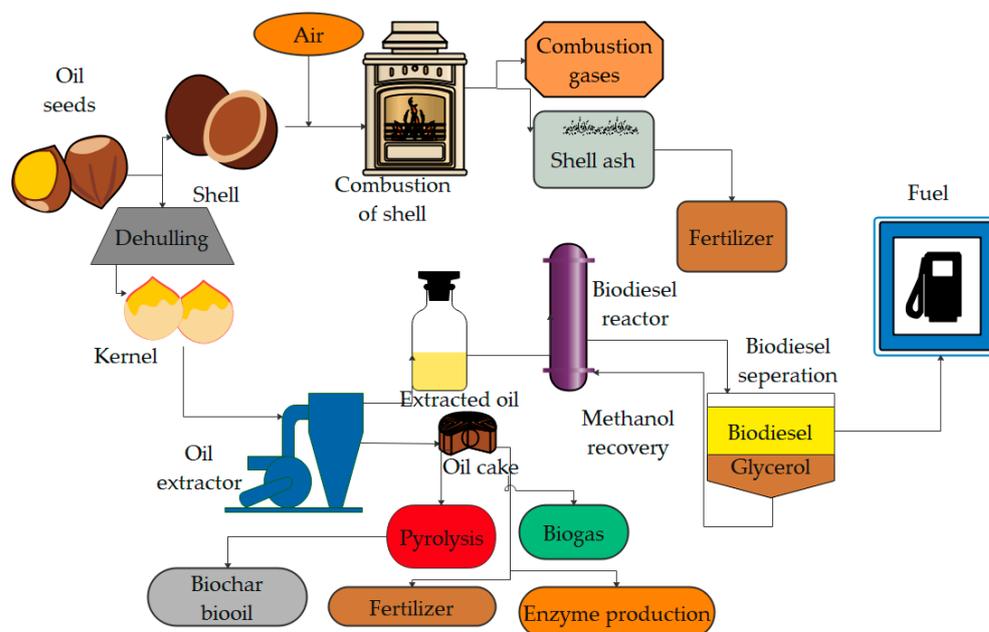


Figure 5. An outline of by-products and fuel generation from oil seeds.

## 9. Sustainable Biodiesel Production

Successful biofuel production in terms of sustainability can be achieved by the following methods:

- (1) Utilization of either green catalysts, biochar, or activated catalysts;
- (2) Application of enzyme catalysts produced from the oil cake of the feedstock;
- (3) Use of waste cooking oil as a feedstock for biodiesel synthesis;
- (4) Implementation of circular economy in biodiesel production.

The use of enzyme catalysts in biofuel synthesis is not suitable on a commercial scale due to its high costs. Hence, the application of bio-based enzymes obtained from biomass is an alternative for the transesterification process. These green catalysts are highly efficient, eco-friendly, and non-corrosive and reduce water usage in biodiesel production [249]. These catalysts are found in abundance and are low-cost materials that are easily biodegradable in the environment [250,251]. A few studies have utilized char from hardwood, peanut hulls, pine log residues, and wood chips for biodiesel synthesis. Biochar was subjected to sulfonation and obtained a yield of 92% biodiesel. The catalyst showed a larger surface area and higher porosity of the catalyst, which increased the performance of the catalyst [252,253]. This catalyst can be reused for biodiesel production. Higher biodiesel production of 87.57% was achieved using a sulfonated rice husk catalyst, compared to amberlyst-15, which yielded 45.17% [254]. Activated carbon from peanut hulls showed efficiency of 90% in biodiesel conversion, but these catalysts lost their catalytic activity after the fourth cycle [253]. The utilization of sulfonated corn straw activated carbon was shown to achieve a 98% FAME yield [255]. Usually, most of the non-edible feedstocks used in biodiesel production have higher free fatty acid content and thus require a larger amount of alcohol (esterification and transesterification), and they also need acid and alkali catalysts for synthesis. The application of green catalysts minimizes the impacts created by the usage of acid and alkali catalysts. It also minimizes the alcohol quantity required for the transesterification reaction. Thus, it can reduce the effect created by the use of alcohol and chemical catalysts in biodiesel synthesis.

Oil cakes are the most often used substrates among the agricultural wastes used to produce lipase. Oil cakes (oil meals) are leftovers from the extraction of oil from seeds. They have been described as ideal substrates for the synthesis of microbial enzymes because they still contain nutrients that can act as carbon and nitrogen sources [256]. One of the earliest reports of lipase production using oil cakes dates back to the 1950s. Their residual oil content is a lipase production inducer [257]. In addition, there have been reports of several agricultural leftovers used to produce lipase, including brans, oil cakes, and bagasse. Solid-state fermentation offers a practical substitute for the manufacturing of industrial enzymes at reduced prices, with the benefit of using agro-industrial leftovers as fermentation substrates, many of which are viewed as inexpensive because they represent processing waste products [258]. In developing nations, enormous amounts of agricultural waste are produced, and their disposal is a significant environmental concern. Utilizing these residues as a source of nutrients for enzyme manufacturing will also lower the overall production costs [258]. Wheat bran, soybean cake, rice husk, gingelly oil cake, olive oil cake, sugar cane bagasse, babassu oil cake, and shea nut cake were among the agro-industrial leftovers investigated [259]. Thus, utilizing the oil cake in lipase production may have a great impact on the biofuel industry and food industry because of the mass production of the lipase from various agricultural resources. This not only generates a valuable compound from waste material but also addresses the environmental management and safe disposal of oil cakes.

Waste cooking oil utilization in biodiesel production is beneficial to the environment because it recycles waste cooking oil and produces renewable energy with less pollution. It can substitute some petrochemical oil imports while simultaneously lowering the waste management costs. Biodiesel synthesis from waste cooking oil offers three benefits: economic, environmental, and waste management [254,260]. Because of its cheaper cost, WCO is more likely than other raw materials to play a role in future biodiesel production [261]. Recycling low-cost feedstocks into high-value products, on the other hand, is a critical pillar in the development of a sustainable circular economy, which is an emerging economic paradigm [262]. As a result, converting WCO to bioenergy and biofuel might simulta-

neously improve energy security, reduce waste and pollution, protect food safety, and promote a circular economy and sustainable development [263].

The application of a circular economy in the biodiesel production process will increase the likelihood of successful biofuel applications. The production of valuable compounds such as enzymes and biochar not only creates new products; it also creates new job opportunities. The cost of biodiesel can be reduced by the application of the circular economy. Thus, it could generate more positive impacts, such as reduced pollution, better resource management, energy synthesis, and new product synthesis, as shown in Figure 5. The circular economy (CE), with a special emphasis on sustainable waste management strategies, aims to slow, narrow, and shut down supply chain loops by converting materials and waste back into resources, so as to create a sustainable and zero-waste environment [264].

## 10. Conclusions

The current work emphasizes the need to process oil seeds to increase the yields of oil. We demonstrate that few studies have reported on the processing of seeds for oil extraction. Using resource- and energy-efficient techniques for oil extraction and biodiesel synthesis will help to make the process more economical. Further, research on defatted biomass after oil extraction is required for waste minimization and the generation of revenue. Glycerol synthesis from the biodiesel production process also needs to be studied for use in various applications; for example, it can be used as a carbon source for the production of valuable compounds. We also recommend that future studies perform a complete LCA, incorporating both agricultural and industrial processes, which will give a clear picture of the sustainability of biofuel utilization.

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