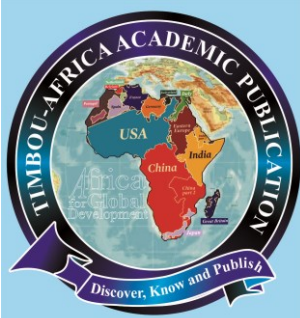




ABSTRACT

Biodiesel, derived from renewable sources such as non-edible oils, offers a sustainable alternative to fossil fuels amid growing concerns over energy security, greenhouse gas emissions, and resource depletion. This review focuses on rubber seed oil (RSO) from *Hevea brasiliensis* as a promising feedstock, given its abundance as a by-product of rubber plantations and high oil content (40 to 50% by weight). Key aspects covered include RSO characterization, biodiesel production

RECENT ADVANCES IN BIODIESEL PRODUCTION FROM RUBBER SEED OIL: FEEDSTOCK CHARACTERIZATION, PRODUCTION PROCESSES, ENGINE PERFORMANCE, AND ENVIRONMENTAL IMPACTS

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Introduction

Global concerns about fossil fuel depletion, greenhouse gas emissions, and energy security have driven growing interest in biodiesel as a renewable substitute fuel. Other available alternative fuels prompt the demand for higher use of these substitutes for conventional fuels. Continuous usage of coal and petroleum-based fossil fuels has negatively affected the ozone layer, while price volatility and other adverse effects limit their demand in industrial and environmental applications. Alternative energy sources, including wind, solar, hydro, and biofuels, offer sustainable and renewable options with lower environmental impact (Dwivedi et al., 2013). Vegetable oils and animal fats converted into fatty acid methyl esters (FAME) represent major routes for biodiesel production. However, the use of edible oils competes with food supplies. Hence, nonedible, underutilized oils are of interest. Rubber seed oil (RSO) from *Hevea brasiliensis* offers an attractive option due to large rubber plantation



methods, physicochemical properties, engine performance, and environmental implications. Challenges such as high free fatty acid (FFA) content necessitating pretreatment, oxidation stability issues due to unsaturation, and feedstock logistics are discussed. Engine tests reveal comparable performance to diesel, with reduced CO, HC, and particulate emissions. The review highlights the potential of low cost heterogeneous catalysts from wastes for efficient production. Future directions emphasize catalyst innovation, blending strategies, and life cycle assessments to enhance viability. Overall, RSO biodiesel promotes energy diversification, reduces environmental impacts, and supports circular economies in rubber-producing regions, though scaling requires addressing economic and technical hurdles.

Keywords: Biodiesel, Sustainable, Emissions, Renewable, Innovation.

areas, high seed kernel oil content (relative to kernel mass), and the fact that seeds are largely a byproduct of latex and wood production. Rubber seeds have potential as a material for manufacturing biofuels that can substitute traditional fuels (Kazeem et al., 2023).

Homogeneous base catalysts such as NaOH, KOH, and sodium or potassium methoxides are commonly used for esterification and transesterification of oils low in free fatty acids. However, associated issues including difficulty in separating the product from the catalyst, high initial catalyst costs, soap formation, low grade glycerol byproducts, reactor corrosion, and the need for large amounts of washing water have prompted research into ecofriendly heterogeneous catalysts for biodiesel production from non-edible oils rich in free fatty acids (Roschat et al., 2012). This paper critically reviews recent advances in the production and utilization of biodiesel derived from rubber seed oil, focusing on feedstock characterization, production methods, physicochemical properties, engine performance, and associated environmental impacts.

Biodiesel feedstock

The rubber tree, with the botanical name *Hevea brasiliensis*, originates from South America, specifically Brazil and genus *Hevea* includes ten species: *Hevea camargoana*, *Hevea benthamiana*, *Hevea brasiliensis*, *Hevea guianensis*, *Hevea rigidifolia*, *Hevea microphylla*, *Hevea nitida*, *Hevea pauciflora*, *Hevea camargoana*, and *Hevea spruceana*. All *Hevea* species contain rubber latex, and 99% of natural rubber is produced by *Hevea brasiliensis* (Aravind et al., 2015).



Figure 1: Rubber tree (Britannica, 2023)

Biodiesel production relies on lipids and short chain alcohols as essential feedstock. Feedstock costs, ranging from 60% to 95% of total production expenses, significantly impact biodiesel affordability (Morshed *et al.*, 2011). Concerns over the food to fuel debate have spurred investigations into alternative sources, such as nonedible and waste oils, for sustainable biodiesel production (Onoji *et al.*, 2016a).

To prevent food crises, nonedible oil bearing plants like the rubber tree, *Jatropha curcas*, and *Pongamia pinnata* have been identified as viable sources for biodiesel. The rubber tree stands out due to its high seed oil yield (35 to 60%) and ability to produce natural latex for various rubber products (Atabani *et al.*, 2013). Given its extensive applications in biofuels and automotive industries, rubber is considered the bioenergy crop of the 21st century.

Biodiesel and its origins

Biodiesel possesses excellent features such as renewability, biodegradability, and low emission properties, along with good lubricity. Triglycerides are the main constituents of vegetable oils and consist of three fatty acid chains (acyl groups) connected to a



glycerol backbone. Common fatty acid chains in plant derived triglycerides typically contain 10 to 24 carbon atoms (Guo *et al.*, 2010).

The primary distinction among different plant oils lies in the composition of fatty acids connected to the triglyceride molecules. Rudolf Diesel (1858–1913) developed his engine to improve upon the hazardous steam engines of the late 19th century (Marchetti and Errazu, 2008). At the 1900 Paris Universal Exhibition, he demonstrated a new engine running on peanut oil (Marchetti and Errazu, 2008). Later, diesel engines became the preferred powertrain due to their performance, reliability, and low fuel consumption.

Rubber seed and its industrial applications

Recent scientific research has shown that rubber seeds and seed oils can be utilized in producing paint materials, semi drying oils (Eka *et al.*, 2010), ink (Igeleke and Omorusi, 2007), and many other industrial applications (Vipin *et al.*, 2016). Additional uses include fertilizers and animal feed (Iyayi *et al.*, 2008), grease (Aravind *et al.*, 2015), activated carbon (Okieimen *et al.*, 2005a), and liquid soaps and shampoos (Igeleke and Omorusi, 2007), which serve as carriers for copper fungicides in cosmetics (Kittigowittana *et al.*, 2013). Banković-Ilić *et al.* (2012) reported that fresh rubber seeds consist of 40 to 50% kernel, 37% husk, and 20 to 25% shell, including moisture content (Gimbun *et al.*, 2012). Dried kernels contain 40 to 50% oil, while seeds include protein and both essential and nonessential amino acids (Eka *et al.*, 2010). Rubber seeds have cyanogenic glycosides (0.186 g) and 0.638 to 0.749 g HCN/kg in freshly harvested seeds (Iyayi *et al.*, 2008; Eka *et al.*, 2010). Storage at ambient temperature for 60 days can reduce HCN concentration (Iyayi *et al.*, 2008).

Rubber seed processing

Biodiesel production from RSO involves oil extraction, pretreatment, and transesterification. Oil is extracted from seeds, purified to remove impurities and moisture, then transesterified with alcohol (methanol) and a catalyst (NaOH or KOH) to produce biodiesel.

Seeds are assessed for freshness, cleaned with distilled water and dried at ambient temperature for 48 hours (Onoji *et al.*, 2017a). Husks are separated by winnowing. Kernels (about 100 g) are oven dried at 105°C for 5 hours to determine initial moisture. Remaining kernels are conditioned to 15% moisture for optimal oil yields. Conditioned kernels are milled and sieved into sizes to determine the size yielding highest extraction efficiency (Onoji *et al.*, 2017a).

Rubber seed oil extraction

Key parameters influencing extraction include solvent type, kernel particle size, seed/solvent ratio, time, and temperature (Elkhaleefa and Shigidi, 2015). Solvent



selection considers cost, matrix affinity, and toxicity. Five particle sizes (0.5 to 2.5 mm) were evaluated; 50 g of ground kernels were extracted with 225 mL n-hexane at 60°C for 45 minutes using Soxhlet extraction (Onoji *et al.*, 2016b).

Acid catalyzed esterification of seed oil

Reducing FFA to less than 1% prevents soap formation and ensures high yields (Betiku and Ajala, 2014). 100 mL RSO was heated to 105°C to remove moisture, then mixed with 45 mL methanol and 1.5 vol.% H₂SO₄, stirred at 600 rpm and 60°C for 1 hour. The mixture was settled for 2 hours, separated and excess methanol evaporated. Experiments varied H₂SO₄ (3 to 6 vol.%) to achieve less than 1% FFA (90.5% conversion) (Onoji *et al.*, 2017b).

Transesterification of rubber seed oil

Transesterification is a method for generating fatty acid mono alkyl esters (biodiesel) by reacting vegetable or animal oils with alcohols in the presence of a suitable catalyst (acidic, enzymatic, or basic), yielding glycerol as a byproduct (Onoji *et al.*, 2016a). Catalyst choice depends on moisture and FFA content. Common homogeneous base catalysts for RSO transesterification include carbonates, alkoxides of sodium and potassium, NaOH, or KOH (Ahmad *et al.*, 2014a). Homogeneous acid catalysts like HCl and H₃PO₄ are used for pretreatment (Bokhari *et al.*, 2012). Heterogeneous catalysts, such as ion exchange resins and metal oxides, tolerate high FFA and can be reused without significant yield decline (Omorogbe *et al.*, 2013). Gimbun *et al.* (2012) achieved 96.9 wt.% yield using a CaO based catalyst from cement clinker. Krishnakumar *et al.* (2013) reported 98 wt.% yield with solid CaO calcined at 850°C for 1.5 hours.

The best method depends on factors like reactant type, temperature, catalyst type, reaction time, and cost. Low-FFA edible oils typically use homogeneous bases like NaOH or KOH. Crude RSO's high FFA leads to soap formation with base catalysts. A two steps process esterification with acid (H₂SO₄) and excess alcohol to reduce FFA, followed by base catalyzed transesterification, yields high biodiesel and glycerol. However, high costs and post treatment challenges persist. For high FFA oils, heterogeneous catalysts promoting both esterification and transesterification are preferable: selective, efficient at low temperatures, cost effective, and derivable from wastes (Di Serio *et al.*, 2008).

Factors influencing transesterification of rubber seed oil

Free Fatty Acid (FFA) in RSO ranges from 23.471% to 45% (Omorogbe *et al.*, 2013). Reducing FFA in crude RSO is crucial to prevent soap formation and ease downstream processes with heterogeneous catalysts (Ibrahim and Pillai, 2011). Acid catalyzed esterification with H₂SO₄ and methanol reduces FFA. Catalyst concentration and methanol ratio are more influential than temperature and time (Ahmad *et al.*, 2014b).



Methanol to Oil Molar Ratio significantly influences yield. Stoichiometrically, transesterification requires three moles of alcohol per mole of triglyceride to yield three fatty acid esters and one glycerol (Ma and Hanna, 1999). Ratios up to 30:1 have been reported for acid catalyzed reactions, 6:1 for base catalyzed (Abdulkadir *et al.*, 2014). With KOH, maximum yields of 75 to 96.8 wt.% occur at 6:1 (Ahmad *et al.*, 2014b). Excess methanol beyond optimal levels causes separation issues.

Catalyst Concentration is the most influential factor (Ahmad *et al.*, 2014b; Widayat and Kiono, 2012). High concentrations darken biodiesel color (Widayat *et al.*, 2013). Dhawane *et al.* (2015) achieved 89.30% FAME yield at 3.50 wt.% with a carbonized eggshell catalyst; higher loadings reduced yields due to soap formation and increased viscosity.

Higher temperatures enhance reaction rates and yields (Gimbun *et al.*, 2012). Dhawane *et al.* (2015) identified 60°C as optimal for methanol-based transesterification. Exceeding methanol's boiling point (65°C) reduces yields due to vaporization (Gimbun *et al.*, 2012). Most studies indicate 60 minutes is sufficient for base catalyzed reactions; longer times may cause catalyst leaching (Dhawane *et al.*, 2015).

Stirring overcomes mass transfer limitations from immiscible reactants. Dhawane *et al.* (2016) found 500 rpm optimal, yielding 94.5%; higher speeds (750 to 1,000 rpm) reduced yields due to catalyst desorption.

Catalysts and catalysis

A catalyst is a substance that modifies the rate of a reaction (positively or negatively) without being significantly changed during the process. Catalysts have been used in various sectors for over 2,000 years and are neither reactants nor products (Levenspiel, 2005). This adhesion occurs through two processes: chemisorption (chemical adhesion) and physisorption (physical adhesion) (Mechrafi, 2002). Physisorption involves weaker bonds between the adsorbate and solid surface, primarily via Van der Waals forces, and can involve multiple irreversible layers (Madani, 2004). It resembles condensation, with low heat release (42 to 63 kJ/mol) (Fogler, 2008). In contrast, chemisorption involves bonding similar to atomic chains (Fogler, 2008). Due to stronger bonds, chemisorption is irreversible and occurs at higher temperatures, releasing heat comparable to chemical reactions.

Catalysis involves the study, application, and utilization of catalysts and processes, aiming to enhance efficiency and accuracy (Fogler, 2008). Catalysts fall into two main categories: (1) synthetic catalysts (homogeneous and heterogeneous) functioning at elevated temperatures, and (2) enzymes functioning near room temperature in biochemical systems. Homogeneous catalysis occurs when the catalyst is dissolved in the same phase as the reactants. Heterogeneous catalysis involves distinct phases; reactants are typically fluids or gases, while the catalyst is solid. Reactions occur at or near the fluid solid interface. A large surface area is crucial for high reaction rates,

facilitated by porous catalysts with large internal areas. For example, a cracking catalyst like aluminosilicate has a pore volume of $0.60\text{cm}^3/\text{g}$, an average pore diameter of 4 nm, and a surface area of $300\text{m}^2/\text{g}$ (Fogler, 2008).

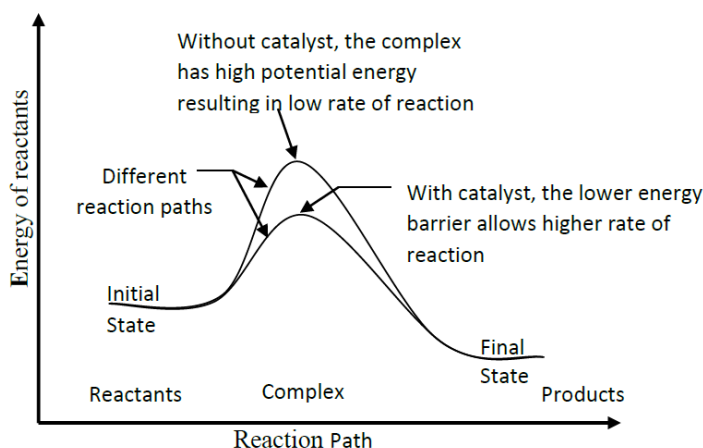


Figure 2: Representation of the action of a catalyst (Levenspiel, 2005)

Biodiesel production methods and blending techniques

Various methods exist for biodiesel production from feed stocks like RSO. The most common is

transesterification, converting triglycerides to biodiesel by reacting with alcohol and a catalyst. Blending biodiesel with petroleum diesel improves compatibility with engines and infrastructure. Blends range from B5 (5% biodiesel, 95% diesel) to B40 (40% biodiesel, 60% diesel) and blend ratios influence fuel properties and engine performance (Omorogbe et al., 2013).

Biodiesel and fuel properties

Fuel properties indicate combustion, ignition, and quality. Post-transesterification, RSO biodiesel shows reduced viscosity, density, and acid value, meeting ASTM D6751 and EN 14214 standards. Flash points around 150°C enhance safety (Hamzah et al., 2019).

Table 1: Physical Properties of Rubber Seeds (Onoji et al., 2016a)

Property	Value
Kernel (%)	40–50
Husk (%)	37
Shell (%)	20–25
Moisture (%)	20–25

Table 2: Comparison of Physico-Chemical Properties and Other Characteristics of Rubber Seed Oil (Onoji et al., 2016a)

Property	RSO Value	Diesel Value
Density (kg/m^3)	910–920	830–860
Viscosity (mm^2/s)	30–40	2–5
Flash Point ($^\circ\text{C}$)	150–170	>55
Calorific Value (MJ/kg)	38–40	42–45



Table 3: Fuel Properties of Biodiesel According to Standards

Property	ASTM D6751 Limit	EN 14214 Limit	RSO Biodiesel Value
Acid Value (mg KOH/g)	≤0.50	≤0.50	0.45
Viscosity (mm ² /s)	1.9–6.0	3.5–5.0	4.2
Flash Point (°C)	≥93	≥101	150

Engine performance and emissions

Studies evaluated RSO biodiesel in engines. Onoji et al. (2020) found higher BSFC for biodiesel/blends than diesel due to lower heating value, but B20 matched diesel at 2750 rpm (0.20 kg/kWh). Reductions in CO, HC, and smoke density occurred, with slight CO₂ increases. BSFC for B100 was 5% higher.

Table 4: Typical Engine Performance and Emission Data

Parameter	Diesel	B20 RSO	B100 RSO
BSFC (kg/kWh)	0.20	0.20	0.23
BTE (%)	32	31	29
CO (g/kWh)	2.5	2.0	1.8
HC (g/kWh)	0.5	0.3	0.2

Environmental and emission considerations

RSO biodiesel reduces greenhouse gas emissions due to its renewable origin and lower carbon intensity. Emissions show reductions in CO, HC, and particulates. Benefits include reduced fossil fuel use and potential carbon neutral lifecycle (Onoji et al., 2020). High unsaturation lowers oxidation stability, requiring antioxidants or blending with saturated oils like palm biodiesel (Zamberi et al., 2018).

Challenges

High FFA in RSO complicates base catalyzed transesterification (soap formation, low yields); pretreatment add cost. High unsaturation causes poor oxidation stability and deposits. Feedstock logistics are challenging despite extensive plantations; collection is seasonal and dispersed. Some methods like supercritical are energy intensive. Long term engine durability, cold flow properties, and storage stability need exploration. Ensuring compliance with standards across blends is essential.

Conclusion

Rubber seed oil emerges as a viable, nonedible feedstock for biodiesel production, addressing key challenges in energy security and environmental sustainability. Its high oil yield, compatibility with existing transesterification processes, and favorable engine performance coupled with reduced emissions of CO, HC, and particulates



position it as a promising alternative to fossil fuels. Heterogeneous catalysts from wastes offer cost effective, ecofriendly solutions, enhancing production efficiency and glycerol quality. However, issues like high FFA content, oxidation instability, and logistical hurdles must be mitigated through innovative pretreatments, blending strategies, and optimized catalysts. The environmental benefits, including lower greenhouse gas emissions and support for circular economies in rubber-producing regions, underscore RSO biodiesel's potential. Future research should prioritize scalable technologies, comprehensive LCAs, and long term engine studies to ensure economic viability and global adoption. By leveraging RSO, we can advance toward a more sustainable energy landscape, reducing reliance on depleting fossil resources while minimizing ecological impacts.

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