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Development of Biodiesel Production Strategies for Blending Purposes in Biorefineries: A Review

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ABSTRACT

The rising demand for diesel fuel amidst declining fossil reserves, volatile oil prices, and stringent emission regulations has driven the expansion of biodiesel production. Biodiesel, primarily produced as fatty acid alkyl esters via catalytic transesterification of triglycerides, offers advantages over fossil diesel, including environmental friendliness, non-toxicity, and enhanced lubricity. However, its limited oxidation stability, energy density, and cold flow properties restrict blending ratios with conventional diesel to prevent engine performance issues. Alternative methods, such as hydrotreated vegetable oils (HVOs), face challenges related to hydrogen dependency and cost. This review explores current biomass-derived diesel production methods and proposes a cost-effective strategy for industrial-scale biodiesel with improved stability, energy content, and cold flow characteristics. This approach aims to enable higher blending ratios with mineral diesel, reducing dependency on finite fossil resources while promoting cleaner, renewable energy use.

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1. Introduction

The increasing demand for diesel, coupled with declining petroleum reserves, fluctuating oil prices, and stricter environmental regulations, has fueled the expansion of the biofuels industry, with biodiesel emerging as the leading commercial alternative to conventional diesel. The popularity of diesel engines over gasoline engines has been fueled by the relatively high volumetric energy density of diesel [1]. Owing to the growing transportation and industrial sectors, the daily global diesel consumption is predicted to rise to about 5.7 million liters by the year 2035 [2]; however, petroleum crude oil scarcity is expected within next fifty years as a result of the depletion of the current estimated oil reserves [2, 3]. Additionally, pursuant to the Paris Climate Deal, most countries around the world adopted stringent environmental regulations and policies toward the suppression of the adverse environmental and health impacts of the direct combustion of fossil fuels.

Lipid-based liquid fuels such as biodiesel and renewable diesel are broadly accepted as clean and renewable fuels [4], that can complement or even replace mineral diesel [5]; commercial success nonetheless, has been enjoyed by biodiesel. Biodiesel, in this context is defined as a mixture of mono-alkyl esters of fatty acids produced from the transesterification of lipids with an alkyl donor, such as an alcohol [6-8]. The physicochemical properties of biodiesel closely resemble those of petroleum diesel, allowing it to be blended with conventional diesel in virtually any proportion or used in its pure form in existing diesel engines without requiring modifications [9-11]. Biodiesel as a renewable alternative to petroleum diesel, could contribute to the mitigation of GHG emissions and thus, improve public health, at the same time decreasing dependence on petroleum products [12-14]. In addition to its renewability, biodiesel has gained wide acceptance because of it has good lubricity, biodegradability and non-toxicity [15-17]. Many countries have introduced policies and regulations of different mandatory blending percentages of biofuel with petroleum-based fuels, with the support of the Renewable Fuel Standard in a quest to limit the GHG emissions [11, 18, 19].

However, biodiesel is not entirely favorable to the diesel engine because of its inferior oxidation stability, cold flow properties, and energy density relative to mineral diesel [20]. This is because of the compositional and structural variations of biodiesel from mineral diesel. As such, the prolonged usage of biodiesel in engines induces excess wear of engine components [21]. Accordingly, the blending fraction of biodiesel with mineral diesel has been limited to 7 vol.% max, in accordance with the EN 590 standard [22-24]; and 20 vol.% biodiesel in accordance with the ASTM D7467 fuel standard specification [25]. This restricts the realization of the benefits of using renewable sources of energy such as, lower environmental pollution and better energy security. The mainstream biomass-derived diesel production strategies are reviewed in this work, leading to the development of a strategy that can be cost-effectively applied for industrial scale production of oxygen-free, saturated biodiesel, with relatively short carbon chains, in order to prevent engine damage, and perhaps realize higher blending ratios. This review also examines the assessment and optimisation of biodiesel production techniques to improve its blending capability in biorefineries. It specifically seeks to discover economical production methods that enhance biodiesel's stability, energy content, and cold flow characteristics, enabling increased blending ratios with conventional diesel.

2. Biodiesel Synthesis Feedstocks

The cost and availability of feedstocks significantly influence biodiesel production across different regions of the world [26]. Feedstock costs alone account for 60% to 88% of the total biodiesel production expenses, making them a critical factor in determining biodiesel's economic viability [27-29]. The availability of feedstocks depends on geographical location and the type of oil resources present [30-32]. Additionally, both the feedstock and the production process play a key role in determining the final properties of biodiesel.

Biodiesel feedstocks include a variety of lipid-containing materials, such as approximately 350 oil-producing crops, animal fats, waste oils, greases, algae, and other microorganisms [33-35]. These feedstocks are categorized into three generations: first-generation feedstocks consist of edible vegetable oils; second-generation feedstocks include non-edible oils, animal fats, and waste oils; while third-generation feedstocks are derived from algae and other microorganisms [36]. The ideal feedstock is one that minimizes processing costs while maximizing lipid yield and quality [37]. Key attributes of interest in biodiesel production are lipid content, fatty acid composition, and the availability of the feedstock [38].

2.1. Food Competition

First-generation feedstocks were initially the most commonly used for biodiesel production [29, 30, 39]. However, the use of edible oils has sparked concerns due to their impact on global food prices and reduced availability, driven by the food-versus-fuel debate [9, 11, 40]. Biodiesel produced from edible oils is also reported to be costly, sometimes exceeding the price of petroleum diesel [16, 17, 41].

To address these issues, the industry has shifted towards second-generation feedstocks, which offer a more cost-effective alternative by reducing reliance on food-grade materials [13, 28, 42]. Waste oils, in particular, have emerged as a sustainable and economical option, capable of lowering feedstock costs by up to 70% [26]. Millo *et al*. highlighted that international biofuel policies have been revised to promote second-generation biofuels. For instance, the European Parliament capped the use of biofuels derived from agricultural feedstocks at 6% of the total 10% target, with the remaining share to be fulfilled by second-generation biofuels [11].

2.2. Land Competition

The sustainability of using first- and second-generation crop-based feedstocks for biofuel production is challenged by their competition with food crops for arable land and freshwater resources [2, 26, 36]. Additionally, the conversion of forests and undeveloped land into feedstock cultivation areas negatively impacts biodiversity [32, 43]. Certain non-edible oil plants, such as jatropha, offer a partial solution as they are drought-tolerant and can grow on arid or marginal lands, reducing competition with food crops [30, 31]. Similarly, utilizing waste-based second-generation feedstocks for biodiesel production provides a sustainable approach to addressing waste management challenges [2, 27, 43]. Microalgae present another promising alternative feedstock, as they can be cultivated on marginal lands or in wastewater, thereby mitigating the land-use conflicts associated with food-based feedstocks and offering a potential solution to the food-versus-fuel debate [30, 44, 45].

2.3. Oil Yield

The lipid content of a feedstock is directly proportional to its biodiesel yield [45] and inversely proportional to its production cost [46]. Therefore, feedstocks with higher lipid content and rapid growth rates, leading to better availability, are more desirable for biodiesel production. Table **1** highlights the yield characteristics of common feedstocks, demonstrating that first- and second-generation feedstocks produce significantly lower oil yields compared to microalgae [9, 47, 48]. As a result, large amounts of these conventional feedstocks are needed to meet the demand for petroleum-based fuels, requiring extensive cultivation areas [43, 47, 49].

In contrast, microalgae can produce 23 to 300 times more oil per acre than traditional plant-based biodiesel feedstocks [18, 34, 43]. This advantage is attributed to their higher photosynthetic efficiency and oil content [18, 43, 50]. Microalgae also exhibit rapid growth, capable of doubling their biomass within less than a day and growing up to 100 times faster than terrestrial energy crops [27, 45, 51]. Thus, in terms of both oil yield and growth rate, microalgae are a more cost-effective and efficient alternative to conventional biodiesel feedstocks [32].

Lipid content, however, varies depending on the specific strain and cultivation conditions of the feedstock [38, 43, 45]. Genetic engineering and environmental modifications, such as altering nutrient levels, light exposure, and water availability, can enhance lipid production [9, 36, 52]. While some genetic engineering approaches have successfully improved biodiesel yields at the laboratory scale, scaling up these methods for commercial production remains a challenge, as it must be done without compromising performance [9, 43].

2.4. Availability

The selection of feedstock for biodiesel production is largely determined by regional climatic conditions [28, 31]. In temperate regions, crops such as rapeseed, sunflower, corn, and other legumes or cereals are commonly utilized, while in tropical areas, palm oil and soybeans are preferred due to their local availability [33, 54, 55]. Recently, alternative feedstocks like microalgae, jatropha, and waste oils have gained attention for their adaptability across diverse geographic conditions [9, 32]. Microalgae are particularly advantageous due to their rapid growth, high productivity, and independence from seasonal variations, unlike traditional agricultural and forestry crops [27, 56]. Jatropha, known for its ability to grow across various altitudes, possesses desirable traits such as drought tolerance, ease of propagation, and fast growth. However, its oil yield can be significantly enhanced with proper irrigation, fertilization, and management practices [14, 27, 48].

Table 1: Oil yields for the common biodiesel feedstocks [2, 18, 27, 28, 43, 53, 80].

Feedstocks	Oil Yield (L/ha Year)	Global Average Water Footprint (m^3/ton oil)	Seed oil Content (%oil by wt Biomass)	Land Use (m^2 Year/kg Biodiesel)	Capacity of Land Needed (mha)	Potential Sources
Calophyllum	4680		65			
Castor	1307-1413	24740	43.5-48	9		Brazil, Iran, Kenya
Coconuts	2689	4490	63-65		99	Indonesia, Philippines, Thailand
Corn	172	2575	44-48	66	1540	
Cotton Seed	325	3957	18-25			Brazil, Greece
Groundnuts	1059	7529	47.8			USA
Hemp	363		33	31		
Jatopha	741-1892	870	28-60	15	140	Australia, China, Cuba, India, Indonesia, Iran, Mali, Pakistan, Peru Thailand, Zimbabwe
Jojoba	1818		45-50			
Linseed	478	9415				Spain
Microalgae.7	136900	-	70	0.1	2	Iran
Microalgae.3	58700	-	30	0.2		
Microalgae.5	97800	-	50	0.1		
Moringa			40			Cuba
Mustard	572	5600				Canada
Olives	1212	14578	45-70			
Palm Oil	5366-5950	5186	30-60	2	45	Brazil, Ghana, Indonesia, Iran, Malaysia, Singapore, Thailand
Rapeseed	974- 1190	4301	38-46	12	223	Canada, China, France, Germany, India, Italy, Sweden, Turkey, UK
Rice Bran	828		15-23			
Safflower	779	16046				
Sesame	696	21793				
Soybean	446-636	4190	15-20	18	594	Argentina, Brazil, Canada, India, USA
Sunflower	952-1070	6792	25-40	11		France, India, Italy, Spain, Turkey

Waste oils, a byproduct of human activities, offer another sustainable feedstock option. Examples include waste oils from machinery, tallow, and used cooking oil [2, 57, 58]. Waste cooking oil is particularly abundant, with global production estimated at around 18.6 million tonnes annually [2, 26, 55]. It is widely sourced from food processing industries, such as potato processing plants, and industrial fryers in fast-food establishments [2, 59].

Additionally, waste cooking oil is approximately 40–70% cheaper than fresh vegetable oils [55], making it a cost-effective and environmentally beneficial feedstock for biodiesel production, contributing to efficient waste management [2, 31, 61].

2.5. Extraction

After harvesting, oilseeds are subjected to drying, decortication, and oil extraction processes [10, 32]. The extraction of lipids can be achieved through mechanical, chemical, or enzymatic methods, or a combination of these techniques. Additionally, methods such as ultrasound-assisted extraction, supercritical fluid extraction, and microwave-assisted extraction are often used as complementary techniques for oil extraction from plant sources [28, 32]. The mechanical press extraction method can be coupled with solvent extraction to yield oil with a higher purity, although this approach is more costly [32]. The solvent extraction process utilizes chemical solvents with high selectivity and solubility for lipids, including hexane, dichloromethane, chloroform, and toluene [32, 43]. However, these chemical solvents pose significant toxicity risks to both humans and the environment [27]. The solvent can be separated from the extracted oil through distillation following the lipid extraction process [32]. Supercritical extraction is another efficient method, but its application on an industrial scale is often not economically feasible [18]. In the supercritical state, the fluid's thermophysical properties change drastically, making it a super-solvent that enhances extraction efficiency. The most commonly used supercritical fluid is CO_2, which offers several advantages over chemical solvents: (a) it allows easy post-extraction separation at ambient conditions; (b) it is non-toxic, providing a non-oxidizing environment that helps prevent oxidation of extracts; and (c) the relatively low critical temperature of CO_2 reduces the risk of thermal degradation of the extracted products [27].

For microalgae, the harvesting process is followed by drying the biomass before lipid extraction can occur [27, 43]. The drying step, which is necessary to remove the approximately 90% water content of the microalgal biomass, is one of the most energy- and time-intensive stages in biodiesel production [7, 62]. Various drying techniques are employed, such as solar drying, lyophilization, oven drying, drum drying, spray drying, and vacuum drying [32]. After drying, the microalgae cells undergo a cell disruption process to facilitate lipid extraction. This step is crucial because the thick cell walls can inhibit the release of intracellular lipids during extraction [27]. Methods like bead beating, pressing, autoclaving, and homogenization are commonly used for cell disruption [27, 43, 63], after which the lipids are separated from other cellular components [43]. For dry microalgal biomass, chemical solvent extraction is typically employed, while supercritical fluid extraction is more suitable for wet-paste biomass [27]. However, the industrial use of microalgae as a biodiesel feedstock remains economically unfeasible due to the high processing costs [18, 62]. As a result, direct conversion of wet microalgae biomass into biodiesel has been suggested as a cost-effective alternative, as it bypasses the energy-intensive drying process [62].

2.6. Lipid Composition

The lipid composition profiles of feedstock oils used in biodiesel production are distinct to their respective sources [64], and these profiles play a significant role in determining the properties of the resulting fuel [9, 28]. The lipid composition is influenced by the source strain of the feedstock and the conditions under which it is cultured [28, 31]. Table **2** below presents the lipid composition profiles of several common biodiesel feedstocks. The physicochemical properties of biodiesel are primarily influenced by the characteristics of the fatty acids, including their degree of saturation, chain length, and the extent of branching [28, 31, 65]. Fatty acids with high saturation typically lead to biodiesel with poor cold flow properties [54], although they provide excellent oxidation stability [65]. The quality of biodiesel can be improved by blending it with other diesel fuels from different sources, which modifies its fatty acid composition [9].

3. Biodiesel Synthesis Strategies

Currently, several methods are available for producing biodiesel from biomass-derived oils, including direct blending, micro-emulsion, pyrolysis, and transesterification [13, 53, 61]. Among these, transesterification is the most effective in producing a fuel with properties similar to petroleum diesel, particularly in terms of viscosity, purity, and volatility [28, 53]. Due to its relatively low cost and high conversion efficiency, transesterification is the most widely adopted and established process for commercial biodiesel production [33, 59, 66]. This process involves the reaction of triglycerides with an alkyl donor, typically a short-chain alcohol, resulting in the formation of biodiesel as fatty acid alkyl esters, with glycerol as a byproduct [19, 57, 67]. Variants of transesterification used in biodiesel production include esterification and interesterification. Esterification involves the reaction of free fatty acids with alcohol, producing water as a byproduct [40, 68, 69], while interesterification refers to the exchange of alkyl groups between different esters [31].

Table 2: Lipid composition profiles of vegetable oils [28, 46, 64, 65].

Fatty Acid	Castor	Coconut	Cotton Seed	Jatropha	Mustard	Neem	Olive	Palm	Polanga	Pongamia	Rapeseed	Soybean	Sunflower	Tallow	UCO
Arachidic	0.3			0.2-0.3	0.7	1.9		0.06-0.11		2.2-4.7		0.3	0.4		0.55-2.3
Behemic										4.2-5.3		0.1			0.65
Erucic					32.81			0							
Gadolic				3.6	10.44			0.33		9.5-12.4					3.6
Gondoic	0.7														
Lauric		46.5		0.1				0.2-0.9					0.5		
Lignoceric						0.3			2.6						0.04
Linoleic	4.2	2.2	55.2	31.9-36.0	11.64	17.9	5.8	9.59-12.2	13.7	10.8-18.3	14.1-32	51.8-53.7	52.34-66.2	2.9	13.5-36.0
Linolenic	0.3	0	0.6	0.2-0.3	8.61	0.4		0.17-0.2	2.1	1.1-3.5	1.8-8.8	6.5-8.6	0.8-8.19	0.9	0.2-0.8
Myristic		19.2	0.7	0.1	0.05	0.2-0.26		0.9-1.14			1	0.1	0.2		0.19-0.9
Oleic	3.0	6.9	19.2	38.6-44.7	24.98	43.9	82.3	39.9-42.6	42.7	44.5-72.2	55.0-77.8	16.5-24.8	20.6-22.52	42.4	18.3-52.9
Palmiric		9.8	20.1					42.8			5.5	0.2			20.4
Palmitic	1.0	9.8		14.1-14.6	2.8	14.9	9.7	37.8-43.79	17.9	3.7-9.8	3.49-4.0	10.4 – 24.8	4.8-10.58	23.3	4.1-26.5
Palmitolei				0.5-0.7	0.16	0.1	0.46	0.15-0.4	2.5			0.1-2.0	0.8	0.1	0.8-2.4
Ricinoleic	89.5														
Stearic	1.0	3	2.6	6.8-7.6	1.09	20.6	1.74	2.7-4.76	18.5	2.4-8.9	0.55-2.3	2.6-4.7	4.76-5.7	19.3	1.6-4.8

3.1. Transesterification

Transesterification, also known as alcoholysis, is a chemical process that converts lipids, such as triglycerides and free fatty acids, into fatty acid alkyl esters (biodiesel) by exchanging the alkyl group with an alcohol source [33, 46, 70]. This process involves a series of three reversible reactions. First, triglycerides are converted to diglycerides, which are subsequently transformed into monoglycerides, and finally into fatty acid esters and glycerol [27, 32]. Each reaction step produces an ester molecule, ultimately yielding three fatty acid alkyl monoester (FAAE) molecules and one glycerol molecule from each triglyceride molecule [35, 42, 65].

Since transesterification is an equilibrium reaction, an excess of the alcohol donor is typically used to shift the equilibrium towards the product side, thereby maximizing biodiesel yield [27, 32]. The general mechanisms of the transesterification process and its variations are shown in the equations below, with a detailed review provided in the subsequent sections.

3.1.1. Process Description

In the transesterification process, oil and alcohol are typically combined in a reaction vessel, forming two immiscible polar phases due to their limited miscibility [32]. This immiscibility hinders the reaction and reduces biodiesel yield [26]. To enhance mass transfer between the oil and alcohol, several techniques can be employed, including the use of catalysts, increasing reaction temperature, agitation of the reaction mixture, or adding a solvent. These methods can be applied individually or in combination to optimize the reaction.

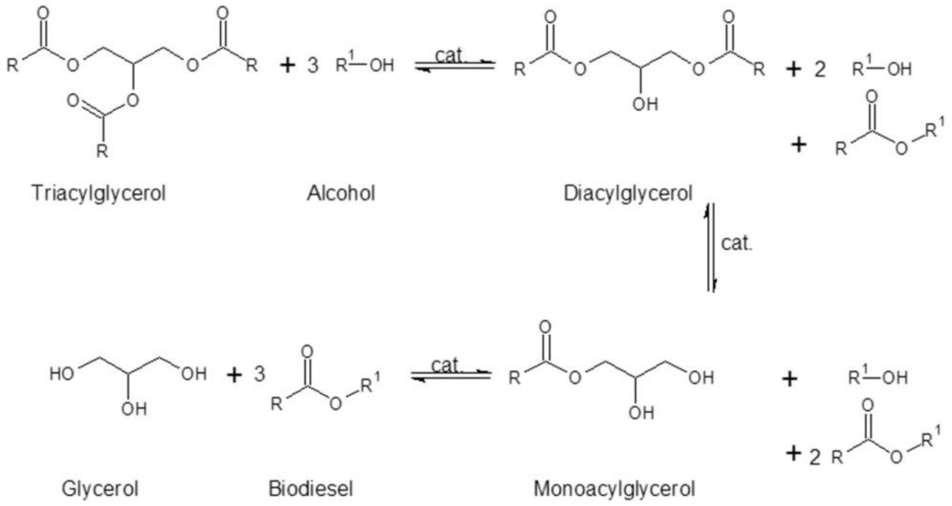

Figure 1: Overall transesterification reactions of triglycerides; where R^1, R^2, R^3 are long chain hydrocarbons [54, 71, 72].

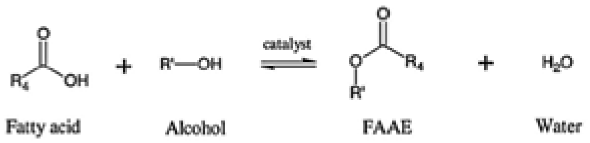

Figure 2: Esterification reaction of fatty acid with alcohol; R^4 is an acyl residue, R' is the alcohol moiety [42, 44, 67].

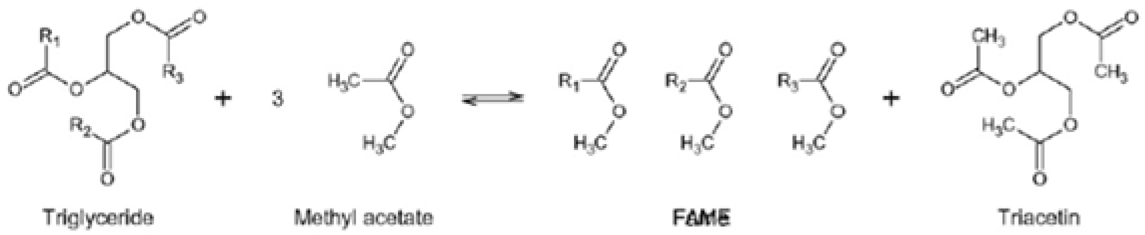

Figure 3: Interesterification reaction of TG with methyl acetate [31, 70, 73].

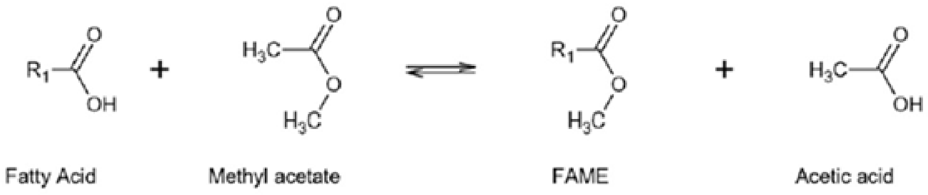

Figure 4: Stoichiometric reaction schemes for the esterification of fatty acids with methyl acetate [70, 73].

Once the reaction is complete, the mixture is allowed to separate into two distinct phases, enabling the removal of glycerol. Any unreacted alcohol and catalyst are then recovered from both the ester and glycerol phases and recycled back into the reactor [32]. Finally, the biodiesel undergoes purification and drying processes to ensure it meets industry-approved quality standards, which are critical for maintaining engine performance, durability, and reducing harmful emissions during combustion [74].

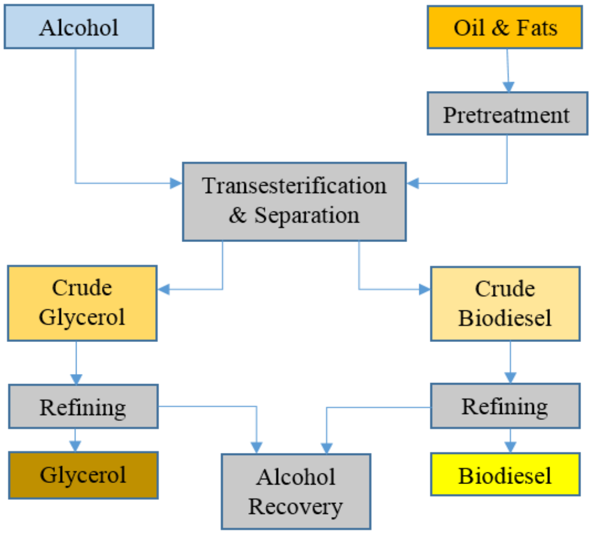

Figure 5: Biodiesel production through transesterification block diagram [26, 28, 53].

The transesterification process can be carried out using either catalytic or non-catalytic methods [46, 54, 66]. Catalytic transesterification can be facilitated by chemical catalysts, such as acids and alkalis [43, 76], or by enzyme catalysts, such as lipase [46, 57, 72]. In contrast, non-catalytic transesterification typically occurs under supercritical conditions, where elevated temperature and pressure drive the reaction without the need for a catalyst [31]. While supercritical processes require extreme conditions, catalytic methods operate under milder conditions, offering better control over the reaction and the quality of the final products [32]. The use of a catalyst accelerates the reaction and improves yield by promoting the breakdown of reactant molecules, facilitating the formation of fatty acid esters [27, 43].

3.1.2. Chemical Catalytic Transesterification

Biodiesel synthesis through transesterification is typically conducted in the presence of a chemical catalyst [50]. These catalysts are broadly categorized into homogeneous and heterogeneous types based on their physical state [46, 65, 70]. Homogeneous catalysts are utilized in liquid form, while heterogeneous catalysts are solid; both types can function as either acidic or basic catalysts [31, 37]. In heterogeneous catalysis, the reaction involves three distinct phases—alcohol, lipid, and catalyst—which introduces mass transfer resistance among the phases, necessitating higher optimal conditions for efficient conversion [26, 37].

The conversion rate in heterogeneous catalysis is influenced by the particle size of the catalyst, with smaller particles offering higher conversion rates due to their increased specific surface area and, consequently, more active sites [3, 37, 76]. Examples of heterogeneous acid catalysts include heteropoly acids, tungstated zirconia, and sulfated zirconia, while heterogeneous alkali catalysts include basic zeolites, aluminum and zinc oxides, hydrotalcites, and calcium-based mixed metal oxides (CaO–MgO) [32, 37, 69]. Homogeneous acid catalysts commonly used are hydrochloric, phosphoric, and sulfuric acids, whereas homogeneous alkali catalysts include sodium hydroxide, potassium hydroxide, potassium methoxide, and sodium methoxide [28, 43, 77].

One of the primary challenges in chemical catalysis is achieving high product purity, as side reactions such as hydrolysis and saponification can occur, complicating downstream product recovery [40, 50, 54]. Consequently, the economic viability of the process largely depends on the cost of product recovery, which can account for more than half of the total production expenses [42].

- *Heterogeneous vs Homogeneous*

In industrial-scale transesterification processes, homogeneous catalysts are often favored over heterogeneous ones due to their ability to operate under milder conditions, such as lower pressure and temperature, and reduced alcohol requirements [26, 46, 76]. Heterogeneous catalysts typically yield lower biodiesel outputs compared to homogeneous catalysts, primarily due to mass transfer limitations and the leaching of active catalytic sites [42, 69]. Homogeneous catalysts generally exhibit high catalytic activity, resulting in faster reaction rates and higher product yields, and they are more cost-effective than most currently available heterogeneous catalysts [2, 37, 70].

However, homogeneous catalysis is sensitive to the presence of free fatty acids (FFA) and water in the feedstock, which can negatively affect the reaction [78]. Additionally, post-reaction purification steps—such as neutralization, flushing, and separation—are required, adding complexity to the process [19, 68]. These purification steps are often environmentally unfriendly due to high water consumption and the disposal of strong acids and bases [69, 76, 78].

In contrast, heterogeneous catalysts are more environmentally sustainable, as they allow for easier recovery of both the product and catalyst, are non-corrosive, and can be reused in multiple reaction cycles [37, 40, 76]. Their reusability and the potential for regeneration make them suitable for continuous biodiesel production processes, unlike homogeneous catalysts, which are typically single-use [27, 32, 42]. Furthermore, heterogeneous catalysts are more tolerant of extreme reaction conditions compared to both homogeneous and enzyme catalysts, enhancing their operational flexibility [37].

In homogeneous-catalyzed reactions, the alcohol and catalyst are typically premixed in proportions tailored to the FFA content of the feedstock before being introduced into the biodiesel reactor. These reactions can proceed rapidly under ambient pressure and at temperatures between 60°C and 80°C [27, 37].

- *Base Preference*

In industrial-scale transesterification, homogeneous alkaline catalysts are generally preferred over both homogeneous acid and enzyme catalysts due to their lower cost and high reaction efficiency under mild operating conditions [55, 57, 76]. Alkaline metal alkoxides, in particular, exhibit the highest catalytic activity, as they can achieve high biodiesel yields within short reaction times, even with minimal catalyst usage, as noted by Mujeeb *et al*. [27]. In contrast, acid catalysts have lower catalytic activity, necessitating higher reaction temperatures and excessive alcohol to achieve comparable biodiesel yields. Additionally, mineral acid catalysts are highly corrosive and can lead to contamination of the product, complicating the downstream purification of biodiesel.

Although alkaline catalysts offer significant advantages over acid catalysts in transesterification, they are highly sensitive to the presence of moisture and free fatty acids (FFAs) in the feedstock oil [37, 55, 65]. Water triggers the hydrolysis of triglycerides, leading to the formation of glycerol and FFAs instead of undergoing transesterification [40, 43]. Meanwhile, alkaline catalysts react with FFAs to form soap through saponification [19, 26, 77]. This soap formation complicates the separation of biodiesel from glycerol [37, 56] and can cause the mixture to gel under ambient conditions, making the process more challenging [46].

The presence of FFAs also diminishes the catalytic activity of alkaline catalysts, which directly reduces biodiesel yield [27, 57, 65]. To achieve optimal transesterification efficiency, feedstock oils should have a moisture content below 0.06 wt.% and an FFA content under 0.5 wt.% when using alkaline metal hydroxides as catalysts [27, 37, 40]. Therefore, pretreatment of feedstocks to remove excess moisture and FFAs is essential to meet these specifications and prevent side reactions [19, 43]. The saponification reactions of FFAs and esters are shown below [32]:

Equation 1: FFA reaction with metallic alkoxide in the presence of heat to produce a salt and water and Equation 2: Ester reaction with metallic alkoxide in the presence of water to produce salt and water.

$$R - COOH + NaOH \rightarrow R - COONa + H_2O \qquad \text{Equation 1}$$

$$R - COOR' + NaOH \rightarrow R - COONa + H_2O \qquad \text{Equation 2}$$

Feedstocks with high free fatty acid (FFA) content can be converted into biodiesel via acid-catalyzed esterification with an alcohol, as FFAs do not react with acid catalysts [37, 46, 57]. Acid catalysis can facilitate both the esterification of FFAs and the transesterification of triglycerides, with these reactions often occurring simultaneously when an acid catalyst is employed [31, 42, 43]. For feedstock oils with FFA content greater than 1 wt.%, a two-step method can be used, involving acid catalysis for FFA esterification followed by base catalysis for triglyceride transesterification [31, 41, 65].

Although water is a by-product of the esterification process, continuous water removal is essential to prevent catalyst dilution and to shift the reaction equilibrium toward biodiesel production. This practice also reduces the amount of alcohol needed for the reaction [32, 73]. Compared to base catalysis, acid-catalyzed transesterification is typically reserved for feedstocks with high FFA levels but is associated with slower reaction rates, lower selectivity, and higher oil-to-alcohol molar ratios [32, 78]. Thus, the selection of the transesterification method and catalyst type is primarily influenced by the FFA and moisture content of the feedstock oil [27, 37, 57].

3.1.2.1. Two-step Method

The two-step chemical catalysis process involves first performing acid-catalyzed esterification of free fatty acids (FFAs) to reduce their content to below 0.5 wt.%, followed by alkali-catalyzed transesterification of the remaining triglycerides in the feedstock [38, 48, 79]. The primary advantage of this method is its ability to accommodate feedstock oils with varying moisture and FFA content, as the acid-catalyzed esterification step serves as a pretreatment for the base-catalyzed transesterification, preventing saponification [46, 78]. This approach allows for high biodiesel yields from feedstocks with significant levels of FFAs and moisture [38, 65].

During the esterification step, the water byproduct is removed before introducing the alkaline catalyst for the transesterification process [32, 38, 46]. Shiu *et al*. suggest that excess alkaline catalyst can be added after the esterification to neutralize the acid catalyst, with the remaining base catalyst facilitating the transesterification. When sulfuric acid (H_2SO_4) is used for acid catalysis, this neutralization step may improve moisture tolerance, as the resulting metal sulfates can act as moisture absorbents during the reaction [38].

3.1.3. Enzyme Catalyzed

Enzymes, particularly lipases, are biocatalysts commonly used in the production of biodiesel [27, 41]. Lipases can catalyze a variety of reactions, including hydroesterification, interesterification, and transesterification, with high specificity and under mild conditions, often at ambient temperatures [37, 46, 50, 81]. The main forms of biocatalysts used in biodiesel production include free lipases, immobilized lipases, whole cells, and fermented solids [32, 41, 78].

Lipases are derived from various sources, such as plants, animals, fungi, and bacteria [31], but microbial lipases are the most commonly employed in biodiesel synthesis due to their relatively low cost, rapid production, and the ease with which they can be immobilized on inexpensive media [46, 78]. Microbial lipases are also known for their high yield, enhanced stability, and the potential for genetic modification to improve performance compared to those from other sources [32, 46, 81]. One significant advantage of lipase-catalyzed transesterification is its reduced sensitivity to feedstock impurities, such as moisture and free fatty acid (FFA) content, which can inhibit the performance of alkaline catalysts [37, 41, 78].

Enzyme catalysis also produces biodiesel with higher purity than chemical processes, likely due to the reduction of side reactions like saponification [30, 41, 57, 67]. As a result, the downstream processing required for product recovery and purification is simpler compared to chemical methods [28, 31, 37]. Furthermore, enzymes are environmentally friendly and can be reused multiple times while maintaining high catalytic activity [38, 46, 67, 81].

Despite the advantages, enzyme catalysis for transesterification in biodiesel production faces several limitations. These include low catalytic activity, which leads to longer reaction times and a higher requirement for catalyst quantities to achieve significant biodiesel yields, as well as the high cost of lipases [50, 56, 57]. These factors pose challenges to the economic viability of enzyme catalysis for industrial-scale biodiesel production [27, 38, 66]. Additionally, enzyme catalysis is hindered by the inhibitory effects of short-chain alcohols and glycerol [31, 56, 70].

Methanol, the most commonly used alcohol donor, can be toxic to enzyme catalysts and cause deactivation at high concentrations [50]. Therefore, controlling alcohol concentration throughout the reaction is crucial to prevent lipase deactivation [31, 46, 50]. To maintain optimal alcohol levels, stepwise alcohol addition is often employed during the reaction [67], ensuring that lipase activity is preserved for longer periods [32]. One method to achieve this is by using alcohol-impregnated silica gel, which gradually releases alcohol over time, maintaining the desired concentration without exceeding the threshold that could deactivate the lipase [31].

Alternatively, co-solvents may be used to control the concentration of methanol and prevent enzyme deactivation. Another strategy is to use longer-chain alkyl donors, such as methyl acetate or dimethyl carbonate, which can lead to higher conversion rates without the deactivating effects of methanol [70].

Enzymes, particularly lipases, exhibit varying degrees of thermal stability, reaction speed, and methanol tolerance [32, 50]. Only a few lipases maintain stability in the presence of methanol, particularly at the optimal methanol-to-oil ratios required for the process, which are typically higher than 3:1 [67]. To enhance the practicality of lipase catalysis, enzymes are often immobilized. Immobilization simplifies enzyme recovery from reaction mixtures, allows for repeated reuse, and ensures the production of high-quality biodiesel [28, 37, 70, 41]. It also improves enzyme stability in organic solvents, including increasing tolerance to inhibitory substances like polar short-chain alcohols and glycerol [50, 40].

The enhancement in stability is attributed to several factors, including the stabilization of the enzyme's hyper-activated form, better dispersion of the enzyme on the support surface, protection from harsh reaction conditions through rigidification, and/or promotion of diffusional limitations by porous supports [31]. Lipase immobilization can be achieved through various methods, such as encapsulation on silica aerogel, adsorption onto microporous resin, chemical binding to chitin, and entrapment in hydrophobic sol-gels [31, 40]. Studies have shown that immobilizing lipases on appropriate supports, combined with optimal reaction conditions, can result in high biodiesel yields through enzyme-catalyzed transesterification [27, 46].

However, immobilization may sometimes negatively affect enzyme activity and selectivity, and can alter the enzyme's structural form, which may reduce biodiesel yield. To enhance the economic feasibility of enzyme catalysis, efforts to develop efficient methods for regenerating lipase activity and ensuring its reuse are essential [46].

3.1.4. Non Catalytic

Non-catalytic transesterification reactions typically occur under supercritical conditions, where the alcohol is in a supercritical gaseous state and the triglycerides dissolve into a homogeneous phase [32]. This method has advantages over conventional transesterification due to the enhanced solubility of triglycerides in supercritical alcohol, leading to higher reaction rates [26, 27, 31, 37, 38]. Supercritical methanol, for instance, helps overcome the mass transfer issues typically associated with alcohol/oil mixtures by forming a homogeneous phase, which is facilitated by the lower dielectric constant of supercritical methanol [27].

The non-catalytic nature of this process eliminates the need for a catalyst, simplifying the downstream separation and purification processes, as there are no side products such as soap formed [26, 46, 73]. Moreover, the supercritical process is less affected by moisture and free fatty acid (FFA) content in the feedstock, allowing for the concurrent transesterification of triglycerides and esterification of free fatty acids [37]. This makes the process more environmentally friendly compared to traditional methods [27].

However, supercritical transesterification has some significant drawbacks, including its high capital and energy requirements [26, 32]. The process requires larger quantities of alcohol compared to conventional methods, and the excess alcohol must be recovered and reused, which adds complexity to the process design [32]. Typical reaction conditions for supercritical transesterification involve temperatures between 200-400°C, pressures of 10-60 MPa, and alcohol-to-oil ratios of 20:1 to 45:1 [27, 31, 38]. These extreme conditions require specialized equipment, making the process more expensive than conventional transesterification methods [32, 46]. Despite its advantages, these challenges present significant barriers to the widespread industrial adoption of supercritical biodiesel production.

3.1.5. Alkyl Donor

Methanol and ethanol, which are low molecular weight primary alcohols, are the most commonly used alkyl donors in transesterification reactions [31, 32]. However, higher molecular weight alcohols, as well as secondary and branched-chain alcohols, can also be used as alkyl donors. The choice of alkyl donor significantly influences both the process conditions and the biodiesel yield [37]. When considering alternative alkyl donors, several factors need to be evaluated, including the solubility of the alcohol in the reactants, its toxicity towards the catalyst, renewability, health and environmental impact, the quality of the fuel produced, and the overall economics of the process [38].

- *Alcohols*

Methanol is widely preferred as the alkyl donor for commercial biodiesel synthesis primarily due to its low cost [44, 65], as well as the ease of post-transesterification glycerol separation through settling [32]. In contrast, ethanol, derived from biomass, is renewable and environmentally friendlier than methanol, which is a fossil fuel byproduct [30, 34, 37]. For biodiesel to be considered fully renewable, all of its reagents must come from renewable sources. Longer-chain alcohols, when used in biodiesel synthesis, result in biodiesel with better thermal stability, though oxidation stability tends to be poorer, particularly when the alcohols are branched [27, 31, 37]. Additionally, linear alcohols typically yield biodiesel with better ignition properties compared to their branched-chain counterparts [54]. The miscibility of alcohols with oils increases with the length of the alcohol chain [44], but this also makes post-reaction product separation and purification more challenging compared to methanol [65, 82], leading to lower biodiesel yields as the chain length increases [37, 50]. Reactions with secondary alcohols are generally slower than those with primary alcohols, likely due to steric hindrance [31]. Methanol's relatively high polarity explains its low solubility in oil compared to higher molecular weight alcohols [30, 34, 38]. To enhance mass transfer during transesterification, various methods like adding a solvent, stirring, or heating can be employed. However, methanol is a toxic solvent [19], and as noted, exposure to concentrations exceeding one molar equivalent of methanol can cause lipase deactivation and denaturation [31]. Therefore, ethanol or higher alcohols may be more suitable for enzyme-catalyzed transesterification due to their less toxic effect on lipase [31, 78]. Furthermore, a combination of methanol and ethanol can be used in the same reaction to leverage the benefits of both solvents, although methanol is consumed at a faster rate [31].

- *Short Chain Esters*

Recently, short-chain esters such as acetates and alkyl carbonates have been explored as alkyl donors in biodiesel synthesis, yielding high biodiesel production along with valuable byproducts [19, 31, 38]. These esters offer a significant advantage over alcohols by mitigating issues related to glycerol production, which can deactivate lipases during transesterification [19, 50]. This opens up the potential for lipase recycling without the need for additional pretreatment, which is often necessary when alcohols are used as alkyl donors [78]. Byproducts like triacetylglycerol (triacetin), which is produced from the interesterification of lipids, can enhance the cold flow properties and viscosity of biodiesel, and can also serve as an anti-knock agent in petroleum products [31, 35, 73, 70]. Additionally, using methyl acetate as the alkyl donor suppresses the saponification reaction by reacting with free fatty acids (FFAs) to form biodiesel and acetic acid, further improving the efficiency of the process [38, 73].

However, the interesterification process with esters is characterized by lower reaction rates and higher requirements for ester-to-oil ratios and catalyst concentrations compared to the use of alcohols as alkyl donors [31, 78]. This reduced reactivity is likely due to steric hindrance caused by the relatively larger and more complex molecular structure of ester-alkyl donors. Furthermore, esters, being alcohol derivatives, are more expensive than conventional alcohols [38, 50]. Using alkyl carbonates as reagents leads to the formation of byproducts like glycerol carbonate and glycerol dicarbonate, which require environmentally harmful solvents like methyl tert-butyl ether for separation from the fatty acid alkyl esters (FAAE) and fatty acid glycerol carbonate monoesters mixture [70]. Therefore, there is a clear need for improved methods to regulate product selectivity during interesterification, particularly with reagents like dimethyl carbonate, and for the development of renewable sources for producing methyl acetate.

3.1.6. Factors that Affect Transesterification

The conversion, selectivity, and reaction rate of biodiesel synthesis can be influenced by several process variables, including the alkyl donor to oil molar ratio, reaction temperature, free fatty acid and moisture content, catalyst type and concentration, mass transfer conditions, use of co-solvents, and reaction time [30, 34, 60]. Among these, the key parameters typically optimized for the transesterification reaction include reaction temperature, alkyl donor to oil molar ratio, catalyst concentration, reaction time, and mixing rate [31, 41, 65]. Analyzing the interactions between these variables and selecting the optimal conditions for the process can significantly enhance biodiesel yield while minimizing operational costs [34].

3.1.6.1. Molar Ratio

The molar ratio of alcohol to oil is a critical factor that significantly impacts biodiesel yield [60, 65, 70]. Since transesterification is an equilibrium reaction, an excess of alkyl donor is required to shift the reaction toward the continuous production of biodiesel [34, 56, 73]. Singh and Patel investigated the effect of methanol to oil molar ratios and found that higher methanol concentrations reduce the viscosity of the reaction mixture, enhancing mass transfer rates by promoting better contact between the reagents and the catalyst [59]. However, while increasing the alcohol molar ratio improves biodiesel yield up to a certain point, it can lead to a decrease in yield beyond this optimal ratio. This drop in yield occurs due to the emulsification of the transesterification products induced by the polar hydroxyl group of the alcohol, which facilitates the reverse reaction and lowers overall FAAE yield [65]. In enzyme-catalyzed transesterification, high concentrations of polar short-chain alcohols can also disrupt the lipase's aqueous environment, leading to irreversible enzyme deactivation [30, 78].

The stoichiometric alcohol to oil ratio for transesterification is typically 3:1, but the optimum ratio for maximum yield and reaction rate can vary depending on the specific reaction conditions [65, 70, 83]. In conventional transesterification processes, a 6:1 molar ratio is commonly used [27, 34, 44]. In reactions where methanol functions both as a solvent and a transesterification reagent, very high alcohol to oil molar ratios—sometimes reaching hundreds or even thousands—may be necessary to achieve high biodiesel yields [34, 44]. Additionally, higher reaction temperatures tend to increase the optimal alcohol to oil ratio, with supercritical transesterification typically requiring ratios as high as 42:1 to achieve higher yields [70]. To improve the process economy, unreacted alkyl donor can be recovered, purified, and recycled for further biodiesel production [55, 65].

3.1.6.2. Reaction Temperature

The reaction temperature plays a significant role in determining both the rate of reaction and the biodiesel yield [46, 65], and its impact varies depending on the catalyst used [44]. Reactions conducted at ambient temperatures typically exhibit low reaction rates and biodiesel yields due to mass transfer limitations between the oil and methanol. However, increasing the reaction temperature leads to higher reaction rates and improved yields [34, 75]. Elevated temperatures help shift the reaction equilibrium in favor of biodiesel production, which is consistent with the endothermic nature of esterification [30, 41]. As a result, high temperatures are associated with faster reaction times and higher yields [27, 60]. The mass transfer between oil and alcohol improves with temperature due to the reduction in oil viscosity as temperature increases [37, 55, 70]. Additionally, higher temperatures increase the frequency of collisions between molecules, which enhances material transfer and accelerates the reaction rate [30].

However, studies suggest that the influence of temperature on reaction kinetics is effective only within specific temperature ranges [34], which depend on the type of catalyst used. Catalyzed reactions are generally carried out between ambient temperature and the boiling point of the alcohol [38]. Beyond this range, increasing the temperature may lead to alcohol evaporation, which has minimal effect on biodiesel yield [37, 44, 59]. Enzyme catalysts, in particular, are sensitive to temperature and can undergo thermal denaturation above 60°C, resulting in a decrease in reaction rate [30, 31]. At high temperatures, thermal decomposition of the transesterification products begins after equilibrium is reached, and prolonged reaction times can lead to further decomposition, thereby reducing the biodiesel yield [70]. Optimizing reaction temperature and duration is crucial to achieving rapid biodiesel production with high yields while minimizing thermal decomposition of the products.

3.1.6.3. Moisture Content

The moisture content in the transesterification reaction mixture plays a crucial role in influencing both the reaction rate and the biodiesel yield [81]. Lipase catalytic activity depends on the aqueous-organic interfacial area, and a minimum moisture level is necessary to maintain the active conformation of the lipase, ensuring optimal catalytic performance [78, 84]. A moderate moisture content can enhance the interfacial area between water and organic phases, potentially improving lipase activity and increasing the biodiesel yield [70]. However, excessive moisture can lead to enzyme aggregation, which reduces the enzyme's catalytic effectiveness [78, 81].

Furthermore, high moisture content can cause hydrolysis of the biodiesel produced, reversing the transesterification reaction and converting the biodiesel back into free fatty acids and methanol, thereby reducing the overall yield [30, 42, 57]. Therefore, the optimal moisture content in enzyme-catalyzed transesterification must balance the need to prevent hydrolysis while preserving lipase conformation for maximum biodiesel yield [30, 31, 78].

Excessive moisture also promotes the hydrolysis of triglycerides into soap and glycerol during alkaline-catalyzed transesterification, further lowering the yield of fatty acid alkyl esters (FAAE) and complicating the separation process [70, 32, 44]. In addition, high moisture levels dilute homogeneous acid catalysts, necessitating the use of larger quantities of alkyl donor to achieve the desired biodiesel yield. Therefore, using moisture-free raw feedstock can reduce the amounts of reagents and catalysts needed, optimizing the reaction [34]. For acid esterification systems that produce water as a byproduct, a water management strategy, such as carrying out the reaction in a membrane reactor to remove water during the process, is beneficial [32].

3.1.6.4. Reaction Pressure

The effect of reaction pressure on biodiesel yield is closely linked to its impact on fluid density and solubility under supercritical conditions. As pressure increases, the density of the supercritical fluid also rises, enhancing its ability to dissolve reactants, which in turn improves biodiesel yield [70, 73]. Yield tends to increase with pressure up to a certain optimal point, after which further increases in pressure do not significantly boost the yield [73]. The typical optimum pressure for supercritical transesterification is around 20 MPa, at which the entire system reaches a supercritical state [70].

3.1.6.5. Additional Solvent

The use of solvents, such as hexane, in transesterification reactions can accelerate the extraction process (in the case of reactive extraction) and enhance the solubility between reagents, thus promoting more efficient biodiesel production under milder conditions [31, 32, 34]. By reducing the polarity of the reaction mixture, the addition of non-polar solvents improves solubility, which may allow for lower alcohol-to-oil molar ratios, optimizing the reaction [38, 44]. Co-solvents are particularly beneficial in enzyme-catalyzed transesterification, where they help mitigate the inhibitory effects of methanol and glycerol on lipase activity [31, 32, 70]. In supercritical in situ transesterification, using supercritical CO_2 as a co-solvent can lower the temperature and pressure required to reach the supercritical state, improving efficiency [70]. However, co-solvents can alter the selectivity of the transesterification products and introduce challenges in product recovery and separation, potentially affecting the purity of the biodiesel [44]. Additionally, some solvents may have toxic environmental impacts, raising concerns about their effect on the life cycle carbon emissions of the biodiesel [31, 44]. It is essential to control the amount of solvent in the reaction mixture to avoid dilution of the catalyst and reagents, which could decrease the reaction's productivity [38]. While solvents add to production costs—both in purchasing and in post-reaction recovery—they may be worth the investment if the advantages they offer outweigh the added expenses.

3.1.6.6. Stirring

Agitation through stirring enhances mass transfer in the transesterification reaction by increasing the interfacial area between the reactant phases. This improvement in mixing intensity leads to higher reaction rates and better biodiesel yields [32, 34, 44]. When combined with co-solvents, high mixing intensity can also lower the optimum temperature required for the reaction due to the enhanced solubility and mass transfer between reagents [32]. However, the benefits of agitation have limits; beyond a certain mixing intensity, no significant improvement in reaction performance is observed. Excessive agitation can cause shear stress, which may disrupt the structure of enzymes, particularly in lipase-catalyzed reactions, reducing enzyme activity and leading to a lower biodiesel yield [31, 34]. Studies suggest that continuous stirring and alternating stirring both yield similar results, with alternating stirring recommended for energy savings [44].

3.1.6.7. Catalyst Concentration

Transesterification typically requires a catalyst to achieve a reasonable reaction rate and high yields under mild conditions [44]. Chemical homogeneous catalysts are often preferred for their lower methanol-to-oil molar ratio requirements compared to enzyme and heterogeneous chemical catalysts, likely due to fewer phase transfer limitations [38]. Biodiesel yield increases with catalyst concentration up to a certain point, after which further increases in catalyst concentration can reduce the yield. This is due to the promotion of side reactions such as emulsion and gel formation, which complicates product recovery and reduces the overall yield [60, 65]. Homogeneous alkaline catalysts are particularly susceptible to such issues [37]. While strong acid catalysis can require higher catalyst concentrations, it also necessitates neutralization in the product stream, adding to the operational costs [44].

3.1.7. Biodiesel Characterization

Biodiesel is a clear, amber-yellow, non-aromatic, non-toxic liquid fuel with physiochemical properties comparable to petroleum diesel. It is derived from renewable oils through the transesterification process [14, 27, 32]. The quality of biodiesel is typically characterized by its physiochemical properties, which include cold flow properties, density, cetane number, heating value, oxidation stability, and viscosity [28, 32, 53]. To be suitable for commercial use, biodiesel must meet globally prescribed certification standards such as EN 14214 (2003) and ASTM D 6751, as outlined in Table **3** [54, 83, 85].

Biodiesel quality is influenced by various factors, including the characteristics of the feedstock, the production process, post-production handling, and the storage environment [2]. The following sections will explore some of the crucial properties of biodiesel in greater detail.

3.1.7.1. Cold Flow Properties

Cold flow properties are critical in determining the flow performance of biodiesel in low-temperature environments, and they are a major factor in the fuel's usability in colder regions [85]. When exposed to low temperatures, biodiesel tends to crystallize, causing blockages in filters, increasing viscosity, and resisting flow. This can lead to operational issues, such as fuel starvation in engines and overloading of the fuel pump [28, 37, 47]. Cold flow properties are typically characterized by three key metrics: Cloud Point (CP), Pour Point (PP), and Cold Filter Plugging Point (CFPP) [37, 47, 54, 85].

Biodiesel generally exhibits poorer cold flow performance compared to petroleum diesel [28, 85]. The CFPP of biodiesel is strongly influenced by the length and saturation level of its fatty acid chains [47]. Fatty acids with higher saturation levels (more double bonds) typically result in lower cold flow performance, leading to poorer cold flow properties. This is because saturated fatty acid chains tend to crystallize more readily at lower temperatures. On the other hand, unsaturated fatty acid chains help improve cold flow properties, as they tend to remain fluid at lower temperatures, though this may result in reduced oxidation stability and heat of combustion [54].

Table 3: ASTM D 6751 and EN 14214 specifications for biodiesel [2, 27, 28, 53, 54, 60, 82, 83].

	Limit	Method	Limit	Method
Density at 15ºC	870-890 kg/m^3	ASTM D4052-91	860-900 kg/m^3	EN ISO 3675, EN ISO 12185
Flash Point	130°C minimum	ASTM D93	>101°C minimum	EN ISO 3679
Viscosity at 15ºC	1.9-6.0 mm^2/s	ASTM D445	3.5-5.0 mm^2/s$^{.}$	EN ISO 3140
Sulfated ash	0.02% m/m	ASTM D874	0.02% m/m maximum	EN ISO 3987
Cloud Point	Report to customer	ASTM D2500	Based on national specification	EN ISO 23015
Copper Strip Corrosion	Class 3 maximum	ASTM D130	Class 1 rating	EN ISO 2160
Cetane Number	47 minimum	ASTM D613	51 minimum	EN ISO 5165
Water Content and Sediment	0.05 (%v) maximum	ASTM 2709	500 mg/kg maximum	EN ISO 12937
Acid Number	0.5 mg KOH/g maximum	ASTM D664	0.5 mg KOH/g maximum	EN 14104
Free Glycerin	0.02% (m/m) maximum	ASTM D6584	0.02% (m/m) maximum	EN 1405/14016
Total Glycerol	0.24% (m/m) maximum	ASTM D6548	0.25% (m/m)	EN 14105
Methanol Content	0.2% (m/m) maximum	EN14110	0.2% (m/m) maximum	EN14110
Phosphorus	10 mg/kg maximum	ASTM D4951	10 mg/kg maximum	EN 14107
Distillation Temperature	360°C	ASTM 1160	-	-
Sodium and Potassium	5ppm maximum	EN14538	5 mg/kg maximum	EN 14108/EN 14109
Oxidation Stability	3h minimum	EN ISO 14112	6h minimum	EN ISO 14112
Carbon Residue	0.05 wt.%	ASTM D4530	0.3% (m/m) maximum	EN ISO 10370
Calcium and Magnesium	5ppm maximum	EN14538	5ppm maximum	EN 14538
Iodine	-	-	120g/100g maximum	EN 14111

The cold flow behavior of biodiesel also improves as the fatty acid chain lengths decrease, meaning shorter-chain fatty acids tend to give better cold flow performance [85]. To enhance the cold flow properties of biodiesel, several strategies can be employed, including:

1. **Blending**: Mixing biodiesel with mineral diesel or other biodiesels with better cold flow properties can improve its cold flow behavior [28].
2. **Using branched-chain alcohols as alkyl donors**: This can result in the formation of biodiesel with better cold flow properties [54].
3. **Winterization**: This process involves reducing the amount of saturated fatty esters in biodiesel, which can help improve cold flow properties [47].

These methods can help optimize biodiesel's cold flow properties, ensuring better performance in colder climates.

- *Cloud Point*

The Cloud Point (CP) of a fuel is the temperature at which the first visible cluster of solid crystals forms as the fuel is cooled in a low-temperature environment. This temperature represents the highest melting point of the constituents within the fuel [37, 47, 85]. As the temperature continues to decrease beyond the cloud point, the crystallization process accelerates, leading to further solid formation, which thickens the fuel and can block fuel filters and injectors in engines, causing operational issues [47].

The Cloud Point is a critical parameter for determining the cold flow behavior of biodiesel and is commonly measured using ASTM standards, including D2500, D5771, D5772, and D5773 [54].

The fatty acid composition of biodiesel plays a significant role in predicting its cloud point. Specifically, biodiesel with a higher degree of i.e., more saturated fatty acid chains) will typically have a higher cloud point. This is because saturated fatty acid chains have a tendency to crystallize at higher temperatures than unsaturated chains, which remain liquid at lower temperatures.

In equation form, the cloud point of biodiesel (CP) can be expressed as a function of its fatty acid composition. While the specific formula may vary based on experimental conditions, it generally suggests that:

$$CP = f(\text{Degree of Saturation in Fatty Acids}) \qquad \text{Equation 3}$$

Where, as the degree of saturation increases, the cloud point of biodiesel also increases, making it less suitable for use in colder climates unless modified by blending or other techniques.

This relationship emphasizes the importance of understanding the fatty acid composition when assessing the cold flow properties of biodiesel and its potential performance in various environmental conditions.

- *Pour Point*

The Pour Point (PP) of a fuel is the temperature at which the fuel becomes semi-solid and can no longer flow or be pumped. It is lower than the Cloud Point (CP), which marks the temperature at which the first visible crystals form in the fuel. At the pour point, the clusters that formed at the cloud point begin to coagulate, resulting in a thicker, gel-like substance that impedes fuel flow [37, 47, 53].

Biodiesel generally has a higher pour point compared to petroleum diesel, making it more prone to flow issues at lower temperatures [53]. The pour point is critical in determining the performance of biodiesel in cold weather, as it indicates the temperature at which the fuel becomes unusable due to its semi-solid state.

The pour point of biodiesel can be determined using various ASTM standards, including:

- ASTM D97
- ASTM D5949
- ASTM D5950
- ASTM D5985
- ASTM D6749
- ASTM D6982 [54].

To improve biodiesel's cold flow properties, methods such as blending with lower pour point fuels, modifying the fatty acid composition, or using additives may be employed. However, the higher pour point of biodiesel compared to petroleum diesel remains a challenge for its use in colder regions.

- *Cold Filter Plugging Point*

The Cold Filter Plugging Point (CFPP) is the minimum temperature at which a specified fuel can still flow through a standard filter when subjected to low temperatures in a controlled environment. It is an important parameter for assessing the low-temperature performance of biodiesel and other fuels. According to Altaie *et al*. and Sierra-Cantor and Guerrero-Fajardo, the CFPP is defined as the highest temperature at which 20 ml of fuel fails to pass through a 45 µm wire mesh filter under a 0.02 atm vacuum within 60 seconds [37, 47, 53].

CFPP is a critical indicator of biodiesel's operability in cold conditions. The CFPP increases with the degree of saturation in the fatty acid chains of the biodiesel. In other words, biodiesel with a higher degree of saturation (more saturated fatty acid chains) has a higher CFPP, meaning it is more likely to form crystals that plug the fuel filter at lower temperatures. On the other hand, biodiesel with lower saturation (unsaturated fatty acid chains) generally has a lower CFPP, making it more suitable for colder climates.

$$CFPP = (0.8537 \times CP) - 4.72 \quad \text{Equation 3}$$

Estimation of CFPP: CFPP can be estimated based on the fatty acid composition of the biodiesel, with higher unsaturation (i.e., more double bonds in the fatty acid chains) leading to a lower CFPP. The exact estimation would depend on the relationship between the fatty acid chain length, degree of saturation, and the CFPP.

In practical terms, biodiesel producers and users aim to minimize the CFPP to ensure that the fuel can be used effectively in colder climates, possibly through blending with diesel or modifying the biodiesel composition.

3.1.7.2. Kinematic Viscosity

The kinematic viscosity of a fuel is a critical parameter in determining its behavior in internal combustion engines, particularly regarding fuel atomization, combustion efficiency, and engine performance. High kinematic viscosity tends to hinder fuel atomization, leading to poor combustion and reduced engine power. This can also result in increased exhaust emissions and lower overall engine efficiency [5, 28, 34, 46]. Conversely, higher viscosity improves the lubricity of the fuel, reducing engine wear and minimizing fuel leakage, which is beneficial for engine longevity [28, 53].

Biodiesel typically has a higher kinematic viscosity compared to petroleum diesel. This is due to the larger chemical structure and higher molar mass of the biodiesel molecules, which are composed primarily of fatty acid methyl esters (FAME) with relatively long carbon chains and high saturation levels [28]. The kinematic viscosity of biodiesel is inversely related to temperature, meaning that as the temperature decreases, the viscosity increases, making the fuel more resistant to flow and atomization [28].

Kinematic Viscosity of Biodiesel:

- At 40°C, the kinematic viscosity of biodiesel typically ranges between 1.9–6 mm^2/s (ASTM D6751 standard) and 3.5–5 mm^2/s (EN14214 standard) [34, 46].
- Biodiesel's kinematic viscosity is influenced by the degree of saturation and chain length of its fatty acid chains. Higher saturation (more single bonds in the fatty acid chains) leads to higher viscosity [5, 54, 60]. Additionally, longer fatty acid chains also contribute to a higher viscosity.

Implications:

- **High viscosity** may hinder efficient fuel atomization, leading to incomplete combustion and poor engine performance.
- **Low viscosity** is desirable for better atomization and combustion, but extremely low viscosity might reduce lubricity and increase engine wear.

In practical biodiesel use, achieving the right balance in viscosity is crucial. Typically, biodiesel with high levels of unsaturation (i.e., more double bonds in the fatty acid chains) tends to have lower viscosity, which improves atomization and combustion efficiency while maintaining sufficient lubricity for the engine. However, very low viscosity biodiesel may compromise engine protection, so ensuring compliance with industry standards for viscosity is essential.

3.1.7.3. Density

Density, defined as the mass-to-volume ratio of a fuel, plays a crucial role in its atomization and combustion efficiency, directly impacting engine power output due to the volume-based operation of the fuel injection system [14, 28]. As density increases, the flow resistance of the fuel also rises, which leads to reduced fuel injection efficiency [53], resulting in poorer combustion quality and, consequently, higher engine emissions [28]. Biodiesel generally has a higher density than petrodiesel, which can be attributed to its greater molecular mass [53].

3.1.7.4. Flash Point

The flash point of a fuel is an important safety measure for its handling and storage. It is defined as the lowest temperature at which fuel vapors ignite and the flame propagates beyond the ignition source under standard test conditions [85]. Biodiesel has a higher flash point compared to petrodiesel, indicating that it is less flammable and thus safer for handling and storage [14, 49]. According to ASTM D6751-12 and EN14214 standards, the minimum acceptable flash point for biodiesel and its blends is 93°C and 120°C, respectively [46, 53].

3.1.7.5. Cetane Number

The cetane number (CN) of a fuel measures the time delay between its injection into the combustion chamber and its auto-ignition, also referred to as ignition delay time [49, 56]. It reflects the fuel's ignition quality, particularly under cold operating conditions [27, 28, 85]. A higher CN indicates a shorter ignition delay, which typically leads to quicker engine starts and smoother operation [14, 27, 28, 49, 53]. Conversely, fuels with lower cetane numbers experience longer ignition delays, often resulting in increased hydrocarbon (HC) and particulate matter (PM) emissions [28, 49, 53].

The CN of a fuel is influenced by the saturation level and chain length of its carbon molecules, with higher saturation and longer chains leading to an increased cetane number [34, 36, 49]. Biodiesel generally exhibits a higher cetane number compared to petrodiesel, primarily due to the presence of oxygen and long-chain fatty acid methyl esters in its composition [28, 53]. Typical cetane values for biodiesel range between 40 and 70, whereas diesel usually falls between 47 and 55 [27, 53, 56]. The cetane number of diesel can be improved with the addition of specific additives, such as fatty acid amides [83].

The cetane number of biodiesel can be calculated using the following equation:

$$CN = \sum X_{ME(wt.\%)} \times CN_{ME} \qquad \text{Equation 4}$$

where CN is the overall cetane number of the biodiesel, X_{ME} represents the weight percentage of individual methyl esters in the biodiesel, and CN_{ME} denotes the cetane number of each methyl ester component [85].

3.1.7.6. Oxidation Stability

The oxidation stability of a fuel indicates its ability to resist reactions with atmospheric oxygen over a specified storage period. For biodiesel, oxidation stability depends on its composition, particularly the presence of natural antioxidants and the structure of its fatty acid esters [37, 85]. Biodiesel with a higher proportion of unsaturated compounds is more prone to oxidative degradation, as these unsaturated molecules facilitate auto-oxidation processes [6, 60, 86].

When unsaturated fatty acids or esters undergo oxidation, they form hydroperoxides, gums, and sediments, which can negatively impact engine performance [47, 54, 86]. Additionally, the oxygen-containing functional groups in biodiesel may react with engine and refinery components, causing corrosion and contributing to the formation of deposits that impair storage stability, clog filters, and leave residues on fuel pumps [87].

While the degree of unsaturation plays a significant role in determining oxidation stability, other factors such as the presence of water and contaminants introduced through external exposure or thermal degradation can also accelerate oxidation [85]. To improve oxidation stability, measures such as limiting exposure to moisture, oxygen, and light, as well as the use of antioxidant additives, are recommended [6, 54, 86].

3.1.7.7. Heating Value

The heating value of a fuel refers to the thermal energy released during the complete combustion of a specific unit of the fuel [28]. The gross heating value (GHV) is determined by cooling all combustion products to their pre-combustion temperature, including condensing the water vapor, whereas the net heating value (NHV) considers only the heat associated with water vapor remaining in its gaseous state. The NHV can be calculated by subtracting the latent heat of vaporization of water from the GHV [28, 85].

Biodiesel typically has heating values in the range of 39–40 MJ/kg, which is approximately 10% lower than that of conventional diesel, which ranges between 42–46 MJ/kg [32]. This reduction in heating value is attributed to the oxygen content in biodiesel, leading to lower carbon and hydrogen concentrations compared to petroleum diesel [25, 88]. Consequently, a larger volume of biodiesel must be injected into the engine to achieve the same power output as petroleum diesel [14, 89, 90]. According to the EN 14313 standard, the minimum acceptable heating value for biodiesel is 35 MJ/kg [28].

3.2. Deoxygenation

Deoxygenation (DO) is a process that removes oxygen from biomass-derived oils in the form of water (via hydrodeoxygenation), carbon dioxide (via decarboxylation), and/or carbon monoxide (via decarbonylation). This process, carried out in the presence of a catalyst, yields hydrocarbons with properties comparable to those of conventional diesel [4]. The hydrocarbon products from deoxygenation, mainly consisting of n-alkanes and n-alkenes, are commonly referred to as Renewable Diesel [4]. In terms of chemical composition and combustion characteristics, renewable diesel more closely resembles petroleum diesel than biodiesel produced through transesterification [20, 21]. As a result, renewable diesel can be utilized directly in existing diesel engines without requiring further modifications [91].

Compared to transesterification-based biodiesel, renewable diesel produces lower emissions of particulate matter and carbon dioxide while emitting fewer nitrogen oxides (NOx) and hydrocarbons [4]. Additionally, renewable diesel exhibits superior net heating value, oxidation stability, and cold flow properties [92].

The hydrodeoxygenation (HDO) process removes oxygen by reacting lipids with hydrogen, producing n-alkanes and water in the presence of metal or oxide catalysts [93, 94]. The hydrotreatment of triglycerides typically begins with β-elimination, leading to the formation of fatty acids, which are subsequently deoxygenated to yield n-alkanes [88].

In contrast, decarboxylation (DCX) and decarbonylation (DCN) are oxygen removal processes that do not require hydrogen. These reactions occur in the presence of catalysts and produce carbon dioxide (CO_2) and carbon monoxide (CO), respectively, along with diesel-range n-alkanes and n-alkenes [93].

The dominant deoxygenation pathway depends on the specific reaction conditions, though multiple pathways may occur simultaneously [20, 95]. However, hydrogen-based deoxygenation is often expensive due to the high hydrogen requirements (typically 300–420 m^3 H_2 per m^3 of vegetable oil) [95], as well as the need for specialized high-cost reactors [87]. Moreover, hydrogen is predominantly derived from fossil fuels, raising concerns about sustainability [96]. To address these challenges, ongoing research is focused on reducing or eliminating hydrogen usage by optimizing DCX and DCN processes, thereby enhancing the economic and environmental sustainability of deoxygenation [96].

Deoxygenation reactions can be conducted in either batch or continuous systems, with typical operating temperatures ranging from 250°C to 450°C [21]. Fig. (**6**) illustrates the three primary deoxygenation pathways, which are discussed in detail in subsequent sections.

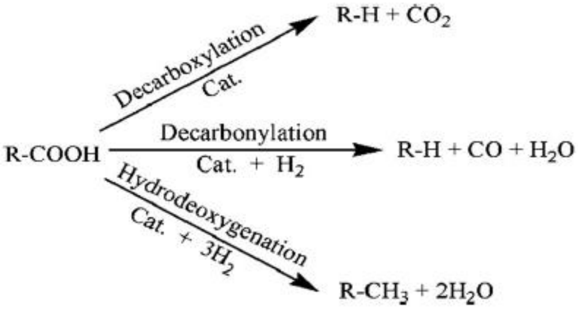

Figure 6: The three deoxygenation pathways for fatty acids [20, 21, 91, 93].

3.2.1. Hydrodeoxygenation (HDO)

Hydrodeoxygenation is an exothermic chemical reaction during which the carboxyl groups in triglycerides and/or fatty acids are reduced by hydrogenation and oxygen removal to produce diesel range n-alkanes and water [21, 97], in the presence of a catalyst [4, 93]. HDO is the most hydrogen intensive DO pathway which is characterized by a series of hydrogenation and hydrogenolysis reactions [96, 98] at higher temperature and H_2 pressures compared to other pathways [20, 96, 99]. During the hydrogenation process, the hydrogen dissolves in the oil and diffuses onto the catalyst surface where molecular hydrogen is dissociated into hydrogen atoms [64]. Hydrodeoxygenation may be accompanied by indirect decarbonylation so that the resultant n-alkanes have one carbon number less than the initial fatty acids, otherwise the product retains the reactant's carbon number [20, 100]. It is suggested in literature that the hydrogenation of the hydroxyl group produces the water and an aldehyde intermediate, which subsequently undergoes indirect DCO if the intermediate experiences C-C scission [96, 99]. Alternatively, the separation of oxygen happens via the C=O bond hydrogenation followed by the C–O bond rupture during the HDO reaction [21, 99]; the selective formation of larger hydrocarbons is enabled by catalyst's presence which restrains the C–C bond breaking while facilitating the hydrogenation of the C=O bond and splitting of the C–O bond [21]. The reduction of the Oxygen to Carbon ratio while increasing the Hydrogen to Carbon ratio leads to the production of higher energy hydrocarbons. Elevating the reaction temperature and the hydrogen to oil ratio facilitates HDO, however extremely high reaction temperatures may induce thermal cracking thereby negatively impacting the reaction selectivity[20]. Hydrodeoxygenation require continuous hydrogen supply for the attainment of a satisfactory product selectivity, however, optimum amounts should be used in order for the process to remain economically viable [21]. Recently, hydrogen donor solvents or coreactants have been employed for in situ hydrogen generation through aqueous phase reforming or decomposition, as a hydrogen gas requirement reduction technique for the HDO reactions [95].

3.2.2. Decarboxylation/Decarbonylation (DCO_x)

Decarboxylation (DCX) and Decarbonylation (DCN) are effective methods for decomposing the carboxyl groups in fatty acids to produce n-alkanes, with oxygen being released as either carbon dioxide (CO_2) in the case of DCX or carbon monoxide (CO) in DCN [20, 93, 98]. During these reactions, oxygen is removed from the fatty acid structure in the form of CO_2 or CO, depending on the specific pathway [99]. The deoxygenation process via DCX and DCN is comparable to hydrocarbon chain cracking, as it involves the breaking of at least one C–C bond, resulting in hydrocarbons with a reduced carbon chain length [96, 97, 99].

Unlike hydrodeoxygenation (HDO), DCX and DCN require minimal or no hydrogen, making these pathways simpler and more cost-effective [97, 98]. However, the presence of hydrogen can inhibit the DCX reaction, with the inhibitory effect increasing as hydrogen pressure rises [96]. In these reactions, CO_2 and CO are released when the C–C bond is broken, followed by hydrogenation of the carbon pool to yield hydrocarbons [22]. Operating at higher hydrogen pressures during deoxygenation suppresses the formation of aromatic compounds, thereby improving hydrocarbon selectivity [21].

While hydrogen-free deoxygenation of lipids is feasible, it faces challenges related to rapid catalyst deactivation. In addition to preserving catalyst activity, hydrogen also facilitates the complete breakdown of triglycerides into fatty acids, which is necessary for efficient deoxygenation [96]. In hydrogen-free conditions, direct decarboxylation and decarbonylation occur simultaneously, whereas in the presence of hydrogen, the process involves both direct hydrogenation and indirect decarbonylation [21].

Among the DCOx pathways, indirect decarbonylation is the fastest reaction [21]. Compared to HDO, which is more environmentally friendly due to its high hydrogen consumption, the DCOx pathways are more favorable in terms of hydrogen demand and overall process efficiency [20].

3.2.3. Factors that Affect DO

The efficiency of deoxygenation, in terms of both conversion and selectivity for a given feedstock, is influenced by several key process parameters. These include the type and amount of catalyst used, the composition of the reaction atmosphere, the operating pressure and temperature, as well as the duration of the reaction [20, 21]. A detailed discussion of these variables and their impact on deoxygenation performance is presented in the following sections.

3.2.3.1. Catalyst

Although deoxygenation can occur without a catalyst, this method is less favorable due to its low product selectivity and high energy requirements [94]. The type of catalyst plays a crucial role in determining the deoxygenation pathway, conversion efficiency, and product selectivity [20, 21]. Catalysts used in deoxygenation typically consist of an active metal component and a support material, which work synergistically. The metal serves as the active site for the reaction, while the support facilitates hydrogen dissociation or the adsorption of oxygenated compounds [21, 96]. Both noble and non-noble metals have been utilized as active components, either individually or in combination, depending on the desired reaction outcomes. Since catalytic behavior varies with reaction conditions, understanding the mechanism of a particular catalyst is essential for optimizing the deoxygenation process [20]. However, the primary considerations when selecting a catalyst are its activity and cost or availability [96]. Table **4** summarizes some catalytic deoxygenation reactions reported in the literature.

Table 4: Catalytic deoxygenation of lipids.

Catalyst	Support	Feed	Conditions			Atm	Reactor Mode	Conversion	Selectivity	Ref.
			Temperature	Pressure	Time					
NiMoCe (5wt.%Ni, 15wt.%Mo, Ce 5wt.%)	Al_2O_3	Jatropha Oil	370°C	3.5MPa	0.9/h	H_2	Fixed bed	89%	80% C15-C18	[101]
NiMoLa	Al_2O_3	Jatropha Oil	370°C	3.5MPa	0.9/h	H_2	Fixed bed	83%	78% C15-C18	[102]
Ni-PTA	Al_2O_3	Jatropha Oil	360°C	3.0MPa	0.8/h	H_2	Fixed bed	98.5%	84.5% C15-C18	[103]
Sulphided NiMo	γ-Al_2O_3	Soyabean Oil	400°C	9.2MPa	2h	H_2	Batch	92.9%	93.5-97.8% Diesel	[104]
10 wt% NiCo	γ-Al_2O_3	Jatropha FAME	400°C	2MPa		H_2	Fixed bed	78.2%	79% C12-C20	[105]
10 wt% NiCo	SiO_2	Jatropha FAME	400°C	2MPa		H_2	Fixed bed	76.1%	73% C12-C20	[105]
5 wt% Pd	C	Castor oil FAME	340°C	25bar	6hrs	H_2	Batch	100%	96% C17-C18	[106]
25 wt% Ni	SAPO-11	Castor oil	300°C	3MPa	2/hr	H_2	Fixed bed	99%	96% C16-C19	[107]
Sulphided 3Ni15Mo	AC	Jatropha oil	350°C	90 bar	3hrs	H_2	Batch	99.7%	81% C17-C18	[108]
25 wt% Ni	MAC	Stearic acid	260°C	6 bar	10hrs	H_2	Batch	100%	94% C17	[109]
Ni	γ-Al_2O_3	Stearic acid	270°C	8 bar	6hrs	H_2	Batch	100%	90.3 C17	[110]
Ni	MFI type Zeolites	Fatty acid esters	280°C	40 bar	8hrs	H_2	Batch	100%	100 C17-C18	[111]

Sulfided CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts are commonly preferred for hydrodeoxygenation (HDO) reactions due to their high catalytic activity in hydrogen-rich environments [21,100]. However, their performance significantly declines in low-hydrogen or hydrogen-free conditions, as they exhibit limited catalytic activity for decarboxylation (DCX) and decarbonylation (DCN) pathways and suffer from rapid deactivation in the absence of hydrogen [96]. Additionally, these sulfided catalysts often produce sulfur-contaminated hydrocarbons, posing environmental concerns [21].

In contrast, noble metal catalysts, such as palladium (Pd) and platinum (Pt) supported on carbon, have shown superior performance in deoxygenating lipids without requiring sulfiding treatments [21, 100]. Despite their high catalytic activity even under inert atmospheres, the industrial application of noble metals is limited due to their high cost and limited availability [87, 100]. As a result, non-noble metal catalysts like cobalt (Co), molybdenum (Mo), and nickel (Ni)-based systems are often favored due to their high catalytic efficiency and lower cost [91].

Ni/ZrO_2, for example, has been shown by Rogers and Zheng to promote indirect decarbonylation, likely due to its bifunctional properties that facilitate both hydrogenolysis and the subsequent decarbonylation of aldehyde intermediates [96]. Additionally, Hachemi *et al*. demonstrated the reusability of Ni supported on Y zeolites by regenerating spent catalysts from the HDO of fatty acids, restoring the catalytic activity per unit surface area after regeneration [100].

It is also reported that nickel-based bimetallic catalysts, such as NiMo/γ-Al_2O_3, exhibit higher catalytic performance compared to monometallic Ni catalysts, achieving activity levels comparable to those of noble metals [96]. Moreover, alkali and alkaline earth metal catalysts, due to their basic properties, offer favorable conditions for DCX reactions by facilitating carbon dioxide adsorption and desorption [97]. Among these, Mg–Al mixed oxides derived from calcined hydrotalcite stand out as cost-effective options for industrial applications [22].

- *Deactivation*

One of the primary challenges of catalytic deoxygenation processes is catalyst deactivation [91, 96]. Catalyst performance is often compromised by the formation of unstable intermediates and aromatic compounds, especially when hydrogen availability is insufficient [95]. This deficiency results in significant coke deposition on the catalyst surface, leading to rapid deactivation. The issue is particularly severe in inert atmospheres, where the lack of hydrogen to stabilize the carbon pool exacerbates coke formation [96]. Even small amounts of coke can impair both noble and non-noble metal catalysts, emphasizing the need for catalysts that are either resistant to coke formation or can be easily regenerated [91].

In hydrogen-free deoxygenation processes, the tendency for coke formation poses a significant limitation, particularly when processing long-chain reactants. Moreover, these processes face challenges in achieving complete conversion of triglycerides due to restrictions in β-elimination reactions [96]. As a result, hydrogen-free deoxygenation, despite its apparent cost advantages over hydrodeoxygenation (HDO), may not be as economically viable due to its lower catalytic activity, reduced conversion rates, and poor selectivity for desired products.

For sulfided metal catalysts, deactivation can also occur from sulfur depletion caused by oxidation and coke formation. In such cases, sulfur sites on the catalyst may be regenerated by introducing a sulfur source, such as hydrogen sulfide (H_2S), into the reaction. However, catalyst regeneration is only feasible up to a certain extent; beyond a critical point, sulfur site degradation becomes irreversible [96]. Additionally, increasing the catalyst loading during deoxygenation can help slow the rate of deactivation, thereby extending catalyst life and maintaining process efficiency.

- *Catalyst Support*

As previously discussed, the synergy between the active metal and its support is crucial for optimal catalytic performance. Commonly used catalyst supports include carbonaceous materials and SiO_2, which are favored for their inertness toward the deoxygenation reactants and products [96]. Other materials, such as zeolites and alumina, have also been utilized as supports in lipid deoxygenation processes [87]. These materials are considered acidic supports, with zeolites containing a significant number of Brønsted acid sites, while alumina supports predominantly feature Lewis acid sites [96]. On the other hand, reducible oxide supports like ZrO_2, TiO_2, CeO_2, and Cr_2O_3 are less suitable for hydrogen-free reaction atmospheres, as they require activation by hydrogen [96].

3.2.3.2. Reaction Temperature

The reaction temperature plays a crucial role in controlling catalytic activity and product selectivity during the deoxygenation process [94]. Since DCOx reactions are endothermic, they generally favor higher temperatures compared to the exothermic HDO reaction, where selectivity can decrease at elevated temperatures [96]. However, excessively high temperatures can negatively affect the selectivity of the deoxygenation process, regardless of the reaction pathway. This is due to the increased rate of thermal cracking and the formation of aromatic compounds at higher temperatures [21]. As a result, higher molar ratios of H_2 to lipids are often required to mitigate thermal decomposition and the formation of aromatic compounds. Optimizing reaction conditions remains essential to achieving the best reaction rates, product selectivity, and overall economic feasibility.

3.3. Hydrocracking

Hydrocracking is a catalytic process that breaks down complex organic molecules, such as heavy hydrocarbons, into simpler, lighter hydrocarbons under elevated hydrogen pressures [112]. It is widely used in petroleum refining to upgrade hydrocarbon mixtures into valuable products like diesel, gasoline, and jet fuel [112-114]. The process involves both cracking and hydrogenation reactions, which result in phase separation of the products [115]. Hydrogenation occurs in compounds containing olefins, aromatics, sulfur, nitrogen, and oxygen, while cracking takes place at C–C bonds, leading to the saturation of double bonds, removal of heteroatoms, and isomerization [114]. Non-catalytic hydrocracking (thermal hydrocracking) is nearly impossible because a catalyst is essential to initiate the hydrogenation reactions [116]. The hydrocracking process produces higher-quality products compared to other cracking methods, due to the accompanying hydrogenation reactions, resulting in saturated hydrocarbons that can be used without further processing [113, 116].

The catalysts used in hydrocracking are bi-functional, possessing both acid and metal properties [112]. These dual functions significantly impact the product distribution of the process [117]. The acid function handles cracking and isomerization, while the metal function is responsible for hydrogenation and dehydrogenation [113, 118]. Hydrocracking is sensitive to the thermodynamic equilibrium between the endothermic cracking reactions and the exothermic hydrogenation reactions, meaning hydrogen consumption is influenced by the reaction temperature [115]. High hydrogen partial pressures help suppress unwanted issues like coking, catalyst fouling, and repolymerization [112, 116]. Additionally, the heat energy input drives the cracking of long hydrocarbon chains [116]. The extent of hydrocracking, and hence the product selectivity, is affected by factors such as reaction temperature, catalyst properties, hydrogen partial pressure, and reaction time [112].

3.3.1. Reaction Temperature

The hydrogenation reaction is favored at lower temperatures due to its exothermic nature, meaning that hydrogen consumption increases as reaction temperatures decrease. While lower temperatures result in slower reaction rates, they also help suppress the formation of coke and aromatic compounds [115, 119]. As the temperature increases, conversion rates improve, but this comes at the cost of selectivity for valuable liquid products, as excessive cracking occurs at very high temperatures [116, 119]. At extremely high reaction temperatures, the influence of the catalyst becomes less effective, and controlling the product distribution becomes more challenging. The optimal hydrocracking temperature is one where both high conversion and selectivity are achieved simultaneously.

3.3.2. Hydrogen Pressure

The presence of hydrogen helps suppress the formation of free radicals, which are responsible for cracking and overcracking hydrocarbon molecules [116]. It also promotes the increased yield of saturated hydrocarbons while inhibiting the formation of coke and aromatic compounds by saturating olefins [116, 119]. Additionally, increasing hydrogen pressure improves catalyst activity by regenerating the catalyst's active sites. This occurs through the conversion of coke deposits on the catalyst surface into gaseous organic compounds, which are then released from the catalyst, thereby extending its lifespan [114].

3.3.3. Catalyst

Catalyst activity plays a crucial role in determining product distribution, total conversion, and production costs in hydrocracking processes [119, 120]. A typical hydrocracking catalyst is a heterogeneous solid powder composed of an acidic support with metal impregnated over it [116, 119]; in some slurry-phase hydrocracking processes, homogeneously dispersed catalysts have also been utilized. The acidic support is responsible for cracking reactions, while the metal component catalyzes the hydrogenation reactions [113, 114]. A strong hydrogenation function minimizes coke formation by hydrogenating coke precursors and enhances product selectivity by quenching free radicals generated during cracking reactions, preventing further cracking that could lead to excessive gas formation [114, 116, 119]. Additionally, acid-catalyzed reactions such as dehydrocyclization can occur during catalytic hydrocracking [116].

The performance of the catalyst depends on its composition, preparation method, and the operating conditions [114]. The metallic component can consist of noble or non-noble metals from groups VI-A and VIII-A of the periodic table [97, 114, 116], and it may involve single or mixed metals, such as cobalt and molybdenum combinations [112,113]. However, noble metals are economically unattractive for large-scale applications due to their high cost [97]. The acidic support is typically an amorphous oxide, such as silica-alumina (ASA), ultra-stabilized Y (USY) zeolite, sulfated zirconia, or a combination of these materials [112, 117, 119]. The Brønsted acidity of the support significantly affects product selectivity, with higher acidity promoting selectivity toward lighter products [118]. Lower acidity tends to reduce reaction rates, which can be countered by increasing the reaction temperature [117]. The catalyst's acidity and shape-selectivity also play a role in its resistance to deactivation [120, 121].

An ideal hydrocracking catalyst promotes high hydrocarbon conversion and product selectivity under moderate process conditions, thus improving process efficiency [116, 120]. It should enhance the reaction rate while minimizing overcracking and reducing olefin content in the final products. Catalyst deactivation generally occurs due to the deposition of carbonaceous materials, such as coke, which block the catalyst's pores during the reaction [119]. Regeneration of some catalysts can be achieved by burning them in air or passing hydrogen over them at high temperatures [112]. Modifying the catalyst's textural properties may also extend its lifespan [114]. Catalysts with longer lifespans are more economically viable from both operational and maintenance perspectives [119].

4. Development of the Biodiesel Synthesis Strategy

Based on the literature reviewed in this study, it is evident that the main limitations of transesterification-produced biodiesel—such as poor cold flow properties, oxidation stability, and energy density—are influenced by factors including the degree of saturation, the length of carbon chains, and the presence of oxygen in the structure. The oxygen content in biodiesel originates from the vegetable oils used as feedstocks, which contain oxygen atoms in the form of carboxyl or carbonyl groups [22], as well as from the alcohol used during transesterification.

The key reaction for producing high-quality, diesel-like hydrocarbons is the deoxygenation reaction, which involves the removal of oxygen from biomass-derived oils through hydrodeoxygenation, decarboxylation, and decarbonylation, either separately or in combination [94, 95, 99]. The hydrocarbon fuels obtained from this deoxygenation process typically exhibit a high cetane number (CN), but limitations remain due to poor cold flow properties, often linked to the long carbon chains. To address this, mild hydrocracking following deoxygenation can be employed to improve cold flow properties, yielding biodiesel with characteristics similar to petrochemical diesel [22].

A comparable approach was reported by Kim *et al*. [121], for biojet fuel synthesis. In these studies, the deoxygenation products of triglycerides were subsequently hydrocracked to produce biojet fuel, which meets ASTM specification D7566-14 and can be blended into commercial jet fuel at up to 50% by volume. The removal of oxygen enhances the calorific value and reduces the corrosiveness of the fuel, while hydrogenation helps to saturate carbon chains, improving oxidation stability. Furthermore, hydrocracking reduces the carbon chain length to match that of petroleum diesel (C13-C20), thereby improving cold flow properties [20, 97].

Other researchers have explored hydrotreatment as a means to enhance the properties of transesterification-produced biodiesel. However, the transesterification route is prone to saponification, particularly when using low-cost feedstocks such as waste cooking oils, due to its sensitivity to fatty acids. Additionally, it requires substantial investment in reactors, catalysts, alcohol, and energy. As such, the strategy illustrated in Fig. (**7**) below is proposed for synthesizing biodiesel from castor oil.

The strategy becomes economically viable for industrial applications when catalyzed by non-noble, highly active catalysts, such as Ni-based bimetallic catalysts on suitable supports, with deoxygenation conducted under modest hydrogen conditions. While a single-step hydrodeoxygenation-hydrocracking process is possible, it is not ideal for several reasons. Specifically, the carbon monoxide (CO) generated through decarbonylation can poison the metal component of the catalyst, disrupting the balance between the metal and acid functions in the hydrocracking reaction [121]. This imbalance can lead to overcracking of the hydrocarbons and premature catalyst deactivation due to the excessive formation of aromatic species and coke [95]. As a result, the yield of the final product is significantly influenced by the hydrocracking step, where excessive cracking can lead to the production of undesirable short-chain gaseous hydrocarbons [121, 122].

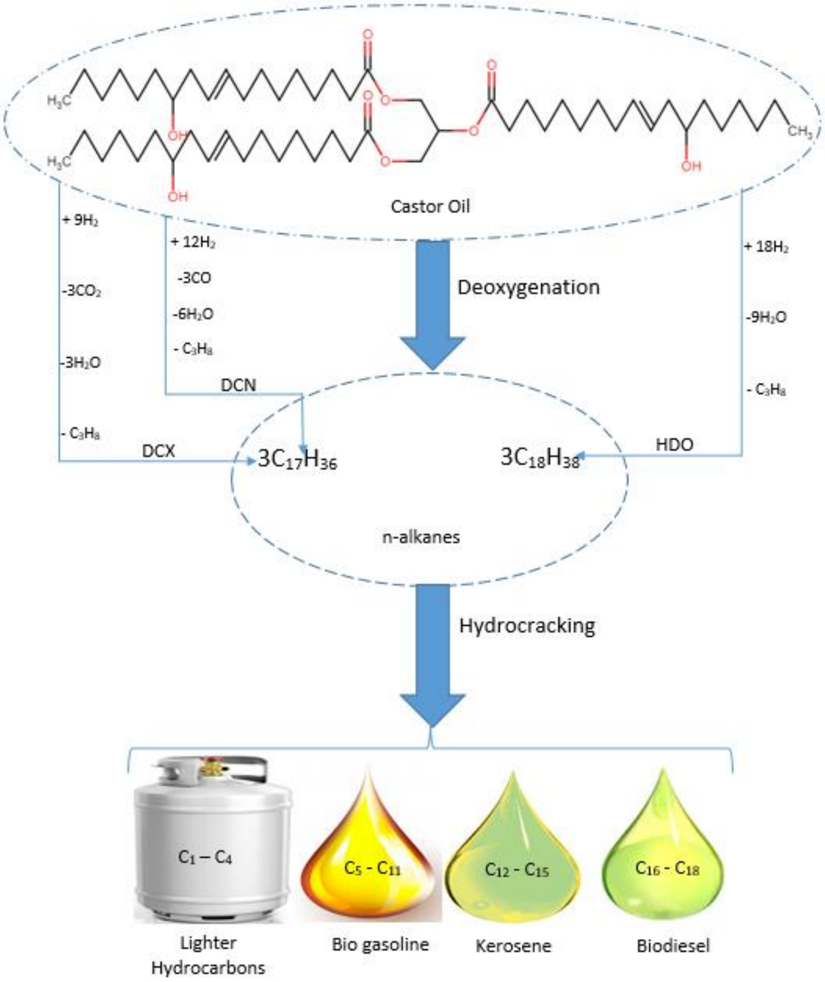

Figure 7: The proposed biodiesel synthesis strategy.

Depending on the reaction conditions, this process can also produce other valuable liquid fuels, such as bio-gasoline and biojet fuels.

5. Conclusions

The currently commercially produced biodiesel, in the form of Fatty Acid Alkyl Esters, faces limitations for use in modern diesel engines due to the oxygen content in its composition. This oxygen presence hinders its use as a pure fuel and restricts the blending proportions with petroleum diesel. The properties of biodiesel are heavily influenced by the feedstock and the synthesis method employed. Deoxygenation is a promising process for producing renewable diesel from vegetable oils, achieved through a combination of hydrodeoxygenation, decarbonylation, and decarboxylation pathways, depending on the reaction conditions.

In hydrogen-rich environments, hydrodeoxygenation predominates and is effective but costly. However, this pathway helps maintain catalyst activity for longer periods compared to hydrogen-free environments. In contrast, the decarbonylation and decarboxylation pathways are favored in hydrogen-free conditions. These pathways produce n-alkanes and n-alkenes with fewer carbon atoms due to the C–C bond scission involved, but they are prone to rapid catalyst deactivation, which reduces the overall yield of renewable diesel.

Lower temperatures promote hydrogenation reactions, whereas higher temperatures favor cracking reactions. However, excessively high temperatures can lead to undesirable aromatization and coke formation, which exacerbates catalyst deactivation and results in hydrocarbons with lower calorific value. Therefore, the development of a two-step biodiesel synthesis strategy, involving separate deoxygenation and hydrocracking processes, is critical for industrial-scale production. This approach minimizes catalyst deactivation, produces biodiesel with no oxygen content, and enhances cold flow properties, making it more suitable for engine use.

Existing literature on biodiesel blending techniques in biorefineries mostly focuses on traditional transesterification and hydrotreated vegetable oils (HVOs), but considerable gaps remain in addressing significant constraints such as oxidation stability, cold flow characteristics, and energy density. Existing techniques usually fail to reach high blending ratios without sacrificing engine performance or needing costly additives and process adjustments. Additionally, the dependency on hydrogen in HVO synthesis raises costs and restricts scalability. There is a need for novel biodiesel production technologies that boost fuel qualities while retaining cost-effectiveness and sustainability, enabling seamless integration into existing refinery infrastructure and lowering dependence on fossil fuels. Future research should focus on optimizing reaction conditions to achieve deoxygenation efficiencies above 95%, while maintaining catalyst stability for extended operational periods, thereby improving the yield and energy density of renewable diesel for large-scale industrial applications

Recommendations

To improve the sustainability and economic feasibility of biodiesel production, prioritising its integration with other biorefinery processes is essential. This method facilitates the joint use of feedstock, enhances process efficiency, and allows for the co-production of valuable by-products including glycerol and bio-based compounds. Nevertheless, issues such feedstock unpredictability, process optimisation, and infrastructure compatibility must be resolved by sophisticated catalytic technologies, efficient separation methods, and governmental assistance. Future research must concentrate on creating integrated biorefinery models that enhance resource utilisation while guaranteeing economical and scalable biodiesel production.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that have appeared to influence the results reported in this paper.

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