

Biodiesel Production by Heterogeneous Catalysis and Eco-friendly Routes

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Abstract

Biodiesel is produced on a large scale as an eco-friendly substitute and additive to fossil fuels. Catalytic homogeneous processes using strong acids, alkalis, and natural oils have been realized in industry. However, these traditional methods have several disadvantages, such as the generation of large volumes of waste, high water and reagent needs, use of hazardous reagents, high operation costs, and utilization of valuable feedstocks and catalysis, respec-

tively. Different solutions have subsequently been investigated, such as cheap alternative feedstocks, co-solvents and catalysts, sustainable operational conditions, advanced reactor designs and scales, and advantageous pre- and post-reaction treatments. This review explores and analyzes the main aspects of current biodiesel technologies and opportunities. It also describes some advanced improvement strategies.

Keywords: Biodiesel, Heterogeneous catalysts, Microfluidics, Sustainable technology, Waste cooking oil

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1 Introduction

Currently, biodiesel represents the most promising renewable fuel for replacing diesel [1,2]. New technologies have constantly evolved to improve the efficiency and quality of production processes and products. Although the biofuel market has been steadily increasing, it has experienced major challenges with feedstocks, industrial operation conditions, and biofuel prices. Current biofuel feedstock is comprised largely of edible vegetable oils from the food sector. Alternative, non-competing feedstocks for the production of biodiesel have been proposed, in particular non-edible and recovered (waste) oils.

Biodiesel is a mixture of long-chain fatty acid alkyl esters (FAAE) produced mainly by esterification, transesterification or both processes concurrently. The most common reaction, i.e., transesterification, occurs between triglycerides (TGL) and alcohols in the presence of a catalyst, such as strong acid or alkali, producing FAAE and glycerol. Manufacturing processes are commonly conducted using batch or continuous large-scale reactors and homogeneous catalysts. However, these methods demand extensive separation and product purification procedures that generate large amounts of waste [3]. Likewise, they require many unit operations and specialized equipment suitable for operations under corrosive and hazardous conditions. Some of these disadvantageous process parameters may be overcome by solid eco-friendly catalysts or continuous-flow operation.

Different sustainable catalysts such as metal oxides, enzymes, zeolites, alumina, and modified waste materials have been studied [4–9]. Heterogeneous catalysts are easily removed and regenerated, safer to use, and commonly less corrosive [10–13]. Bifunctional catalysts for simultaneous esterification and transesterification are promising because they allow mild operational conditions and lower equipment and operation costs. For example, sulfonated metals such as $\text{Al}(\text{HSO}_4)_3$ enable the esterification and transesterification of feedstock with high free

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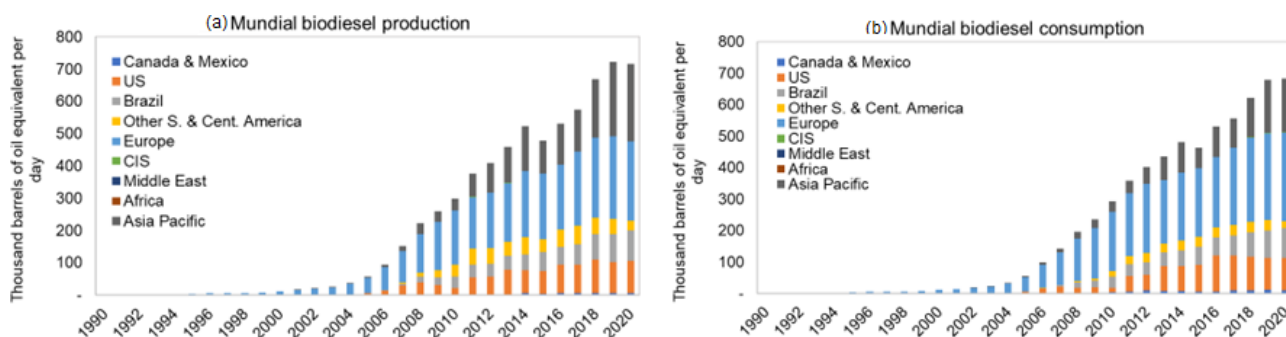


Figure 1. Global biodiesel production and consumption between 1990 and 2020. (a) Biodiesel production, (b) biodiesel consumption. Reprinted with permission from "Statistical Review of World Energy 2021" [31].

fatty acid (FFA) and water contents (i.e., waste cooking oil) without saponification but with easy catalyst recovery and reuse [14]. However, heterogeneous catalysts may leach and deactivate easily [15–17].

A different approach employs heterogeneous photocatalysis, which has been applied effectively to esterification processes [18–21]. The advantages of photocatalytic materials are their generally low cost, high stability, easy handling, post-reaction recovery, and reusability [9,22]. Photocatalysis also does not involve saponification or catalyst leaching. Catalyst-free processes represent another eco-friendly option. For example, supercritical conditions can be applied for esterification and transesterification, but they necessitate extreme operational settings and equipment. High-purity feedstock is furthermore desired because the water content can interfere with the esterification process, favoring hydrolysis.

The implementation of microscale plants offers an attractive alternative to traditional batch operations. Microplants naturally require smaller amounts of catalyst, enable shorter residence times, and provide higher heat and mass transfer, easier management, maintenance, and operational control [23]. Scale-up is typically achieved by serial or parallel operation of several microdevices [24–26]. The inner structures of these devices promote turbulent mixing that increases mass transfer and hence reduces residence times and the amount of alcohol and catalyst required. Although microscale processes commonly employ homogeneous catalysts to avoid clogging, heterogeneous operations have been developed.

Other important operation parameters include catalyst immobilization and reuse, process efficiency, and product quality. This review analyzes some of the most important aspects of biodiesel production, comparing and discussing conventional and recent technologies. Moreover, this paper features eco-friendly routes by evaluating feedstock, catalysts, processes, product purity, and waste generation.

2 Current Status and Challenges

2.1 Biodiesel Market

Since 2005, global biodiesel production has increased by more than seven times [27]. In 2018, biodiesel production equalled 29 % of petroleum-derived diesel production [28]. Similarly, 41

billion liters were produced in 2019 [28], with the US, Brazil, and Europe as the biggest biodiesel markets (Fig. 1). In 2016, its market value reached USD 34.1 billion and was projected to grow to USD 41.2 billion in 2021 [29]. While biodiesel production saw a decline of approximately 10 % in 2020 due to the Covid-19 pandemic, it is expected to reach 46 billion liters between 2023 and 2025 [28]. The prices for biofuels and their feedstocks have developed similarly over the last decade, but there has recently been a sharp decline, with a further reduction expected for biodiesel [30].

Currently, biofuel feedstock mainly comprises of edible oils with almost 8 % of the total grain consumption [32], and has thus been competing with the food sector. While grain production has seen a steady increase in the last decade, this was mainly driven by feed and food sectors (Fig. 2). Because biodiesel costs approximately 40 % more than petrodiesel [33] and because the biodiesel process is between 1.5 and 3 times more expensive [34], low-cost feedstocks for its production are highly desirable. Non-edible oils and waste oils are frequently proposed as alternative, cheap, and non-competing raw materials for biodiesel production. While the use of non-edible oils still competes indirectly with edible oils due to the need for planting, contributing to deforestation, the utilization of used and recovered waste oils is considered a more sustainable option. For example, waste cooking oil (WCO) represents a

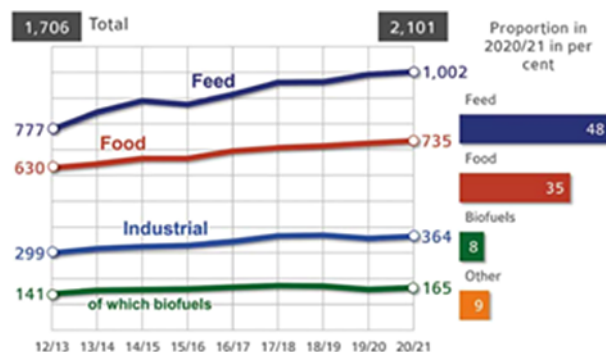


Figure 2. Global grain consumption between 2012 and 2021 estimated in millions of tons. Grains: barley, maize, millet, oat, rye, and wheat. Industrial: production of starch, beer, alcohol, and bioethanol. Other: other industrial uses, seed, and losses. Reprinted with permission from [35], Copyright: © AMI 2021 | Source: IGC.

significant environmental burden that demands urgent solutions. In addition, implementing WCO as feedstock will produce biodiesel at a more competitive price.

The growing importance of biodiesel has naturally led to significant research and technology development efforts over the last years (Fig. 3). As part of this, the interest in the utilization of WCOs and alternative feedstocks with high FFA content has increased, while the use of edible oils such as soybean has decreased. Moreover, new technologies exploiting raw materials with high FFA content, which cannot be converted using conventional alkaline conditions, have been developed.

The use of biodiesel has many advantages over conventional fuels (as defined by ASTM D6751, EN 14214, and IS 15607) [32]:

- Complementation or replacement of fossil fuels without modification of current engines [15].
- Availability from renewable sources, i.e., vegetable oils, WCO, and animal fat [27, 37–39].
- A much higher biodegradability of 90 % for biodiesel (30 days) compared to 24.5 % for petrodiesel [40].
- Lower greenhouse gas (GHG) emissions by as much as 86 % during production and use (lifecycle) [41, 42].
- Zero-sulfur content, which reduces atmospheric pollution. In contrast, petrodiesel fuels contribute up to 80 % of the SO₂ in the atmosphere due to incomplete combustion [41, 43].
- The US biodiesel industry is expected to achieve annual GHG reductions of more than 35 million tons by 2022 [41].
- The flash point (>130 °C) is higher than that of diesel (60–80 °C). A higher flash point makes it more difficult for the vapors to ignite, allowing safer handling [44].

These characteristics are critical in the context of rising global energy consumption. By 2050, the global energy demand and fuel requirement are expected to increase by 53 % [28, 45, 46] and 59 % [45], respectively. Without further intervention, GHG emissions are projected to rise by 39 % by 2030 [45, 47]. For the transportation sector, which is responsible for 58 % of the fossil fuel consumption [48], electric cars have been proposed

as alternative vehicles. However, these require high-capacity batteries and their manufacturing shows unfavorable GHG emissions. Nevertheless, electrification and biofuels have been proposed as complementary technologies to reach Green Deal targets [42].

Moreover, biodiesel represents an alternative fuel for trucks, trains, boats and barges, construction equipment, diesel generators (hospitals and remote areas), and other industrial facilities. The U.S. military uses large quantities of diesel fuel for its vehicles because of its lower flammability and explosivity, which could be substituted with biodiesel [49].

2.2 Feedstock

Triglycerides (TGL) and free fatty acids (FFA) can be used as biodiesel feedstock. Vegetable oils represent the most common raw material, and their contents of TGL and FFA vary, as described in Tab. 1.

Edible oils, such as canola and palm oil, have also been utilized for biodiesel production (Fig. 4), with palm oil being currently the most common worldwide. In contrast, Europe uses more rapeseed/canola oils. However, the consumption of edible oils has decreased (animal fats, canola oil, and soybean oil), except for palm oil, and the use of WCO has increased. Reusing waste oils can improve the cost efficiency of biodiesel production because raw materials account for approximately 60–80 % of the total costs [50]. Another option to reduce the price of raw materials is the use of distilled fatty acids obtained as a by-product from the oil refining process, which are currently used in the production of alkyl resins for paints, lubricant formulation, and animal feed [51].

Waste Cooking Oil (WCO)

Waste cooking oil is a non-edible resource with a high FFA content [63, 64]. During the frying process, the oil is heated in the

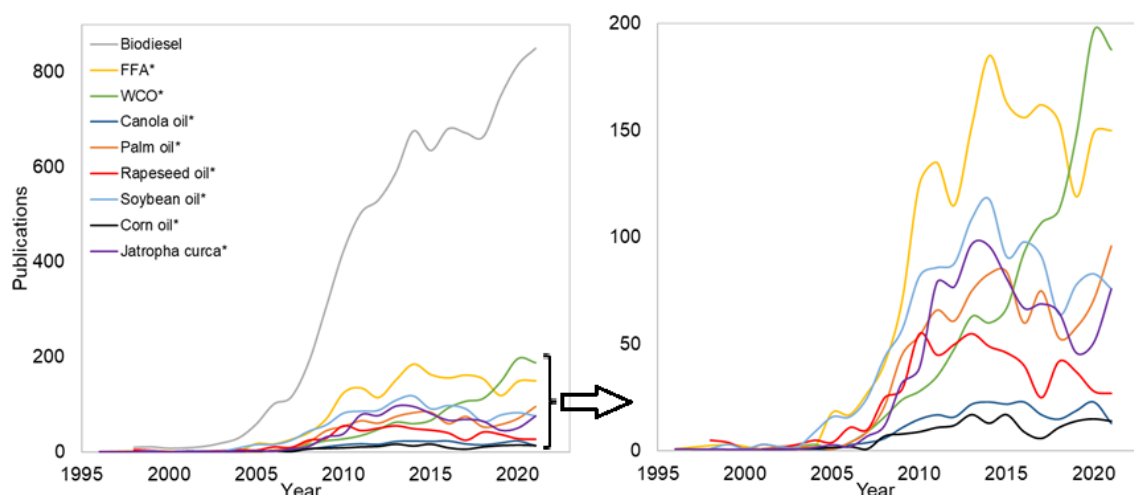
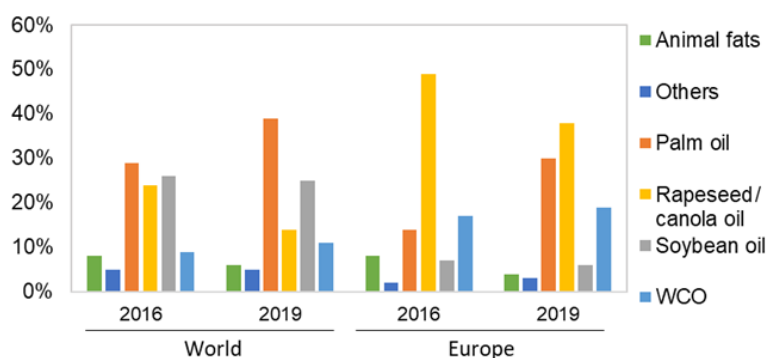


Figure 3. Scientific publications based on biodiesel production. *Considers publication with the “respective subject + Biodiesel”. Database: ScienceDirect [36].

Table 1. FFA content of biodiesel feedstock.

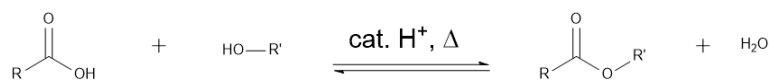
Feedstock	FFA content	Oleic acid (C ₁₈ H ₃₄ O ₂)	Linoleic acid (C ₁₈ H ₃₂ O ₂)	Linolenic acid (C ₁₈ H ₃₀ O ₂)	Palmitic acid (C ₁₆ H ₃₂ O ₂)	Stearic acid (C ₁₈ H ₃₆ O ₂)	Ref.
Animal fat ^{a)}	7–50 %	38 %	–	–	19 %	3 %	[52]
Brown grease ^{b)}	> 15 %	29–46 %	28–43 %	0.8 %	18–23 %	7–13 %	[52–54]
Jatropha oil	15 %	43 %	15 %	–	15 %	7 %	[4, 52, 55]
Palm oil	3–10 %	40 %	10 %	–	43 %	5 %	[56, 57]
Rapeseed/canola oil	10–18 %	61 %	21 %	10 %	–	–	[58]
Soybean oil	< 1 %	23 %	54 %	8 %	7 %	3 %	[52, 55]
WCO	> 10 %	38–44 %	26–32 %	0.2 %	4–26 %	1–10 %	[59, 60]
Yellow grease ^{c)}	< 15 %	22–48 %	21–38 %	1–5 %	10–23 %	13 %	[53, 59, 61]

^{a)}Chicken fat; ^{b)}WCO with FFA content < 15 %; ^{c)}WCO with FFA content > 15 %.


Figure 4. Biodiesel production feedstock. Compiled data from [35, 62].

presence of water from food and air at high temperatures (160–200 °C). This process causes hydrolytic, oxidative, and thermolytic changes. The water and FFA contents in WCO are thus higher than in crude edible oil. These cause an increase in viscosity and specific heat, a change in surface tension, color, and a higher tendency to foam [65, 66]. WCOs with FFA content < 15 % and > 15 % are called yellow and brown grease, respectively [53].

WCO is considered an environmental problem because of its necessary disposal [67]. For example, the European Union collects 0.7–1 million tons of yellow grease annually [68]. Canada produces 120 000 tons of yellow grease (FFA < 15 %) per year [69]. Consequently, WCO has been proposed as an inexpensive and abundant feedstock to produce biodiesel [68]. For this, pretreatment steps are required, i.e., filtration, water content removal, and FFA reduction. The FFA content can be converted to biodiesel by an esterification process. Esterification and transesterification can operate in series or simultaneously. The order of the reactions depends on the catalyst and operational conditions. Biodiesel from WCO is frequently darker. Although ASTM D 6751 does not specify coloration, it can be decolorized easily using an activated carbon bed [70].


Figure 5. Esterification by acid catalysis.

3 Mechanisms of Biodiesel Generation

Esterification and transesterification are the most common routes to produce biodiesel. However, interesterification has been considered as a third option to produce fatty acid ethyl ester (FAEE) [71]. Fischer-esterification describes the reaction between a free fatty acid and an alcohol in the presence of a catalyst, generating biodiesel and water (Fig. 5). The esterification reaction of FFA occurs preferably in the presence of a short-chain alcohol (methanol, ethanol or propanol) [72–76]. A high volume of alcohol is commonly used to prevent the backward reaction (hydrolysis). The most common catalyst is a strong mineral acid, such as sulfuric acid [3]. Esterification is often applied as pretreatment step for oils with a high FFA content such as WCO.

Transesterification is the main reaction applied on large scales industrially and utilizes either strong acids or alkalis as catalysts. Under acidic conditions, the reaction generates biodiesel and glycerine (Fig. 6). In contrast, base-catalysis (saponification) furnishes the corresponding fatty acid salts instead.

Both reactions require high temperatures up to 120 °C [75] and demand considerable energy and specific unit operations when working with short-chain alcohols at temperatures higher than their boiling point. Different technologies have been explored to optimize biodiesel production (Tab. 2) with various operation conditions, catalysts, reactors, and efficiency, respectively.

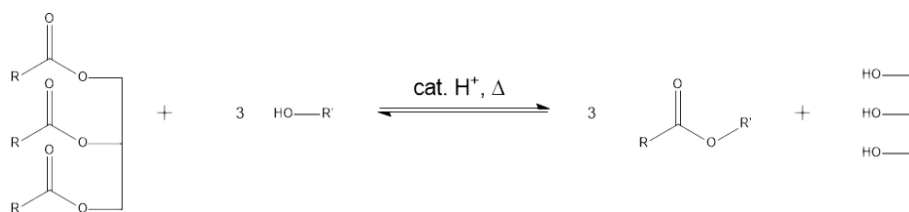


Figure 6. Transesterification by acid catalysis.

Table 2. Biodiesel production by different technologies.

Reactional medium	Advantages	Disadvantages
<i>Homogeneous</i>		
Supercritical conditions	Product with high purity Less or no catalyst [77–81]	High temperature (> 250 °C) High pressure (> 10 mPa) Requires pretreatment to remove water [77–82]
Microwave	High efficiency, fast reaction Mild operational conditions Less or no catalyst [58, 83–87]	Selective heating Overheating of solvent Catalyst and medium hotspots Reagent diffusion limited [88–93]
Strong bases (KOH, NaOH)	Fast reaction [15, 16] Catalyst readily available [64]	Soap formation Requires highly refined oil [15–17] FFA content < 0.5 % [15, 16, 94] Product difficult to purify Catalyst difficult to recover [95, 96] High volumes of wastewater [64]
Strong acid (H ₂ SO ₄)	Applicable to FFA [15–17, 95, 96], Catalyst readily available [64]	Product difficult to purify Catalyst difficult to recover [95, 96] Biodiesel with a sulfur content higher than 100 ppm (standard limit) [64]
<i>Heterogeneous</i>		
Bases (CaO)	Ease of recovery [15–17] Reduced corrosion [64] Reduced toxicity [64]	Low activity Requires high temperature and alcohol content Water poisonous to active sites Easy leaching and active site deactivation [15–17, 95, 96]
Acid Al(HSO ₄) ₃	Simultaneous esterification and transesterification Applicable to feedstock with high FFA and water contents [15–17] Reduced corrosion Reduced toxicity [64]	Requires high temperature and alcohol content Water poisonous to active sites Easy leaching and active site deactivation [15–17]
Metal oxides (Cr.SiO ₂)	Esterification and/or transesterification [97, 98] Reduced toxicity Easy recovery [14,99]	Limited reuse [100] Easy leaching and active site deactivation [15–17] High temperatures [17, 101] Water poisons the active sites [17]

Table 2. Continued.

Reactional medium	Advantages	Disadvantages
Photocatalysts (TiO ₂ +UVA)	Simultaneous esterification and transesterification [98]	Slow reaction
		Parallel and non-desirable reactions
	High physical and chemical stability	Deactivation by impregnation of organic material [21, 98, 102]
	Easy handling	
	Easy recovery	
Biocatalysts (lipases)	High product purity [9, 22]	
	Mild operational conditions [103–107]	Low reaction efficiency
	Esterification and transesterification	Easy leaching and deactivation of active sites [104, 108–110]
	High product purity	
	Low wastewater generation [104, 108–110]	

3.1 Non-catalytic Routes

3.1.1 Supercritical Conditions

Processes under supercritical conditions can be applied for esterification and transesterification (Tab. 3) but require high temperatures (> 250 °C) and pressures (> 10 mPa) [77–82]. The properties of the alcohol employed, such as dielectric constant, viscosity, specific gravity, and polarity, must be considered for supercritical processes [40, 80, 111–113]. The water content can interfere with the esterification process, favoring hydroly-

sis. Similarly, the transesterification of feedstock such as TGLs with high water content, can produce FFA and glycerol [77]. The process can be conducted in the presence of an acid catalyst, subsequently improving the reaction efficiency.

Methanol is the most common alcohol used for biodiesel production under supercritical conditions [77]. It is a polar solvent with hydrogen bonding between molecules. Under supercritical conditions, the degree of hydrogen bonding decreases, reducing its polarity and increasing solubility [77, 114]. Moreover, nonpolar TGLs are solvated by methanol. This feature results in a one-phase mixture with improved mass transfer,

Table 3. Biodiesel production under supercritical conditions.

Reactor	Reaction	System	Feedstock	Alcohol	Oil/ alcohol	T [°C]	Pressure [mPa]	t [min]	Biodiesel [%]	Ref.
Batch	Est	Hom	FFA ^{a)}	MeOH	1:1.6	270	10	30	97	[114]
Batch	Est	Hom	Levulinic acid	EOH	1:09	280	15	10	80	[119]
Batch	Est	Hom	Oleic acid	MeOH	1:20	260	20	60	95	[120]
Batch	Est/Trans	Het	Palm fatty acid distillate	MeOH	1:6	290	40	30	98	[121]
Batch	Est/Trans	Hom	Palm fatty acid distillate	MeOH	1:6	290	40	30	78	[121]
Batch	Est/Trans	Hom	Rapeseed oil	MeOH	1:14	270	15	17	97	[122]
Batch	Est/Trans	Hom	Rapeseed oil	MeOH	1:09	270	30	20	94	[80]
Batch	Est/Trans	Hom	WCO+crambe oil	EtOH	1:02	300	30	20	70	[115]
Batch	Trans	Hom	Jobba oil	MeOH	1:30	287	12.3	23	96	[123]
Batch	Trans	Hom	Chicken fat	MeOH	1:6	400	41.1	6	88	[124]
Cont flow	Est/Trans	Hom	Chicken fat	MeOH	1:20	280	110	60	97	[125]
Cont flow	Trans	Hom	Chicken fat	MeOH	1:9	375	20	10	84	[126]
Microbatch	Interest	Hom	Refined palm oil	Ethyl acetate	1:50	350	200	20	52	[71]
Microbatch	Trans	Hom	Rice bran oil	EtOH	1:5	300	8.5	24	75	[127]

^{a)}Mixture of FFA: 88 % oleic acid, 4.5 % linoleic acid, 3.5 % palmitic acid, and 4 % others.

which consequently improves yields of FAME production [80, 112, 115, 116]. Unsaturated fatty acids (oleic, linoleic, and linolenic) as feedstocks react easier than saturated fatty acids (palmitic and stearic) [40, 80, 111–114, 117, 118]. Different reactor designs have been considered, of which the batch process represents the most commonly applied.

3.1.2 Microwave-Assisted Conditions

Activation with microwaves has been applied for esterification and transesterification (Tab. 4) [87, 128–131]. Through this process, friction and collision occur between molecules, which generate heat. Reaction is achieved quickly under mild operational conditions and with smaller amounts of catalyst [58, 83–87]. Irradiation can be conducted continuously or pulsed [129, 130] and applied to different feedstocks. The limitations of this process are caused mainly by the catalyst [129, 130, 132–134]. Additional drawbacks include selective heating, overheating of polar solvents, the generation of hotspots around solid catalysts, and the limitations of reagent diffusion [88–93].

3.1.3 Miscellaneous Methods

Other methods for esterification and transesterification have been explored (Tab. 5), such as electrolysis, reactive distillation, and assisted plasma [144–151]. These investigations were prompted by the need for mild operational conditions and the utilization of feedstock with high FFA contents. The procedures developed commonly operate with reduced amounts of catalyst or even without.

3.2 Catalytic Routes

Catalytic routes are the most common for the production of biodiesel. Homogeneous or heterogeneous systems were devel-

oped using acids, alkalis, oxides, and biocatalysts in free or immobilized forms. Based on the catalyst used, different operational conditions (e.g., temperature, molar ratio, mixing, catalyst loading, and pH), feedstock (e.g., FFA, crude edible oil, and WCO), reaction types (e.g., esterification and transesterification), and reactor systems (e.g., batch, continuous flow, and microdevices) have been explored.

Bifunctional catalysts have emerged to carry out esterification and transesterification reactions either consecutively or simultaneously. The utilization of bifunctional catalysts that operate in two subsequent steps increases the process costs. While these materials can be easily adapted to existing conventional plants, their complexity naturally makes them expensive to produce. In addition, the implementation of such catalysts may result in low efficiency, poor reusability, or leaching. The use of bifunctional catalysts for simultaneous esterification and transesterification is considered more attractive. The coupled process occurs rapidly under mild operational conditions with low equipment and operation costs. Heterogeneous catalysts are the most commonly employed with the catalytic surface containing acidic and basic sites [156]. However, one-step processes may still be expensive due to the high costs of these advanced catalytic materials, leaching, and rapid deactivation. Their technical implementation also requires changes in the entire industrial plant. The reduction in the catalyst efficiency may affect both transformations, i.e., esterification and transesterification, differently. Additionally, the recovery and reactivation of these tandem materials need to be further investigated.

3.2.1 Homogeneous Catalysis

Strong homogeneous bases or acids as catalysts are widely used in industrial processes (Tab. 6), but they are corrosive, hazardous, and not environmentally friendly [27, 45, 157]. The alkali-catalyzed process is the most common for large-scale operation [39], is applied only for transesterification, and requires harsh

Table 4. Biodiesel production by microwave-assisted irradiation.

Reactor	Reaction	Syst.	Feedstock	Alcohol	Oil/ alcohol	Power [W]	Catalyst	[wt %]	<i>t</i> [min]	Biodiesel [%]	Ref.
Batch	Est	Het	Silk-cotton seed oil	MeOH	1:18	270	CaO	0.3	114s	98	[135]
Batch	Est	Het	PFAD	MeOH	1:9	–	TiO ₂ -GO	4	20	93	[136]
Batch	Trans	Hom	WCO	MeOH	a)		KOH	0.8	7	98	[137]
Batch	Trans	Hom	<i>Jatropha curcas</i> oil	MeOH	7:11	500	H ₂ SO ₄	2	90	61	[138]
Batch	Trans	Hom	WCO	MeOH	1:8	600	KOH	1.2	6	98	[139]
Batch	Trans	Hom	WCO	MeOH	1:6	750	NaOCH ₃	0.8	10	98	[140]
Batch	Trans	Hom	Camelina oil	MeOH	1:6.91	800	KOH	1.26	5.85	95	[141]
Batch	Trans	Het	<i>Spirulina platensis</i>	EtOH	1:8	800	PEG/MgO/ ZSM-5	2	40	96	[142]
Cont Packed bed	Trans	Het	Waste cotton seed cooking oil	MeOH	1:9.6	180	CaO		9.7	90	[143]

a) 59 vol % methanol/vol % oil.

Table 5. Biodiesel production using miscellaneous methods.

Method	Reaction	Feedstock	Alcohol	Oil/ alcohol	Catalyst	[wt %]	<i>T</i> [°C]	<i>t</i> [min]	Biodiesel [%]	Ref.
Corona discharge plasma	Ester	WCO	Methanol	1:6	–	–	2	110	78 ^{a)}	[146]
Electrolysis	Trans	WCO	Methanol	1:12	KOH	–	120	120	99	[148]
Electrolysis	Trans	WCO	Methanol	1:8	Na ⁺ /zeolite–chitosan	1	25	30	97	[152]
Electrolysis	Trans	WCO	Methanol	1:6	HPMo/support graphene oxide	0.85	25	900	91	[151]
Plasma-assisted	Trans	Ethyl acetate	Methanol	1:6	H ₃ (PMo ₃ O ₁₀) ₄ ·H ₂ O (H ₃ PMo)	10	25	90	77	[145]
Plasma-assisted	Trans	Soybean oil	Methanol	1:15	Active carbon	–	65	30	92	[153]
Plasma-assisted	Trans	Soybean oil	Methanol	1:15	Active carbon+H ₂ SO ₄	–	65	30	74	[153]
Plasma-assisted	Trans	Ethyl acetate	Methanol	1:6	NaOCH ₃	0.1	25	30	90	[145]
Reactive distillation	Est	Dodecanoic acid	2-Ethylhexano	1:1	–	–	130	120	40	[154]
Reactive distillation	Est	Dodecanoic acid	2-Ethylhexano	1:1	Sulfated zirconia-	–	130	120	75	[154]
Ultrasound-assisted	Trans	Canola oil	Methanol	1:7.5	CaO	5.35	60	150	99	[150]
Ultrasound-assisted	Trans	Canola oil	Methanol	1:7	Calcium diglyceroxide	9.33	60	135	82	[150]
Ultrasound-assisted	Trans	WCO	Methanol	1:6	KOH	0.75	30	30	97	[155]
Ultrasound-assisted	Trans	Sunflower oil	Methanol	1:6	KOH	0.75	30	30	94	[155]
Ultrasound-assisted	Trans	Soybean oil	Methanol	1:6	KOH	0.75	30	30	98	[155]

^{a)}Obtained by acid number.

pH ranges of 12 to 14 [158]. However, the process is unsatisfactory for low-cost feedstocks such as WCO due to their high FFA content.

An FFA content of less than 0.5 % is instead desirable [15,16,94] to minimize soap formation (Fig. 7) [15], which demands neutralization by acid and washing for product purification. This procedure may result in an aqueous emulsion that makes separating the desired ester and glycerol challenging and necessitates high water volumes. Consequently, the entire process results in a large volume of wastewater that requires further treatment [64].


Figure 7. FFA reaction with strong bases generating soap and water.

In contrast, the acid-catalyzed process can be applied to feedstocks with high FFA contents since it operates by esterification and transesterification. However, the process is slower

than the alkali-catalyzed method [15,16], requires stainless-steel coating due to corrosion hazards, does not allow catalyst recovery, and requires large water volumes for product treatment. The process is also conducted under elevated temperatures (70–120 °C) and extreme pH conditions. The use of mineral acids, such as H₂SO₄, for esterification also leads to high sulfur contents in biodiesel products, with a maximum of up to 10 ppm allowed according to the ASTM D975-21 [44].

Industrially, the process involving high FFA content containing feedstock is frequently carried out in two steps: (1) esterification of FFA by concentrated sulfuric acid and (2) transesterification of triglycerides by strong alkali [16]. The reaction efficiency depends mainly on the feedstocks' purity, alcohol-to-oil molar ratio, catalyst, and temperature [39]. The most economical conventional process uses batch reactors and mechanical stirring but requires prolonged reaction times and high temperatures. These disadvantages have been overcome using microplants [26], ultrasonic irradiation, and co-solvent addition techniques, which reduce the reaction time and demand lower temperatures [16].

Table 6. Biodiesel by homogeneous catalysts.

Reactor	Reaction	Feedstock	Alcohol	Oil/ alcohol	T [°C]	Catalyst	[wt %]	t [min]	Biodiesel [%]	Ref.
Batch	Est	Palmitic acid	MeOH	1:10	65	H ₃ BW ₁₂ O ₄₀	10.9 mmol L ⁻¹	180	99	[159]
Batch	Est/trans	<i>Chrysophyllum albidum</i> oil	MeOH	1:9	65	H ₂ SO ₄	1	40	99	[160]
Batch	Trans	WCO	MeOH	1:8	65	KOH	1	90	90	[161]
Batch	Trans	WCO	MeOH	1:9	70	KOH	1	120	98	[162]
Batch	Trans	WCO	MeOH	1:3	60	KOH	1	60	94	[163]
Batch	Trans	WCO	MeOH	1:6	60	NaOCH ₃	0.8	60	92	[164]
Batch	Trans	WCO	MeOH	1:6	60	KOH	1.2	60	96	[164]
Cont	Est	Oleic acid	MeOH	1:3	120	H ₂ SO ₄	1	120	95	[75]
Cont	Trans	WCO	MeOH	1:6	50	KOH	1	480	96	[165]
Cont micro	Trans	Castor oil	EOH	1:14	50	NaOH	1	10	97	[166]
Cont micro	Trans	Palm oil	MeOH	1:21	60	KOH	4.5	3	95	[167]

3.2.2 Heterogeneous Catalysis

The use of heterogeneous catalysts has seen substantial growth. Important reasons for this development are their easier management and recovery. Different materials have been evaluated, as summarized in Tab. 7 and described below.

Metal oxides can act as a base or acid according to the metal's properties and catalyst's treatment, such as doping with sulfuric acid. Alkalis are generally more active than acids [5, 168], but they can be applied only to transesterification. Acid catalysis occurs with Brønsted or Lewis acids [169]. The active sites of Brønsted acids are fewer than for homogeneous acids. Consequently, the biodiesel process requires more severe conditions (i.e., high temperatures and alcohol contents) [64]. However, Brønsted acids can be used for esterification and transesterification simultaneously. Lewis acids are stronger than Brønsted acids, but they can only be used for feedstock without water and FFA content because these act as poisons.

Alkaline earth oxides (BeO, MgO, CaO, SrO, BaO, and RaO) show base properties and can thus be used for transesterification. They are non-metallic, insoluble in water, and heat-resistant. Alkaline earth metal oxides donate electrons to other substances; beryllium oxide is amphoteric, and barium oxide is the strongest base. Magnesium and calcium oxides are the most abundant [170] and are commonly applied [17, 171]. The activity of the solid catalyst is dependent on the active sites on the CaO or MgO surface [16]. The alkalinity of the active sites is responsible for the reaction, and many studies have improved this property by adding other chemicals and pretreatments or using more than one metal oxide. Active sites can be reconstituted by washing with acetone [172] and calcination to remove CO₂ and H₂O [16]. Despite these advantages, heterogeneous base catalysts require high temperatures, long reaction times, large alcohol contents, and high triglyceride purity, and the catalyst leaches rapidly [17, 101].

Natural waste shells and eggshells with high Ca contents can be used for transesterification. However, they frequently show good efficiency during their initial application (> 90 %) but much lower efficiencies after recovery and recycling (< 30 %) [100]. Subsequent doping has been investigated using alkali metals, resulting in high conversions even for reused catalysts [99].

Transition metal oxides (e.g., TiO₂, CoO, Cu₂O, Cr₂O₃, ZnO, Pt, and ZrO₂) provide a large variety of surface structures and energies. The metal oxide surface atoms can be acidic or alkaline based on the metal cation and oxygen anion coordination. These materials are used for esterification and transesterification reactions, in free or immobilized form and upon optional photoactivation [4, 18, 173]. The wet impregnation method is utilized frequently for zirconia immobilization (Zr) of metal nitrate salts. The final catalysts, e.g., Mg/ZrO₂, Ca/ZrO₂, Sr/ZrO₂ or Ba/ZrO₂, can be applied to simultaneous esterification and transesterification [97].

Alkali metal oxides can be employed for transesterification. These alkali metal oxides (Li₂O, Na₂O, K₂O, Rb₂O, and Cs₂O) are shiny, soft, low-density, and react violently with water to form hydroxides. In addition, they have high thermal and electrical conductivity. Sodium and potassium oxides are the most abundant.

Some metals can be sulfonated and hence become acidic, such as Al(HSO₄)₃. Using this catalyst, high conversions from feedstock with high FFA and water contents (i.e., WCO) by esterification and transesterification without saponification have been achieved. The material can also be easily recovered and reused [14]. However, the catalyst can leach and deactivate rapidly [15–17].

Heteropolyacids (HPA) supported on oxides can be applied to esterification and transesterification reactions. HPAs are soluble in methanol but gain higher activity and stability after

Table 7. Biodiesel produced by heterogeneous catalysts.

Reaction	Reactor	System	Feedstock	Alcohol	Oil/alcohol molar ratio	T [°C]	Catalyst	[wt %]	T [min]	Biodiesel [%]	No. cycles (reuse)	Biodiesel [%] reuse	Ref.
Est	Batch	Het.	Oleic acid	MeOH	1:15	75	Biomass-based polymers	–	180	96	–	–	[174]
Est	Batch	Het.	Oleic acid	MeOH	1:12	90	Fe ₃ O ₄ @PILPW	–	300	93	–	–	[175]
Est	Batch	Het.	Oleic acid	MeOH	1:15	110	[HMIM][HSO ₄]	–	480	95	–	–	[176]
Est	Batch	Het.	Oleic acid	MeOH	1:45	100	HZ zeolite	–	240	55	–	–	[177]
Est	Batch	Het.	Oleic acid	MeOH	1:5	100	LO (lanthanum oxide)	–	420	63	–	–	[178]
Est	Batch	Het.	Oleic acid	MeOH	1:10	60	M-MMT K10 acid	–	180	70	–	–	[179]
Est	Batch	Het.	Oleic acid	MeOH	1:5	100	SLO (sulfated lanthanum oxide)	–	420	98	–	–	[178]
Est	Batch	Het.	Oleic acid	MeOH	1:18	88	SO ₃ -HM-ZSM-5-3	–	600	100	–	–	[180]
Est	Batch	Het.	Oleic acid	MeOH	1:20	50	Sugarcane bagasse -SO ₃ H	–	1440	85	–	–	[181]
Est	Batch	Het.	Oleic acid	MeOH	1:8	150	TiO ₂ /NP-800	–	480	87	–	–	[182]
Est	Batch	Het.	Oleic acid	MeOH	1:40	60	TPA3/MCM-41	–	360	100	–	–	[183]
Est	Batch	Het.	Oleic acid	MeOH	1:9	60	Zr(SO ₄) ₂	–	300	98	–	–	[184]
Est	Batch	Het.	Oleic acid	MeOH	1:20	100	300-Nb ₂ O ₅ /SO ₄ ²⁻	–	240	92	–	–	[185]
Est/Trans	Batch	Het.	Soybean oil	MeOH	1:50	65	40 % CaO–MoO ₃ –SBA-15	6	480	83	5	77	[186]
Est/Trans	Batch	Het.	<i>Jatropha curcas</i> oil	MeOH	1:15	150	Bi ₂ O ₃ -La ₂ O ₃	2	240	93	3	87	[187]
Est/Trans	Batch	Het.	WPO ^[a]	MeOH	1:15	80	7WZC ^{d)}	2	60	94	5	79.3	[188]
Est/Trans	Batch	Het.	<i>Jatropha curcas</i> oil	MeOH	1:30	160	Activated Mg–Al hydrotalcites	5	240	93	4	86	[189]
Est/Trans	Batch	Het.	Palm oil	MeOH	1:20	85	CaO–CeO ₂ (1:1)	5	180	95	18	90	[190]
Est/Trans	Batch	Het.	<i>Jatropha curcas</i> oil	MeOH	1:6	60	CaO–Fe ₂ (SO ₄) ₃	5	180	100	3	80	[191]
Est/Trans	Batch	Het.	<i>Jatropha curcas</i> oil	MeOH	1:25	160	CaO–La ₂ O ₃	3	180	99	5	80	[192]
Est/Trans	Batch	Het.	WPO ^[a]	MeOH	1:9	65	CaO/Al ₂ O ₃	4	240	89	2	80	[193]

Table 7. Continued.

Reaction	Reactor	System	Feedstock	Alcohol	Oil/alcohol molar ratio	T [°C]	Catalyst	[wt %]	T [min]	Biodiesel [%]	No. cycles (reuse)	Biodiesel [%] reuse	Ref.
Est/Trans	Batch	Het.	WSO ^{b)}	MeOH	1:9	65	CaO/Al ₂ O ₃	4	240	98	2	77	[193]
Est/Trans	Batch	Het.	Palm fatty acid distillate	MeOH	1:15	80	CAWS-(7) SO ₄	5	180	80	4	46	[194]
Est/Trans	Batch	Het.	WCO ^{c)}	MeOH	1:15	205	Fe(HSO ₄) ₃	1	240	95	5	91.2	[195]
Est/Trans	Batch	Het.	Rapeseed oil	MeOH	1:6	62	GO-to-NaOH-bentonite	6	270	96	2	80	[196]
Est/Trans	Batch	Het.	WCO ^{c)}	MeOH	1:20	180	K-ITQ-6	5	1440	80	2	35	[197]
Est/Trans	Batch	Het.	<i>Eruca sativa</i> gars seed oils	MeOH	1:9	65	Ly2HPW	9	300	93	5	93	[198]
Est/Trans	Batch	Het.	WCO ^{c)}	MeOH	1:11	182	MgZnO	3.32	360	92	5	87	[199]
Est/Trans	Batch	Het.	WCO ^{c)}	MeOH	1:27	100	Mo-Mn/γ-Al ₂ O ₃ -15 wt % MgO	5	240	91	10	70	[200]
Est/Trans	Batch	Het.	<i>Jatropha curcas</i> oil	MeOH	1:40	160	Zn8@Fe-C400	7	240	100	10	94	[201]
Trans	Batch	Het.	WCO	MeOH	1:0.25 v/v	63	MnCO ₃ /Na-silicate	1	120	95	-	-	[202]
Trans	Batch	Het.	WCO	MeOH	1:15	65	CaO	7.5	360	90	-	-	[203]
Trans	Cont micro	Het.	WCO	MeOH	3:1.7 v/v	62	Kettle limescale	8.9	15	93	-	-	[204]
Trans	Cont micro	Het.	WCO	MeOH	2.25:1 v/v	63	Cow bone	8.5	1	99	-	-	[205]
Trans	Cont micro	Het.	WCO	MeOH	2.25:1 v/v	65	KOH/clinoptilolite	8.1	13	97	-	-	[206]
Trans	Cont micro	Het.	Sunflower oil	MeOH	2.5:1 v/v	60	Chicken bone	10	10	51	-	-	[207]
Trans	Packed bed	Het.	Palm oil	MeOH	1:70	1:1	KOH-TiO ₂ /Al ₂ O ₃	157 g cm ⁻³	60	96	3	89	[208]
Trans	Packed bed	Het.	<i>Jatropha curcas</i> oil	MeOH	1:40	240	Pellets	173 m ² g ⁻¹	17.54	99	5	80	[209]
Trans	Packed cont micro	Het.	Palm oil	MeOH	1:24	65	Calcium oxide	1 g cm ⁻³	9	99	-	-	[210]

^{a)}WPO: waste palm oil; ^{b)}WSO: waste sunflower oil; ^{c)}WCO: waste cooking oil; ^{d)}WZC: tungsten-zirconia (W-Zr)-modified waste shell catalyst.

immobilization on oxides. The most common oxides used are Zr, Ti, Sn, and Nb-based, or mixtures, such as $\text{TiO}_2/\text{SiO}_2$. However, the catalyst is susceptible to leaching and poisoning by water [17].

3.2.3 Photocatalysis

Heterogeneous photocatalysis is widely applied to advanced oxidative processes (AOP), and it is used extensively to degrade organic compounds [211–213]. It can also be employed to synthesize products, such as esters [4, 18, 19, 173]. The process is based on irradiating an inorganic semiconductor such as TiO_2 , ZnO, or CdS. Semiconductors are characterized by their valence band (VB), conduction band (CB), and band gap (BG). When the semiconductor is excited by photons ($h\nu$) with an energy equal to or higher than its BG, electrons migrate from the VB to the CB. The electron-hole pair produced can rapidly recombine or initiate oxidative and reductive reactions, as described in Fig. 8 [214, 215].

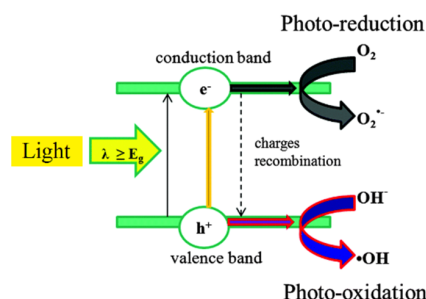


Figure 8. Inorganic semiconductor's activation in the presence of light. Reprinted with permission from [216], Copyright Creative Commons Attribution 3.0.

The use of inorganic semiconductors activated by either ultraviolet light or natural sunlight for esterification has been investigated (Tab. 8) [18–20]. The advantages of heterogeneous

photocatalysts include their low cost, high chemical stability, easy handling, post-reaction recovery, and reusability [9,22].

Titanium dioxide is the most frequently used metal oxide photocatalyst owing to its high photosensitivity, high thermal and chemical stability, corrosion resistance, and non-toxicity [20, 221]. Titanium dioxide is found in three modifications: anatase, brookite, and rutile, each with different physical and chemical characteristics (Tab. 9) and different crystalline structures (Fig. 9). All require UVA light (wavelength: 315–400 nm) for most effective activation, but the band gap energy is also reached by sunlight, which lowers the process cost by replacing electrically powered lamps. Tropical, subtropical, and Mediterranean regions offer advantageous climatic conditions with high UV indices for several months of the year [222, 223], making them interesting locations for solar photocatalytic biodiesel production.

Table 9. Titanium dioxide characterization.

	Anatase	Brookite	Rutile	Ref.
BG [eV]	3.26	3.13	3.05	[224]
Refractive index	2.488	2.583	2.609	[225]
Density [g cm^{-3}]	3.83	4.17	4.24	[226]
Unit cell volume [nm^3]	0.1363	–	0.0624	[225]
Crystal size	< 11	11–35	> 35	[225]
Mohs scale	5.5–6.0	5.5–6	6.0–6.5	[226]
Occurrence	Common	Rare	Common	[227]

The different crystal structures of TiO_2 can be combined, such as in the commercial Aeroxide[®] TiO_2 P25 with 80 % anatase and 20 % rutile [228]. TiO_2 can be modified by doping with nitrogen ions or metal oxides, such as tungsten trioxide, which improves its absorption in the visible range [229], or can be immobilized, e.g., in biopolymers, such as calcium alginate

Table 8. Biodiesel produced by photocatalysis.

Reaction ^{a)}	System	Feedstock	Alcohol	Oil/ alcohol	T [°C]	Catalyst	[wt %]	T [min]	Biodiesel [%]	Ref.
Est	Het.	Oleic acid	MeOH	1:55	55	TiO_2 + UVA	20	240	98	[21]
Est	Het.	Oleic acid	EtOH	1:55	55	TiO_2 + UVA	20	240	21	[21]
Est	Het.	Oleic acid	PrOH	1:55	55	TiO_2 + UVA	20	240	6	[21]
Est	Het.	Oleic acid	MeOH	1:9	40	Au/ TiO_2 + visible light	10	360	85	[217]
Est	Het.	Oleic acid	MeOH	1:12	30	TiO_2 + UVA	12	240	75	[19]
Trans	Het	WCO	EtOH	1:9	65	CuO/ZnO + UVA	5	120	93	[218]
Trans	Het	WCO	MeOH	1:9	60	$\text{TiO}_2/\text{g-C}_3\text{N}_4$ + sunlight	2	60	84	[219]
Trans	Het	WCO	MeOH	1:8	60	TiO_2 + sunlight	Nanotubes	240	91	[220]

^{a)} Batch reactor.

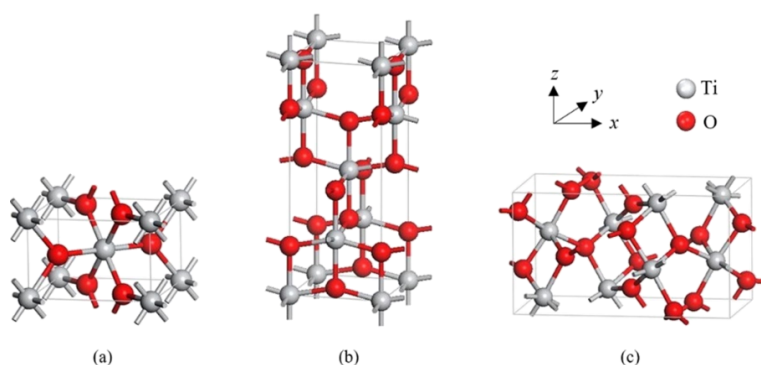


Figure 9. TiO₂ crystalline forms (a), rutile (b) anatase, and (c) brookite. Reprinted with permission from [232], Copyright: Creative Commons CC-BY.

[8, 230]. This immobilization technique has been applied to Triclosan degradation, and the same efficiency was observed for TiO₂ in both its free and immobilized form [231].

3.2.4 Biocatalysts

Biocatalytic reactions often occur under mild operational conditions, reducing energy needs, process hazards, product purification requirements, and wastewater volumes [104, 108, 233–235]. The most common biocatalysts utilized are yeast and enzymes (Tab. 10), which can be applied in their free or immobilized forms.

Yeasts can catalyze esterification and transesterification reactions. Therefore, they are considered a green material for reducing the requirement of feedstock pretreatment, i.e., removal of water and FFA, and product purification. Reactions occur under mild operational conditions (25–45 °C and pH of 5.5–7.0 [236]), but the catalyst requires an incubation period as a pretreatment step.

Likewise, esterification and transesterification can be catalyzed by enzymes, most commonly lipases, which can be derived from animals (dairy and pancreatic), vegetables (soy, cotton, and rye) or microbials (yeasts, fungi, and bacteria) [237, 238]. Lipases achieve high selectivity, high product purity, a reduction in wastewater, and do not cause saponification [239, 240]. Vegetable oils, WCO or animal fat, have been used as feedstock [22, 104, 110, 241–243].

The application of enzymes has a number of disadvantages. In their free form, they show low stability and recoverability, which causes significant process costs and requires strict operational control [240, 244]. The most common free lipases used are *Candida* (28 %), *Thermomyces* (14 %), *Burkholderia* (14 %), and *Rhizopus* (12 %) [245]. Lipase from *Candida antarctica subtilis*, CALB (EC 3.1.1.3), is one of the most common lipases studied [245]. These lipases are hydrolytic enzymes capable of acting over a wide range of pH (6.0–8.0) and temperatures (30–70 °C) [104, 237, 246]. The immobilization of lipases tends to reduce their enzymatic activity, but at the same time increases their chemical stability and facilitates their recovery (Tab. 11) [108, 109, 247].

Double immobilization, e.g., adsorption followed by entrapment, can improve the performance of biocatalytic processes. Following this approach, CALB maintains its enzymatic activity of 70 % after immobilization onto lignin nanospheres confined in calcium alginate hydrogel beads [247], of 94 % when immobilized onto cellulose acetate-coated Fe₂O₃ nanoparticles [248], and of 95 % when immobilized onto Fe₃O₄ magnetic nanoparticles entrapped into chitosan [108], respectively. These studies revealed that double immobilization results in microbead shapes that are small enough to increase the surface area and allow access to the catalyst but large enough to recover and handle the microbeads.

4 Microscale Plants for Biodiesel Production

Microscale plants integrate microfluidic concepts, a technology used to manipulate fluids in microscale processes. Generally, microdevices have a volume between 10 and 1000 μL [263–265]. This technology has been investigated experimentally and numerically in several areas, such as biological systems, liquid-liquid extraction, food and pharmaceutical industries, chemical waste degradation, and biodiesel synthesis [263, 264, 266–269].

Compared with conventional industrial plants, microchannel reactors have several advantages, such as shorter residence times, higher heat and mass transfer, and easier management, maintenance and operational control [23]. Mass transfer tends to be 30 times higher than on traditional scales [23]. Moreover, the better physical and energetic homogeneity increases the process viability without mass and heat spots that can damage the processing system.

The use of micromodules facilitates process maintenance. In the case of saponification, for example, microplants can reduce the volumes of water and reactants. When operated in parallel, only the modules where process problems occur require maintenance, repair or exchange. In contrast, traditional batch systems demand the shutdown of the entire plant. Biodiesel purification by traditional processes includes distillation, filtration, liquid-liquid extraction, or, more often, gravitational separation [270]. When performed in microreactors, gravitational separation is not possible, but other effective separation methods based on liquid-liquid extraction [271, 272], centrifugal forces [273], and micro-heat exchangers [274] have been developed instead.

Flexible scale-up is achieved in serial or parallel microdevices (numbering up), although this requires substantial investment costs [24–26]. Microdevices can be produced by numerous 3D printing techniques (photolithography, soft lithography, moulding microfabrication, and laser ablation) using a range of suitable materials (glass, polymers, metals, and ceramics) [265, 275–278]. For example, Billo et al. constructed a microplant capable of producing 2.8 L min⁻¹ of biodiesel [279]. The

Table 10. Biodiesel produced by biocatalysts.

Reactor	Reaction	Feedstock	Alcohol	Oil/ alcohol	T [°C]	Catalyst	Support	wt	t [min]	Biodiesel [%]	No. cycles (reuse)	Biodiesel [%] reuse	Ref.
Batch	Est/trans	WCO	MeOH	1:4	40	CALB	Fe ₃ O ₄ MNPs@TEOS-TSD	1 g	1800	96	6 (10)	70 (15)	[249]
Batch	Trans	WCO	MeOH	1:6	35	<i>B. cepacia</i>	SPION ^{a)}	25/10/10 ^{b)}	2100	91	5	54	[250]
Batch	Trans	Soybean oil	MeOH	1:4	35	<i>C. rugosa</i>	Magnetic chitosan microspheres		1800	87	4	72	[251]
Batch	Trans	<i>Jatropha curcas</i> oil	MeOH	1:6	37	Lipase from <i>Aspergillus niger</i>	PDA-TiO ₂ NPs	10	1800	92	8	^{c)}	[252]
Microreactor	Trans	Sunflower oil	MeOH	1:2.5	30	Lipase from <i>Thermomyces</i> <i>lanuginosus</i>	–	4 %	–	–	–	–	[253]
Cont micro	Trans	Soybean oil	MeOH	1:7	50	CALB	–	–	53	95	–	–	[254]
Cont micro	Trans	WCO	MeOH	1:90	40	Lipase from <i>Thermomyces</i> <i>lanuginosus</i>	γ-Fe ₂ O ₃	–	20	92	–	–	[255]
MFBR ^{d)}	Trans	WCO	MeOH	1:4	35	<i>Bacillus subtilis</i> cells	Fe ₃ O ₄ -PVA	12 %	2880	89	10	82	[256]

^{a)}Superparamagnetic iron oxide nanoparticles; ^{b)}25 wt %, water content of 10 wt % and *n*-hexane content of 10 wt %; ^{c)}Residual activity: ~9 U mg⁻¹ min⁻¹ (1 cycle) and ~2.5 U mg⁻¹ min⁻¹ (8 cycles); ^{d)} magnetically fluidized-bed reactor.

microplant comprised of 35 manifolds with eight modules of 50 devices each, totalling 14 000 microreactors.

The knowledge of fluid flow behavior and microdevice design is essential to develop optimal systems. Computational fluid dynamics (CFD) techniques are thus linked to process design approaches. CFD generates process information based on different parameters (i.e., density, viscosity, temperature, molarity, concentration, and experimental data) and generates information to optimize the process [280].

The design and structure of the microdevice is fundamental to improving the system efficiency by promoting turbulent mixing spots and increasing the contact area between the reagents. The reactants are pumped into the microchannels in small, interspersed segments, and mass transfer, which facilitates the reaction, occurs across the borders of the reactants [281]. To achieve better mass transfer, the structures of microdevices can be optimized by reducing the channel diameter, using a complex channel geometry, or implementing micromixers.

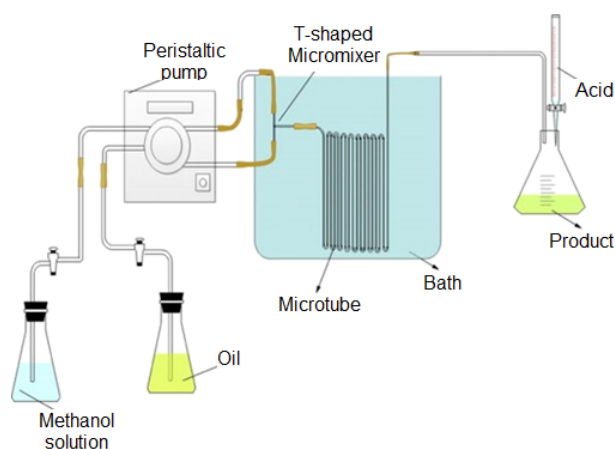
The relevance of the diameter of the channels was evaluated for biodiesel produced from sunflower oil. For a residence time of 252 s, microchannels of 0.96 mm and 0.46 mm diameter resulted in similar conversions of 89 % and 92 %, respectively. The difference was more apparent with 43 % and 80 %, when the residence time was reduced to 112 s [282]. Thus, smaller cross-sections increase conversions by raising the pressure drop, but this approach can cause leaks in the system and requires more energy.

Micromixers attached to the inlet of microreactors and microchannels with complex channel designs have been developed for biodiesel production upon improved reagent mixing. The use of a T-shaped micromixer coupled to a microtube (Fig. 10) was compared with zigzag microchannels with a T-shape inlet (Fig. 11). Following the same operation conditions (1 mol TGL:9 mol MeOH, 1.2 wt % KOH, 60 °C), the micromixer coupled to the microchannel resulted in a conversion of 89 % (residence time of 180 s) [283], while the complex zigzag design resulted in a conversion of 99.5 % (residence time of 28 s) instead [284].

Similarly, laminar versus turbulent flow patterns were evaluated for biodiesel produced from castor oil (EtOH:NaOH 1:9, 1 wt % NaOH, 50 °C, Fig. 12). In turbulent flow mode (Tesla-microchannel design), a 93 % conversion was achieved compared to 76 % by laminar flow (T-shape) and 87 % by intermediary flow (omega-shape). Subsequent experiments were conducted under the same operating conditions and with the same channel designs but using 1 mol TGL:24 mol

Table 11. Comparison of lipase immobilization efficiency by REA analysis.

Enzyme	Support 1	Support 2	REA [%]	Ref.
CALB	AuNPs	–	80	[257]
CALB	Calcium alginate beads	–	88	[103]
CALB	Calcium alginate microbeads	–	100	[8]
CALB	Fe ₂ O ₃	Cellulose acetate-coated	94	[248]
CALB	Fe ₃ O ₄	Chitosan nanoparticles	95	[108]
CALB	Octyl agarose	–	100	[105]
CALB	Lignin nanoparticles	Alginate beads	70	[247]
CALB	Silica-lignin matrix	–	92	[107]
CALB	TiO ₂	–	289	[8]
CALB	TiO ₂	Calcium alginate microbeads	232	[8]
Lipase from porcine pancreas	Cu ₃ (PO ₄) ₂	–	460	[258]
Lipase from porcine pancreas	TiO ₂	Chitosan	100	[259]
Lipase from porcine pancreas	Zn ₃ (PO ₄) ₂	–	147	[260]
<i>Candida rugosa</i> lipase	Glyoxyl agarose	–	50	[242]
<i>Candida rugosa</i> lipase	Fe ₃ O ₄	–	60	[261]
<i>Candida rugosa</i> lipase	Fe ₃ O ₄	Alginate polyaldehyde	60	[262]

**Figure 10.** T-shaped micromixer coupled to a microtube reactor to produce biodiesel. Reprinted with permission from [283] and Elsevier, Copyright (2014) license number: 5360540097272.

EtOH instead of 9 mol EtOH, resulting in 97 %, 93 %, and 95 % conversion, respectively [166]. Hence, the increase in mass transfer due to turbulent mixing caused lower alcohol content requirements.

The microdevice design also impacts on the system's temperature requirement. For microdevices that cannot achieve good mixing, operation at the boiling point of the alcohol may be considered. Hence, the mixture changes from a liquid-liquid interface to a gas-liquid interface, resulting in convective mix-

ing and consequently improving conversion towards FFAE. However, these operation conditions demand more energy, and the reactor system becomes more susceptible to leaks and high-pressure points. Using optimized designs, however, the temperature requirements for optimal conversion may be lower.

Biodiesel obtained by homogeneous alkali transesterification (liquid-liquid interface) was produced in two microdevices (poor mixing versus turbulent spots) at 30, 50, and 70 °C, respectively. The simple system resulted in 66 %, 73 %, and 88 % conversion at these temperatures. In contrast, the device with turbulent spots resulted in 75 %, 93 %, and 93 % conversion over the same temperature range [166]. Hence, the reactor design with turbulent spots reduces the energy requirements as superior conversions were obtained compared to the simple system with laminar flow.

The mass transfer increment through microdevice design optimization improves the efficiency and reduces the alcohol content requirement and the residence time. Thus, microchannels with a design that generates chaotic and turbulent spots of the reactants flow are desirable for an efficient microsystem.

While homogeneous catalysts have been studied extensively for biodiesel production in microdevices, heterogeneous catalysts have similarly attracted attention. The use of low-cost heterogeneous catalysts (KOH/Clinoptilolite [206], kettle limescale [285], and cow bone [205]) to produce biodiesel from WCO were evaluated in microdevices, and conversions of 97 %, 93 %, and 99 % were achieved. A semi-industrial pilot microreactor (200 mL, Fig. 13) was employed for WCO-methanol transesterification using kettle limescale as the catalyst (62 °C, 8.9 wt %

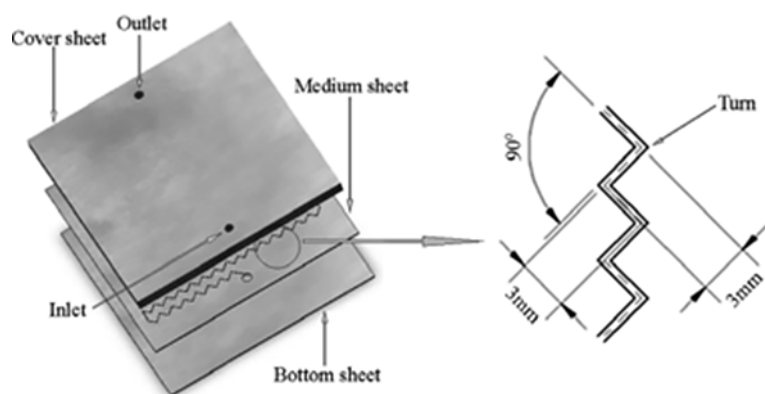


Figure 11. Zigzag microchannel design reactor to produce biodiesel. Reprinted with permission from [283] and Elsevier, Copyright (2009) license number: 5GB494627212.

catalyst, methanol:oil at 1.7:3 oil volume ratio). Optimized process conditions were reached with a residence time of 15 min (93 % conversion), compared to 50 min using the conventional batch reactor process [285].

Lipases are common heterogeneous catalysts applied to biodiesel production by esterification and transesterification. However, these enzymes are expensive, difficult to immobilize, retain, and recover, leach easily, and require careful control of the operational conditions. Implementing microdevices reduces catalyst leaching and loads, and enables better control of the operation conditions. Lipases have consequently been studied in microreactors with edible and non-edible oils [287]. Parallel microdevice modules also minimize enzyme losses in

the case of process complications, as only affected units would have to be stopped, while all remaining units would continue production. A microplant with a microreactor (catalyst: lipase from *Thermomyces lanuginosus* ($723 \pm 19 \text{ U mg}^{-1}$) and microseparator (extraction by deep eutectic solvents (DES)) in series resulted in 94 % conversion using sunflower oil and ethanol (1:10 molar ratio, 40°C , 20 min residence time) [255].

Microflow Photochemistry

Photochemical processes have been investigated in microreactors, e.g., for the synthesis of steroids [288], *L*-pipecolinic acid [289], and pinacol from benzophenone [290], as well as the degradation of pollutants [213,291]. The large surface area and narrow channel depth of microdevices promote better irradiation and improve the photoreaction's efficiency [292]. Naturally, microdevices need to be transparent and manufactured from materials with cut-off wavelengths compatible with the required light, e.g., glass, quartz, silicon, and fluoropolymers [290, 293–295]. Photocatalysts can be introduced as an externally mixed colloidal suspension or can be coated (i.e., sol-gel [296], sputtering [297], spray coating [298], spin coating [299], or vapor+solvent depositing [300]) to the internal microchannel surface. In the latter case, the compatibility between the catalyst and the internal surface of the microchannels needs to be considered. Immobilization also commonly requires pretreatment of the channel material. Silver-coated TiO_2 (0.8 wt % Ag/TiO_2) was immobilized in a microphotoreactor using a

sol-gel method. This device was subsequently utilized for wastewater treatment (Fig. 14) [296].

An efficiency of 99 % was achieved under the optimized operational conditions ($10.22 \mu\text{L min}^{-1}$ flow rate, 12.94 mg L^{-1} inlet concentration, 6.2 initial solution pH, and 7.53 W m^{-2} min UV-LEDs light intensity) [301]. The use of TiO_2 nanotubes has also been evaluated for different processes, such as phenol photoelectrocatalysis in fixed-bed microreactors with 80 % efficiency [302] and biodiesel production from oleic acid and methanol with 86% efficiency [19], respectively. The combination of photochemistry and microfluidics can improve a range of photocatalytic processes and enable efficient and economic processes.

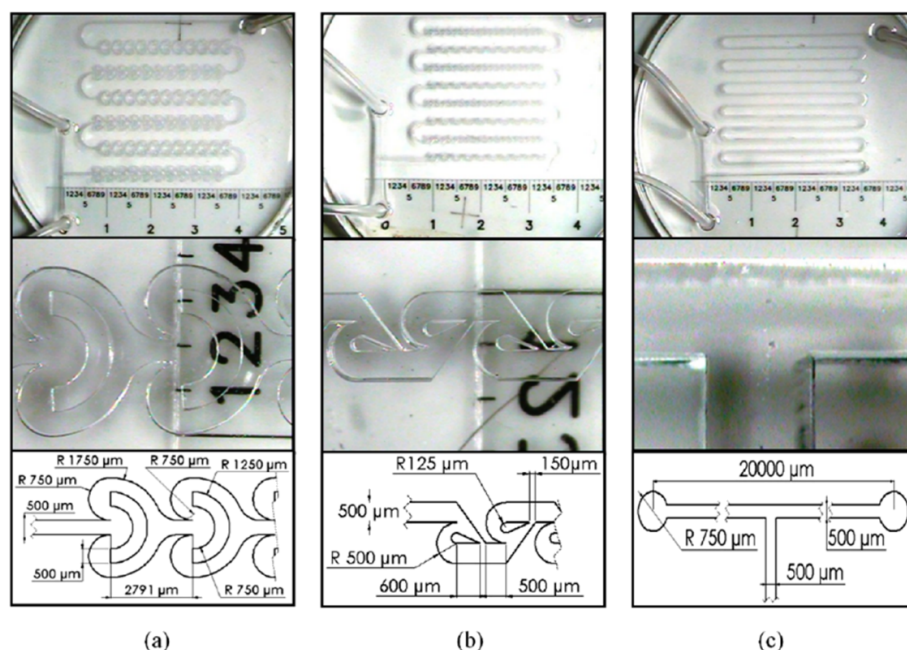


Figure 12. Microchannel designs for microreactors used to produce biodiesel. (a) Omega-shaped, (b) Tesla-shaped, and (c) T-shaped. Reprinted with permission from [166], Copyright (2012) American Chemical Society.

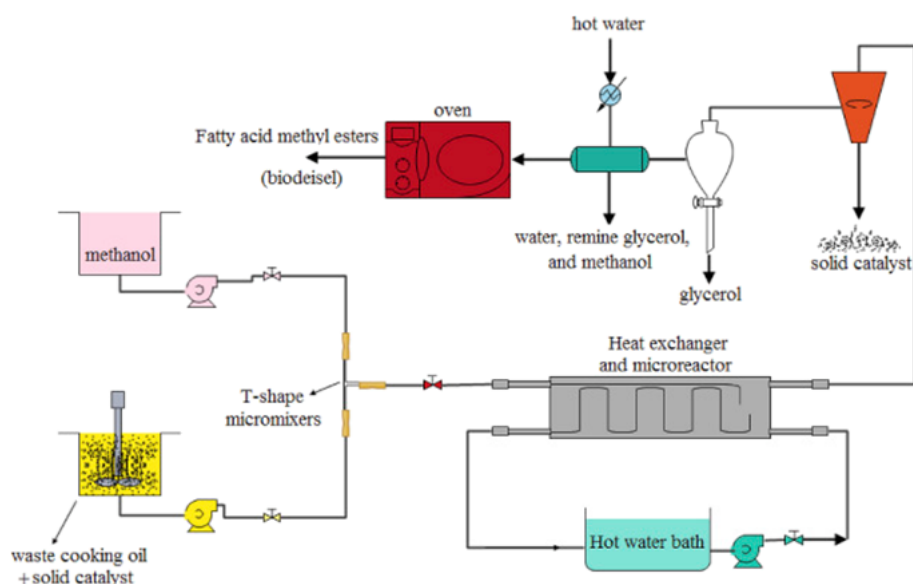


Figure 13. Semi-industrial pilot microplant used for biodiesel production by WCO and kettle limescale as the catalyst. Reprinted with permission from [286] and Elsevier, Copyright (2019) license number: 5360501088909.

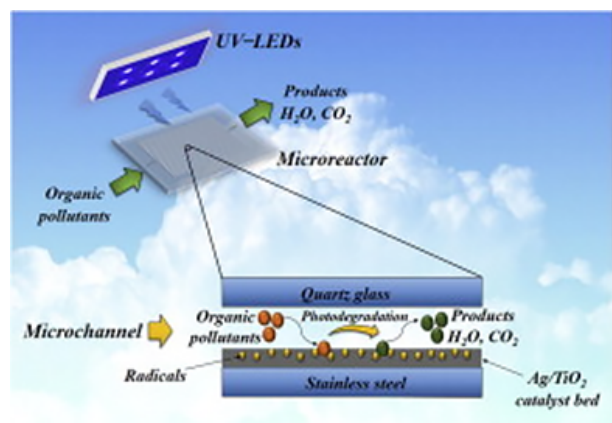


Figure 14. Microphotoreactor coated by Ag/TiO₂ for organic products degradation. Reprinted with permission from [301] and Elsevier, Copyright (2019) license number: 5360550205441.

5 Future Technologies

Due to a large number of advantages of biodiesel compared to petrodiesel, its production and complementary use has been a growing focus of research and government engagements. However, conventional processes, although low cost, do not satisfy environmental concerns, such as waste generation. The use of heterogeneous catalysts for biodiesel production from WCO as feedstock is one of the most promising routes. Nevertheless, these technologies still require more investigations to be applied on large scale. Thus, future studies should focus on their implementation on large scale as a low-cost process. A combined system integrating traditional and novel methods could be the first step to achieve a viable industrial route and boost the use of WCO.

6 Conclusion

Biodiesel production has seen a sharp increase to meet its growing demand as a fuel source. However, new technologies are needed to improve or replace current industrial processes. The use of microdevices and heterogeneous catalysts, such as enzymes and photocatalysts, represent interesting approaches because they overcome many issues encountered in traditional homogeneous processes using strong acids and alkalis. However, further research is urgently needed to reach scalability, obtain kinetic and thermodynamic parameters, and achieve process optimization. WCOs represent an eco-friendly alternative to edible oils, reducing the competition with food industries and solving the environmental burden caused by these waste materials.

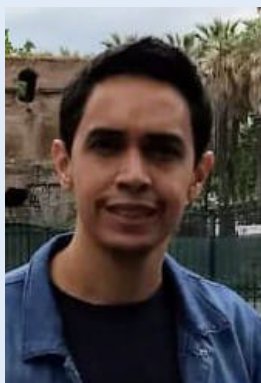
Conflicts of Interest

The authors declare no conflict of interest.



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Abbreviations

AOP	advanced oxidative processes
CB	conduction band
BG	band gap
VB	valence band
CALB	<i>Candida antarctica subtilis B</i>
CFD	computational fluid dynamics
Cont micro	continuous microreactor
Cont flow	continuous flow
Est	esterification
EtOH	ethanol
FAAE	fatty acid alkyl esters
FAEE	fatty acid ethyl ester
FAME	fatty acid methyl ester
FFA	free fatty acid
GHG	greenhouse gas
Het	heterogeneous
Hom	homogeneous
HPA	heteropolyacids
Interest	interesterification
MeOH	methanol
MFBR	magnetically fluidized-bed reactor

REA	relative enzymatic activity
Syst	system
TGL	triglycerides
Trans	transesterification
UVA	ultraviolet A
WCO	waste cooking oil
WPO	waste palm oil
WSO	waste sunflower oil

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Biodiesel is regarded as an eco-friendly substitute and additive to fossil fuels. However, the traditional routes for its production have several disadvantages. Different solutions have been investigated, such as feedstocks, catalysts, reactor designs, and scales. This review explores and analyzes the main aspects of current biodiesel technologies and opportunities, and also describes some advanced improvement strategies.

Biodiesel Production by Heterogeneous Catalysts and Eco-friendly Routes

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