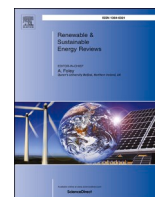




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# Renewable and Sustainable Energy Reviews

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## Status, developments, and sustainability of biowaste feedstock: A review of current progress

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### ABSTRACT

Modification of natural environments for the purpose of their utilisation has led to the degradation of more than 50 % of the world's original forests, highlighting the profound influence of human actions on global ecosystems. The world's cultivated land area has expanded by ~13 % since 1961; however, with the world population doubling since then, we can only rely on half as much land as in 1961 for food production. The rapid exhaustion of natural resources, including land and water, emphasises the necessity for sustainable energy generation. Identifying sustainable energy sources such as biodiesel is critical, particularly when human land use has eradicated half of the planet's forests and agricultural lands are persistently diminishing due to population expansion. Waste cooking oil is a readily available, inexpensive, and widely distributed raw material for biodiesel production. Waste cooking oil is a potential source that can immediately solve the world's needs to generate more useable energy. This review article offers a thorough overview of biodiesel production using conventional methods, intensification processes, and various types of catalysts, along with their advantages and disadvantages. This review delves into optimisation of biodiesel production, including a thorough examination of process parameters such as the methanol/oil molar ratio, catalyst concentration, reaction temperature, reaction time, and stirring speed, and their effects on the biodiesel yield. The kinetics, thermodynamics, and energy consumption of the transesterification reaction, as well as exergy and energy analysis are covered. This article also presents the life cycle analysis and environmental impact assessment. On the whole, the production of biodiesel from waste cooking oil is a cleaner and economical alternative fuel for compression ignition engines.

### Nomenclature

A	Arrhenius constant
ACO	Ant colony optimisation
AFR	Advanced-Flow™ Reactor
Al <sub>2</sub> O <sub>3</sub>	Aluminium oxide
AN	Acid number
ANN	Artificial neural network

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ASTM	American Society for Testing and Materials
B0	Pure diesel
B10	90 % diesel + 10 % biodiesel (by volume)
B100	100 % biodiesel (by volume)
B20	80 % diesel + 20 % biodiesel (by volume)
B30	70 % diesel + 30 % biodiesel (by volume)
B40	60 % diesel + 40 % biodiesel (by volume)

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B50	50 % diesel + 50 % biodiesel (by volume)
Ba <sub>2</sub> TiO <sub>4</sub>	Barium orthotitanate
BaO	Barium oxide
BBD	Box–Behnken design
BP	Brake power
BSEC	Brake specific energy consumption
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
Ca	Calcium
Ca(NO <sub>3</sub> ) <sub>2</sub>	Calcium nitrate
Ca(OH) <sub>2</sub>	Calcium hydroxide
CaCO <sub>3</sub>	Calcium carbonate
CaO	Calcium oxide
CC	Climate change
CCC	Central composite circumscribed
CCD	Central composite design
CCF	Central composite face-centred
CCI	Central composite inscribed
CCRD	Central composite rotatable design
CCS	Centrifugal contact separator
CFPP	Cold filter plugging point
CGDE	Contact glow discharge electrolysis
CH <sub>3</sub> O•	Methoxy radical
CH <sub>3</sub> ONa	Sodium methoxide
CI	Compression ignition
CN	Cetane number
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
CoFe <sub>2</sub> O <sub>4</sub>	Cobalt ferrite
CP	Cloud point
C <sub>p,w</sub>	Specific heat of the calorimeter
CR	Carbon residue
CSS	Calcined scallop shell
CV	Calorific value
DER	Distributed energy resource system
DG	Diglycerol
DHA	Docosahexaenoic acid
DMC	Dimethyl carbonate
DOE	Design of experiments
E10	10 % ethanol + 90 % diesel
E5	5 % ethanol + 95 % diesel
E <sub>A</sub>	Activation energy
EFB	Empty fruit bunch
EN	European standard
EPA	Eicosapentaenoic acid
EU	European Union
FAME	Fatty acid methyl ester
FD	Fossil fuel depletion
FFA	Free fatty acid
FP	Flash point
FS	Ferric sulphate
FTIR	Fourier transform infrared
G	Glycerol
GHG	Greenhouse gas emissions
GRA	Grey relational analysis
GWP	Global warming potential
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid
ha	Hectare
HBPG	Phthalimide-epoxy monomer with glycidol
HC	Hydrocarbon
HC <sup>a</sup>	Hydrodynamic cavitation
HCC	Hemispherical combustion chamber
HEN	Heat exchanger network
HO•	Hydroxyl radical
HVO	Hydrotreated vegetable oil
IV	Iodine value
J	Joule
K <sub>2</sub> CO <sub>3</sub>	Potassium carbonate
K <sub>b</sub>	Mass fraction of biodiesel in the blend
KBr–CaO	Potassium bromide–calcium oxide
KOH	Potassium hydroxide
Kr	Krypton
LCA	Life cycle analysis/assessment
LHV	Lower heating value
Li <sub>4</sub> SiO <sub>4</sub>	Lithium orthosilicate
LiOH	Lithium hydroxide
M10	10 % methanol + 90 % diesel

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M5	5 % methanol + 95 % diesel
m <sub>f</sub>	Mass flow rate of fuel
Mg(NO <sub>3</sub> ) <sub>2</sub>	Magnesium nitrate
MgAl	Magnesium aluminate
MgO	Magnesium oxide
MnFe <sub>2</sub> O <sub>4</sub>	Manganese iron oxide
MOO	Multi-objective optimisation
MOOP	Multi-objective optimisation problem
MSR	Microstructure reactor
MTBE	Methyl tert-butyl ether
N	Rotation rate
N <sub>2</sub>	Nitrogen
Na <sub>2</sub> CO <sub>3</sub>	Sodium carbonate
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NEMO	Acid-base non-eutectic mixture organocatalyst
NIPU	Non-isocyanate polyurethane
NMR	Nuclear magnetic resonance
NOx	Nitrogen oxide
OBR	Oscillatory baffled reactor
OCFE	Orthogonal collocation on finite elements
OD	Ozone depletion
OMC	Ordered mesoporous carbon
OS	Oxidation stability
PB	Palm oil biodiesel
PBR	Packed bed reactor
PC	Porous carbon
PCA	Principal component analysis
PHA	Poly(hydroxyalkanoates)
PM	Particulate matter
PMF	Particulate matter formation
POF	Photochemical oxidant formation
PP	Pour point
q	Fuel consumption of the biodiesel blend
Q <sub>ex</sub>	Heat loss through the exhaust
Q <sub>f</sub>	Fuel energy supply rate
Q <sub>l</sub>	Other losses
Q <sub>w</sub>	Cooling water loss
R	Universal gas constant (8.314 J/mol·K)
R <sub>r</sub>	Rate of reaction
RSM	Response surface methodology
S/N	Signal-to-noise
SN	Saponification number
SEM	Scanning electron microscopy
Sr/ZrO <sub>2</sub>	Strontium/Zirconium dioxide
SrFe <sub>2</sub> O <sub>4</sub> /SiO <sub>2</sub> -SO <sub>3</sub> H	Strontium spinel ferrite/Silicon dioxide–Sulphonic acid
SrO	Strontium oxide
SV	Saponification value
T <sub>0</sub>	Ambient temperature
T <sub>e1</sub>	Exhaust temperature
T <sub>e2</sub>	Exhaust gas temperature for the inlet to the calorimeter
T <sub>e3</sub>	Exhaust gas temperature for the outlet to the calorimeter
T <sub>eq</sub>	Engine torque
TG	Triglyceride
THF	Tetrahydrofuran
TMAH	Tetramethylammonium hydroxide
T <sub>w1</sub>	Cooling water for the inlet
T <sub>w2</sub>	Cooling water for the outlet
(v/v)%	Volume per cent
VOC	Volatile organic compound
W	Watt
(w/w)%	Weight per cent
WCO	Waste cooking oil
XRD	X-ray diffraction
yr	Year
ZIF67	Phosphotungstic acid–modified zeolite imidazolate
ZnO	Zinc oxide
ZrO <sub>2</sub>	Zirconium dioxide
ΔG	Gibbs free energy
ΔH	Enthalpy
ΔS	Entropy

## 1. Introduction

Biodiesel is a convenient alternative fuel for diesel engines since its

characteristics mimic (or are superior to) diesel fuel produced from crude oil, leading to widespread biodiesel production worldwide. Biodiesels are produced from biomass, and are categorised according to the type of biomass used. Biodiesels are typically categorised into four generations according to the type of feedstock [1], as shown in Fig. 1. Table 1 also shown the summaries of the advantages and disadvantages of different classification of biodiesel.

First-generation biodiesel production uses edible raw materials, such as sugar, wheat, palm oil, corn oil, and soya bean oil. This practice, however, raises many questions since the use of edible feedstock for fuel production results in competition with food reserves [1]. The massive use of edible feedstock can result in a shortage of food supply and increase food prices globally. In addition, it can increase the demand for massive agricultural lands. Hence, the use of edible feedstock for biodiesel production threatens the existence of forests and water resources, and is ultimately detrimental to the environment. However, food wastes are available in large quantities, and if they cannot be processed, they can cause serious environmental problems. Therefore, the potential use of food wastes such as waste cooking oil (WCO) is promising for environmental, sustainability, availability, and economic reasons.

Second-generation biodiesel production is more sustainable than first-generation biodiesel production since it uses non-edible feedstocks. The typical non-edible oils used in second-generation biodiesel production are *Jatropha curcas*, *Madhuca longifolia*, *Calophyllum inophyllum*, *Milletia pinnata*, *Ceiba pentandra*, and *Miscanthus giganteus*, as well as agricultural wastes such as empty fruit bunch (EFB). Although second-generation feedstocks are inedible, they require large areas of land for cultivation. Therefore, second-generation biodiesel production also raises issues on land acquisition for cultivation of crops, similar to first-generation biodiesel production. Furthermore, the drawbacks of second-generation biodiesels include the low yields from non-edible crops and the necessity to increase the amount of alcohol in the reaction [2].

Third-generation biodiesel production uses algae as the feedstock. Algae conversion is similar to that of other lignocellulosic biomass conversions into biodiesel, but requires intensification process with high energy input. Algae are highly regarded as a promising feedstock since they are popular as carbon dioxide (CO<sub>2</sub>) capturing agents, and they have a fast growth rate and high oil content [3]. The oil extraction from algae and the conversion of this oil into biodiesel is still in its early phase, and hence, algae have a low conversion rate [4]. With the current state of technology, third-generation biodiesels are not feasible for commercial-scale production, and therefore, they do not provide an immediate solution for the energy security issue.

Fourth-generation biodiesel production emphasises on genetically modified microalgae, which has high adaptability in wastewater systems and poor nutrient environment. The modified microalgae are able to capture more CO<sub>2</sub> than the unmodified microalgae [5]. However, they

**Table 1**

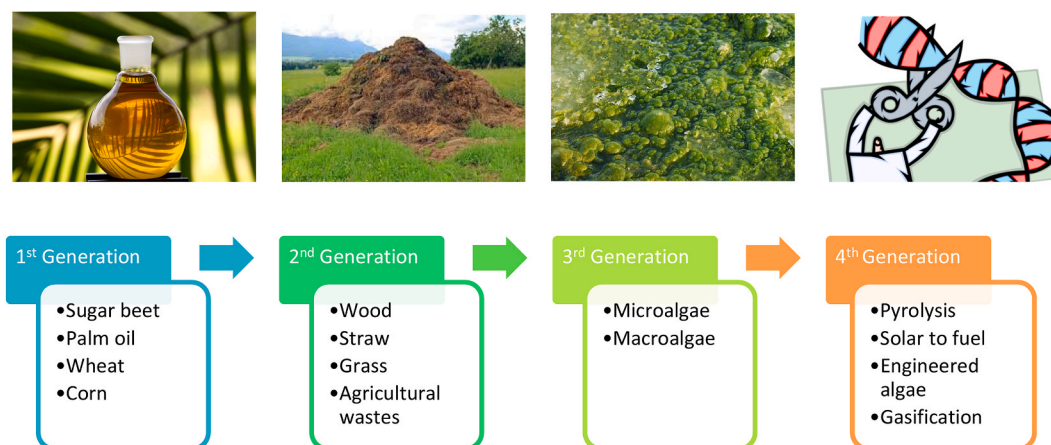
The advantages and disadvantages of different classification of biodiesel.

Classification	Advantages	Disadvantages
First generation	High compatibility with existing engines. Well-established production process.	Competes with agricultural crops such as oil palm and corn. Results in deforestation and a decrease in biodiversity. Requires a large area.
Second generation	Using non-edible raw materials (e.g., <i>Jatropha curcas</i> , agricultural waste). Reducing food-fuel conflict.	Low oil yield requires a higher alcohol ratio in the reaction. Energy-intensive extraction process.
Third generation	Algae efficiently capture CO <sub>2</sub> , with high oil content (~30–70 % lipid by weight). Grows rapidly on uncultivable land.	Not feasible for now owing to low conversion rates. Potential environmental hazards with open systems.
Fourth generation	Genetically modified microalgae enhance carbon dioxide capture and lipid production. Thrive in wastewater/poor nutrient conditions.	Requires advanced biotechnological expertise and substantial funding in research and development.
Waste cooking oil	Redirects waste to the landfill and reduces greenhouse gas emissions by up to 88 % when compared to fossil diesel. Low feedstock costs.	Variable FFA content (5–20 %) requires pre-treatment. Supply chains in emerging markets lack consistency.

may cause other potential environmental issues if they are grown in an open system. The feasibility of modified microalgae is very minimal, and they require more fundamental studies, biotechnology, and genome engineering expertise.

Innocenzi and Prisciandaro [6] found that the use of waste cooking oil (WCO) to replace virgin oil (edible oil) can reduce production costs by 60 % or down to 290–300 €/t. It can be said that WCO will remain as the dominant feedstock for biodiesel production. Therefore, WCO is believed to be a viable alternative to address the issue of food and energy security [7]. Millions of WCO are disposed from the food industry and residences, which poses a significant problem. Using WCO as a new renewable energy source will solve the energy security issue and WCO disposal problem.

Table 2 summarises some reviews on biodiesel production from WCOs. Despite extensive research on biodiesel production from WCOs, little is known on the life cycle cost analysis of cutting-edge technology for biodiesel production from WCOs, posing a challenge in evaluating their commercialisation potential. Numerous studies have also delved deeper into the optimisation of transesterification process parameters,



**Fig. 1.** Classification of biodiesels according to the type of feedstock [1].

**Table 2**  
Previous review studies on biodiesel production from WCOs.

Study Type	Raw Material Sources/ Feedstocks	Conversion Rate	Scope (LCA/ LCCA)	Key Findings/Highlight	Ref
Review	WCO (Vegetable oils)	85–95 % yield	Economic feasibility	Pioneer of process intensification (cavitation, microwaves). Show highlights of possible cost savings.	[8]
Review	WCO Mixed (restaurant/ food waste)	80–90 % yield	Partial LCA	Primary focus on the superiority of transesterification relative to pyrolysis. The availability of raw resources is considered.	[9]
Review	WCO (derived from palm oil)	75–99 % yield	Energy analysis	Identified the energy intensity of supercritical transesterification as a barrier to scalability. High energy requirement (~50 kWh/L) limits scalability; best suitable for large-scale operations.	[10]
Review	WCO Mixed	90–95 % yield	Full LCA	WCO biodiesel reduces greenhouse gas emissions by as much as 75 % compared to fossil diesel, according to modern LCA research. Criticises inconsistent LCA methodology; urges integration of waste management factors. Variations in standardisations.	[11]
Review	WCO (derived from rapeseed)	74–97 % yield	Cost analysis	Heterogeneous CaO catalysts reduce soap formation and costs by up to 30 %.	[12]

\*LCA/LCCA: Partial = mentions environmental impact; Full = Comprehensive analysis.

such as the methanol/oil molar ratio, catalyst concentration, reaction temperature, reaction time, and stirring speed. However, numerous areas remain unexplored such as kinetics, thermodynamics, and energy consumption of the biodiesel conversion process. Furthermore, there is still room to reduce engine wear and carbon deposits on engine components, since most of the reviews are focused on the engine performance and combustion of WCO biodiesel. Therefore, this article examines the potential of WCO as a feedstock for biodiesel production. This review presents a comprehensive discussion regarding the potential of WCO for biodiesel production, explores biodiesel production methods (conventional methods and intensification processes), and details the performance, advantages, and disadvantages of these methods. Moreover, the different types of catalysts (homogeneous, heterogeneous, and enzymatic catalysts) used for biodiesel production are discussed in this review, along with the optimisation of process parameters, physico-chemical properties of the WCO biodiesel, kinetics, thermodynamics, and energy consumption of the transesterification reaction, energy and exergy analysis, engine performance and exhaust emissions of diesel engines fuelled with WCO biodiesel, life cycle analysis, environmental impact assessment, and the value-added products of biodiesel production from WCO, and potential future research direction.

## 2. Edible oils as an unfeasible source for biodiesel production

The non-renewable nature of fossil fuels cannot halt the depletion of crude oil reserves, and therefore, there is a need to develop biodiesels as alternatives to fossil fuels. The sustainability of biodiesels can be observed from the increasing trend in the production of edible oils for more than a decade, shown in Fig. 2 [14,15]. In the last recorded year, the production of palm oil is the highest (36 %), followed by soya bean oil (29 %), rapeseed oil (13 %), sunflower seed oil (9 %), palm kernel oil (4 %), cottonseed oil and peanut oil (both constitute ~3 %), coconut oil (2 %), and least of all, olive oil (1 %) [2,16]. In 2020, the total production of edible oils was 209.2 million metric tonnes, and this amount increases by almost 50 million metric tons within a decade. The production of edible oils is also in line with the population growth, with shows a linear increasing trend.

By referring to the consumption of edible oils, the biodiesel industry accounts for a tiny portion compared with the food industry, as shown in Figs. 3 and 4. More significant edible oil consumption in the food industry is expected since edible oils primarily serve as food. Consequently, the efforts to produce biodiesel from edible oils are questioned since it results in competition with the food industry, raising concerns over global food security. The effect is more severe since the cost of edible oil production is higher than the retail price of petrol and diesel. Despite the steadily increasing demand for some edible oils over time

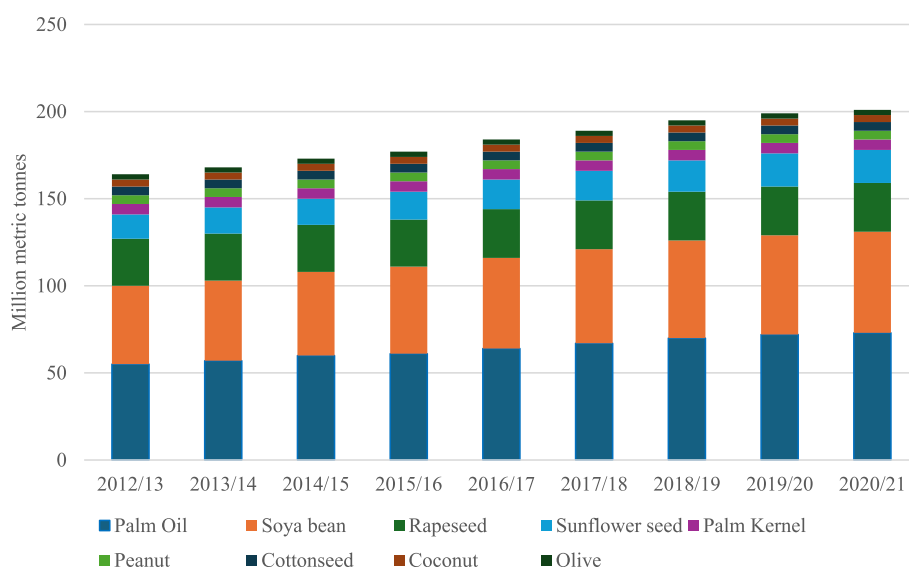


Fig. 2. Production of edible oils worldwide from 2012 to 2020 (in million metric tonnes).

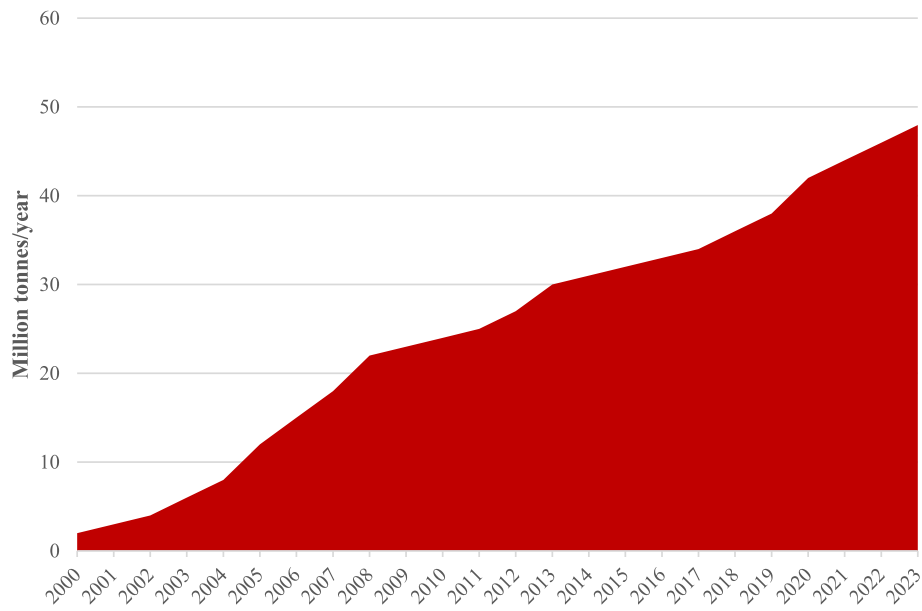


Fig. 3. Production of biodiesels worldwide from 2000 to 2023 (in million tonnes) [14].

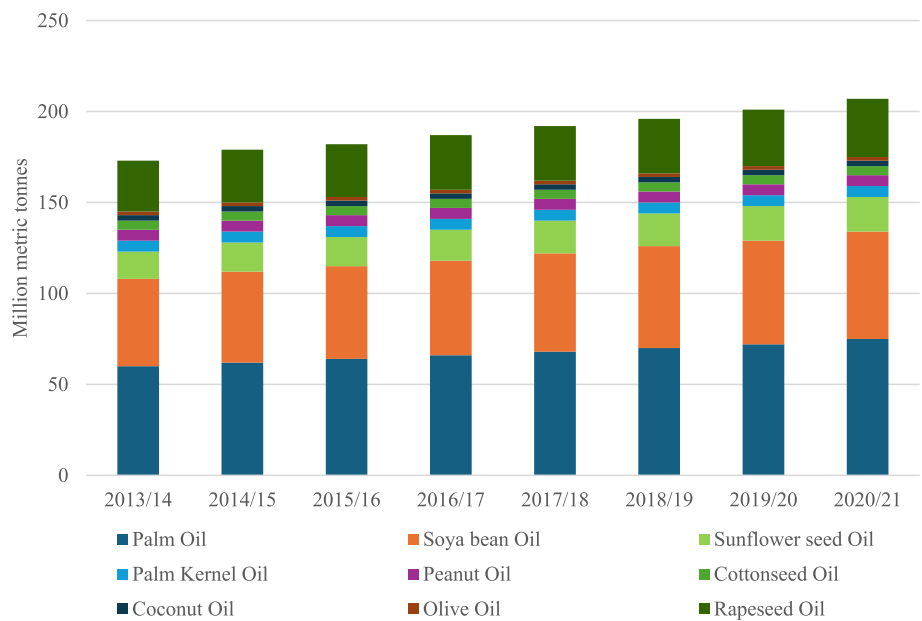


Fig. 4. Consumption of edible oils worldwide according to type from 2013 to 2021 (in million metric tonnes) [15].

(Fig. 4), the inconsistent edible oil prices (Fig. 5) render edible oils unfeasible for biodiesel production in the long term [14].

### 3. Recycling modes worldwide

WCO is a potential source for biodiesel production in many countries such as the member countries of the European Union, Mexico [17], South Korea [18], China, and Japan [15]. The feasibility of WCO for biodiesel production should consider the means of production, economic planning, and WCO recycling scheme. This indicates that a solid supporting system is essential. Government subsidies may catalyse the implementation of WCO recycling schemes. For example, subsidies for recycling companies and domestic incentives for the recyclers may promote the practice. Overall, China lacks in readiness in realising sustainable WCO recycling compared with Japan. The government involvement in terms of subsidies is still low, resulting in a lower

recycling price compared with that of illegal WCO. In addition, there is a lack of technical and administrative support. In terms of logistics, the method of WCO collection, storage and transportation should also be considered. Higher cost-effectiveness and emission reduction can be achieved by having closer collection stations. Additional governing steps, including taxation, legal, and other policies, must be established to form a secure economic environment for WCO in the biofuel industry [19,20]. Illegal WCO sellers will interfere with the system by collecting the WCOs and selling them to the low-level market for cooking after simple filtration. They also illegally market the WCOs to the oleochemical and soap industries. Having an illegal WCO market is also a great concern in other countries such as Columbia and China. At this point, the government must implement rigorous approaches to minimise illegal WCO trading. Besides rules and regulations, raising the public's awareness on the health hazard of using WCO as cooking oil from an illegal market and educating the public on the benefits of WCO

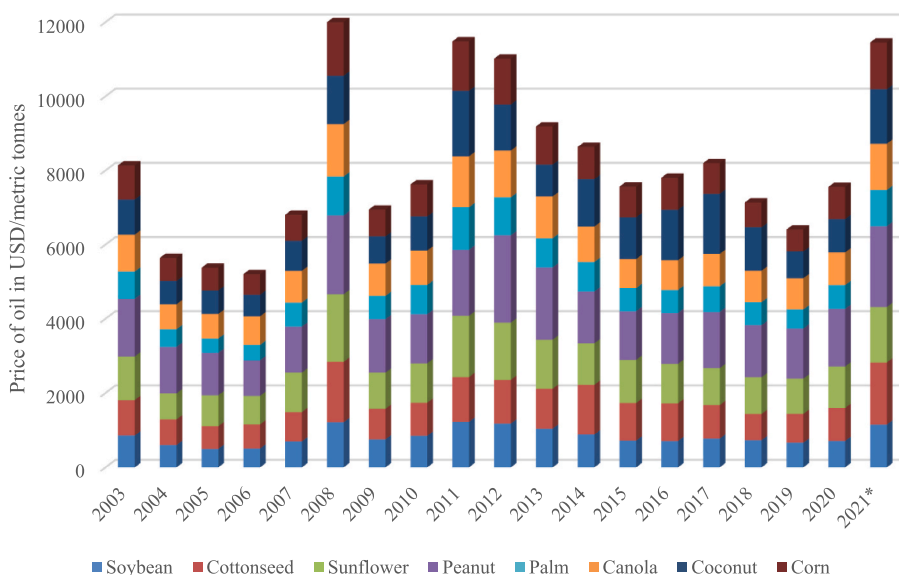


Fig. 5. Prices of various edible oils from 2003 to 2021 (USD).  
\*Note: Up to June 2021 [16].

conversion into biodiesel are equally important. Most residents are unaware of WCO recycling despite the normalcy in paper, metal, and plastic recycling practices. Based on the literature survey, an aggressive subsidy plan is commonly proposed for recycling WCOs for biodiesel production, specifically in regions with a developing economy. This approach is beneficial to promote WCOs in the recycling industry, including promoting supply chain operation in WCO recycling. This will increase profits for both biodiesel industry players and recyclers. Government involvement in creating policies to stimulate the use of WCOs in biodiesel production is essential. This will boost the creation of market size and marketing strategies in the WCO recycling and industry of biodiesel [15]. Fig. 6 shows the recycling modes of WCO for biodiesel production adopted in various countries.

Rapeseed oil is still the dominant biodiesel feedstock in the European Union (EU), accounting for 39 % of the total feedstocks used in 2021 [21,22]. EU is also the main biodiesel producer that uses WCOs [22]. The movement restriction during the COVID-19 has reduced the domestic supply of WCOs in the EU, where EU imports WCOs from China, Malaysia, the United States of America, and Indonesia. China is the country that uses WCOs as their feedstocks to produce biodiesels, but

their yearly production is insufficient to provide large volumes of biodiesels, and the prices of biodiesels are unable to compete with lower-priced diesel. Hence, China exports WCO biodiesels to Europe rather than using them for their own local market. China has recommended the use of gutter oil to produce biodiesel, where gutter oil is used oil collected from the sewage system. Japan is focused on biodiesel production from WCOs, as they are the only feedstocks used since 2017. Encouragement from EU’s Renewable Energy Directive, which provides WCO biodiesel incentives, has boosted the trading market where Japan exported 8.9 million litres of biodiesel to the EU in 2019. Asian countries such as Indonesia, Malaysia, and Thailand use palm oils as their primary feedstocks to produce biodiesel. Indonesia’s biodiesel mandate has imposed the B30 blend, where biodiesels are mainly used for on-road transport, followed by fuel power generation. Indonesia exports biodiesels to Europe (68 %), China (24 %), and South Korea (8 %).

The biodiesel trade between countries is dependent on the biodiesel prices and production policies. The fluctuation prices of the feedstocks will negatively impact the international biodiesel demand. This indicates the importance to ensure the sustainability and price of the feedstock. At present, the prices of edible oils

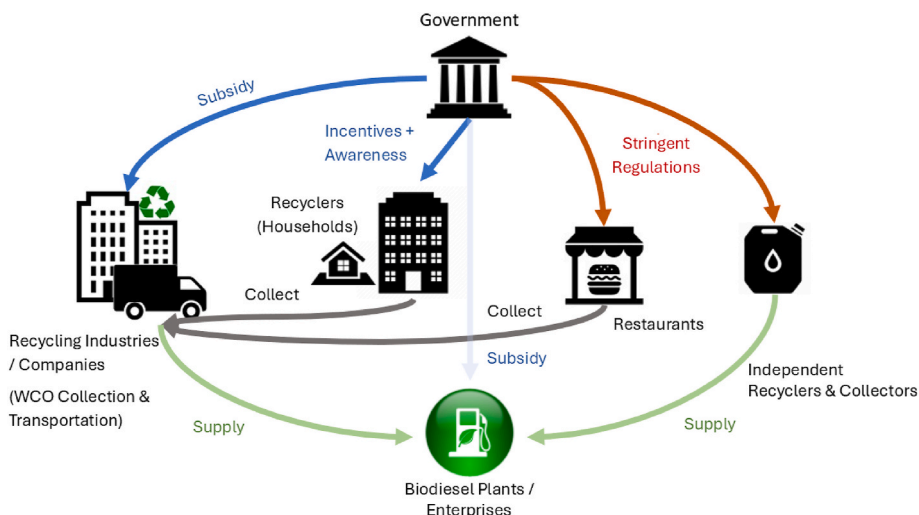


Fig. 6. Recycling modes of WCO for biodiesel production adopted in various countries [15].

remain high, resulting in a surplus in biodiesel production, especially for the biodiesel's dominant supplier country. However, if all of the edible feedstocks are used for human consumption and the WCOs are used for biodiesel production, this will reduce the oil prices, ensure food security, and lead to sustainability of biodiesel feedstocks. Hence, WCO is the cheapest feedstock for biodiesel production, which is not bound by the price of the edible oils, and the EU's Renewable Energy Directive provides incentives to encourage the production of WCO biodiesel.

#### 4. Methods used to convert WCO into biodiesel

##### 4.1. Pre-treatment of WCO

WCO is collected from various food processing industries, fast food restaurants, slaughterhouses, and residences. WCOs are generated from edible oils used for frying such as soya bean oil, sunflower oil, palm oil, mustard seed oil, cottonseed oil, rapeseed oil, and animal fat. During the frying process, a few reactions take place such as hydrolysis, oxidation, polymerisation, decomposition, and isomerisation of the oil. The WCO will release or contain deterioration particles such as aldehydes, ketones, epoxides, polymerides, and cyclic aromatic hydrogen compounds due to the aforementioned reactions. These particles can cause health hazards to the consumers, resulting in safety concerns [23]. Therefore, after frying, this oil is considered as WCO and it is proposed that WCOs are used as sustainable feedstocks for biodiesel production.

WCOs undergo multiple reactions during frying, which deteriorates the oil's properties, and increases the density, kinematic viscosity, acidity, calorific value, free fatty acid (FFA) content, water content, and odour. The hydrolysis reaction generally occurs during frying due to the mixture of the frying oil and the water contained in the food. Hydrolysis increases the FFAs, which in turn, increases the kinematic viscosity, density, and acidity of the oil. Converting WCO into biodiesel by transesterification requires a maximum FFA content of 1–2 (w/w)% [24], as a higher FFA content can result in soap formation. Soap formation is a non-reversible process that will affect the biodiesel yield and quality of the biodiesel. Therefore, many scholars claimed that if the FFA content is above the recommended value, the WCO must be pre-treated to increase its economic value and reduce soap formation [25].

First, the solid impurities that form during the frying process are removed by filtration. Next, water is removed from the oil by pre-heating it at 110 °C for 30 min [26]. The esterification process is the pre-treatment step to reduce the FFA content of the WCO. This process is assisted by various types of catalysts such as homogeneous catalysts (sulphuric acid, hydrochloric acid, hydroiodic acid, and acetic acid) [27, 28], heterogeneous catalysts (heteropolyacids, zeolites, sulphated metal oxides, and ion exchange resins) [29,30], and enzymatic catalysts (*Candida rugosa* lipase, *Thermomyces lanuginosus* fungi) [31,32] with the presence of methanol to facilitate the conversion process. Out of the three methods, enzymatic esterification requires less energy, but it is impractical for industrial-scale biodiesel production as the cost of enzyme cultivation is relatively high, making it infeasible for esterification. Acid-catalysed esterification of WCO has shown remarkable conversion results due to the high reactivity and low cost. At the same time, heterogeneous catalysts are widely investigated in terms of the number of cycles where the catalysts can be reused. The performance of most heterogeneous catalysts will reduce by ~17 % after four cycles [33]. Catalyst regeneration by sulphuric acid is recommended to improve the reusability of the catalyst and maintain the catalytic activity for the esterification process. After the pre-treatment process, the WCO is transesterified to obtain biodiesel. The following sections provide descriptions of the conversion methods, equipment used, and latest advancements in biodiesel production.

##### 4.2. Conventional methods

There are numerous methods used to convert oil into biodiesel such

as gasification [34], pyrolysis [35,36], transesterification [27,37], hydrotreatment [38,39], and deoxygenation [40]. Among these methods, transesterification is well known for its cost-effectiveness, eco-friendly pathway. Transesterification is also the conventional method adopted by the biodiesel industry. The transesterification process breaks down triglycerides in the presence of alcohol to produce ester and glycerol. Fatty acid methyl ester (FAME) and glycerol are the end products of the transesterification process when methanol is used. When ethanol is used, the end products are fatty acid ethyl ester (FAEE) and glycerol. The biodiesel yield is dependent on various parameters such as methanol/oil molar ratio, type of catalyst, catalyst concentration, and reaction temperature [41]. The methanol/oil molar ratio is dependent on the stoichiometry of the transesterification process, where 1 mol of triglycerides react with 3 mol of short-chain alcohol to form 3 mol of esters and 1 mol of glycerol in the presence of a catalyst. However, most scholars prefer a higher methanol/oil molar ratio, up to 30:1 [42] for conventional transesterification. Excess methanol is preferable as it promotes forward transesterification reaction; however, it may increase the solubility of the glycerol, which complicates the separation and purification processes. Hence, the excess use of methanol can be avoided if the conventional process is replaced by an advanced method (intensification process), which will be discussed in the following section. Both acidic and alkaline catalysts are used for biodiesel production, though their purpose is different. Acidic catalysts can be used to reduce the kinematic viscosity (~25 %), dynamic viscosity (~26 %), acid number (~85 %) and FFA content (~85 %) of the oil. These catalysts are needed for oils with high FFA content such as WCO and non-edible oils. Alkaline catalysts are used to increase the conversion efficiency of FAME. Hence, both acidic and alkaline catalysts are needed for successful conversion of non-edible oils into biodiesels. Homogeneous catalysts are commonly used for the transesterification process; however, their concentrations are very subjective. If the concentration of the alkaline catalyst is low, the FFAs in the oil cannot be neutralised completely and the soap formation will not be completely separated. On the other hand, at high alkaline catalyst concentrations, the biodiesel produced undergoes a saponification process, which degrades the quality of the biodiesel. Therefore, it is crucial to optimise the concentration of the alkaline catalyst. An example of the two-step conversion process conventionally used in the production of biodiesel from WCO is described as follows. As shown in Fig. 7, a strong acid is added during esterification. In this case, 1 % of sulphuric acid and ferric sulphate are often used, with a methanol/oil molar ratio of 30:1 and temperature range of 60–80 °C. The purpose of performing an acid-catalysed pre-treatment process is to reduce the FFA content of the crude oil to <1 % for further processing [43]. The formed water must be separated before proceeding to the alkaline pre-treatment. This conversion route carries several drawbacks since an acidic catalyst is used. Acid is a corrosive agent, which should be highly avoided, particularly in a large biodiesel plant. In addition, acid separation is a complicated process. A trace of acid in the biodiesel results in errors in determining the physiochemical properties of the biodiesel. Moreover, the presence of acid in the biodiesel will shorten engine lifetime due to corrosion and emits higher sulphuric oxides. The alternative production route is to replace the acidic-alkaline pre-treatment with enzymatic pre-treatment. The use of enzymatic catalysts is more favourable due to their high selectivity, mild conversion reaction, and low energy consumption [44]. However, the cost of enzymes and their lifespan makes it questionable for industrial-scale biodiesel synthesis.

Many scholars have shown interest in the use of WCOs for biodiesel production. Ho et al. [45] developed acidic heterogeneous catalyst such as SrFe<sub>2</sub>O<sub>4</sub>/SiO<sub>2</sub>-SO<sub>3</sub>H for the esterification process and found that this catalyst helps to achieve 100 % conversion in the transesterification process. In contrast, the conversion was only 85 % when sulphuric acid was used. The separation of the heterogeneous catalyst was less of a hassle. Besides solid heterogeneous catalysts, ionic liquid, which works as a liquid heterogeneous catalyst, has been used for biodiesel

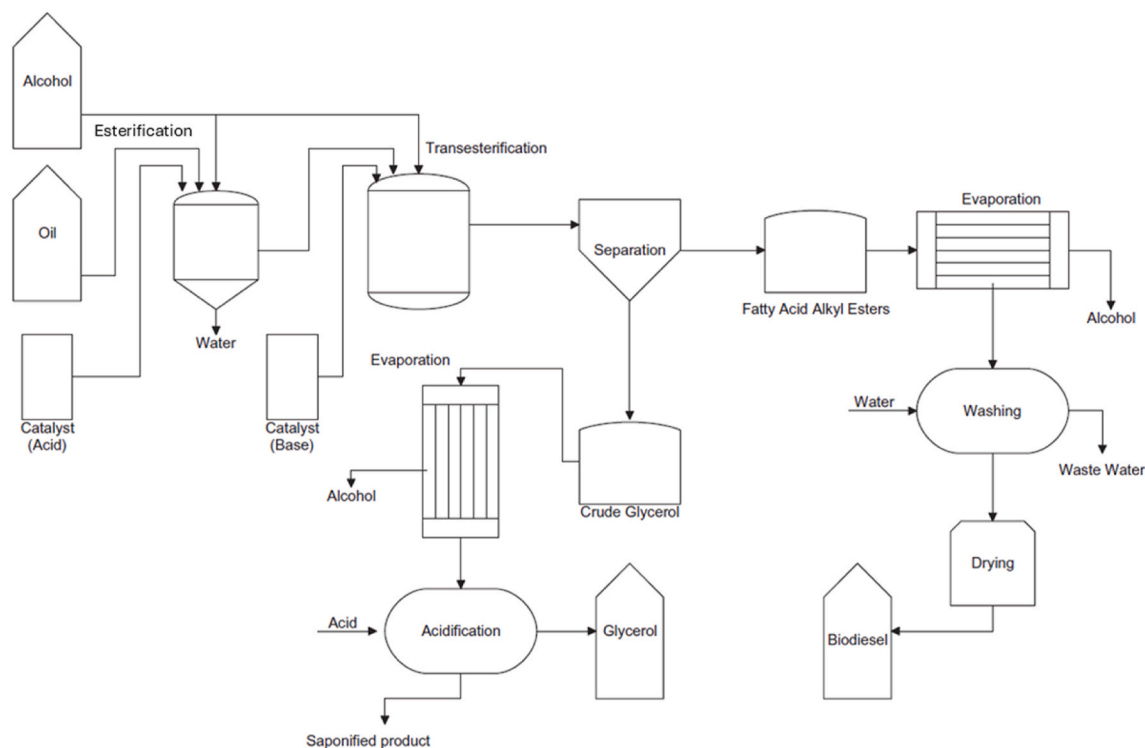


Fig. 7. Conventional two-step biodiesel production process [43].

production. Ionic liquids such as 4-ally-4methylmorpholin-4-ium-bromine [46] blended with NaOH improved the biodiesel yield up to 89.1 %. The ionic liquid was also claimed to be a recyclable and thermally stable catalyst with repeatability up to seven times. Strontium/Zirconium dioxide ( $\text{Sr}/\text{ZrO}_2$ ) was used as a catalyst for the alkaline-transesterification process and the biodiesel yield was 79.7 % [47]. In addition, potassium bromide-calcium oxide ( $\text{KBr}-\text{CaO}$ ) [48], ordered mesoporous carbon (OMC), ferric sulphate (FS), porous carbon (PC) [49], and calcined scallop shell (CSS) [50] were used as a catalyst for biodiesel synthesis. Even though the prices of heterogeneous catalysts are more than 20 times the prices of homogeneous catalysts, heterogeneous catalysts offer benefits such as high reusability, easy separation, environmental friendliness, and less wastewater, rendering them potential candidates to replace homogeneous catalysts. However, heterogeneous catalysts have a few drawbacks such as low mass transfer between the reactant and catalyst, which results in a longer reaction time. However, there is a need to develop a cost-effective heterogeneous catalyst that is as effective as an expensive compound such as platinum, titanium, and other rare earth metal oxides. Therefore, a carbon-based catalyst will be the preferred catalyst as it can be derived from various carbon feedstocks that fulfils the catalyst requirements (low cost and good biodegradability).

Transesterification requires the presence of a short-chain alcohol, and hence, the reaction temperature is dependent on the boiling point of the chosen alcohol. Reaction temperature plays an important part in biodiesel synthesis. The reaction temperature will directly determine the reactivity and miscibility of the reactant and oil, reduce the activation energy, and promote the production of methyl ester. The reaction temperature is also dependent on the type and amount of catalyst. Methanol is the common reactant for the transesterification process. The ideal reaction temperature for a homogeneous catalyst is within a range of 50–70 °C [27,50] at atmospheric pressure. In contrast, heterogeneous catalysts require higher reaction temperatures of 60–116 °C [51]. Some scholars blended methanol with other co-solvents such as n-hexane with oil, to homogenise the liquid phases and improve the biodiesel yield [52]. The addition of a co-solvent can shorten the reaction time.

Homogeneous catalysts typically require a reaction time of 40 min to 3 h [53], whereas heterogeneous catalysts require a minimum reaction time of 60 min to 7 h [54]. All of the benefits and drawbacks of the conventional method for biodiesel production are discussed as above. Scholars have carried out studies to further improve the biodiesel production process to increase the biodiesel yield, improve the economic variability, and make green energy more affordable for the biodiesel industry. Advancements in terms of modified reactor, intensification process, and researching alternative biodegradable catalyst are the steps to produce sustainable clean energy. The intensification process is discussed in the following section.

#### 4.3. Intensification process

Various methods have been used for the intensification process of biodiesel production using WCO as the feedstock. It shall be noted that there is no perfect biodiesel production method, and each has its own advantages and disadvantages. Table 3 present the mechanism, parameters, performance, disadvantages, and advantages of each type of intensification method. Overall, intensifying biodiesel production using the continuous method provides a more efficient process and larger production volume. Ultimately, it can significantly reduce production costs and be used for mass production. In the continuous method, the raw materials can be processed continuously without loading that can increase the production time without additional effort to start each cycle. The development of biodiesel from waste cooking oil (WCO) has been greatly aided using various intensification methods with novel mechanisms for efficiency improvement, scalability, and sustainability. Ultrasonic-assisted biodiesel production involves the use of high-frequency acoustic energy to cause ultrasonic-induced cavitation, resulting in fast collapse of the ultrasonic bubbles creating higher pressures and temperatures. This approach provides improved heat and mass transfer and reduces reaction times from hours to just minutes with yields of over 90 % [55,56]. A schematic of this method is shown in Fig. 8, the ultrasonic reactor configuration, and highlights the dynamics of the ultrasonic bubbles in the liquid phase.

**Table 3**  
Advantages and disadvantages various biodiesel production methods.

Method	Parameters and Performance	Advantages	Disadvantages
Microwave reactor	Catalyst: SrO–ZnO/MOF Reaction time: 5 min Reaction temperature: 80 °C Biodiesel yield: 99 % [70] Catalyst: H <sub>2</sub> SO <sub>4</sub> Reaction time: 10 min Reaction temperature: 60 °C Biodiesel yield: 93–98 % [71] Catalysts: Acid and alkali (two-step) Reaction time: 30 min Reaction temperature: 65 °C Biodiesel yield: 94.6 % [72] Catalyst: KOH Reaction time: 55.26 min Reaction temperature: 50–70 °C Biodiesel yield: 96.65 % [73] Catalyst: CaO Reaction time: 75 min Reaction temperature: 65 °C Biodiesel yield: 98.2 % [73]	<ul style="list-style-type: none"> <li>Higher reaction rate [74].</li> <li>Boosts catalyst performance [75].</li> <li>Direct energy transfer: Ensures uniform reactions at the molecular level [76].</li> <li>Consistent temperature: Prevents localised heating and temperature gradients, unlike conventional methods.</li> <li>Improved catalytic activity by promoting molecular collisions and enhancing catalyst efficiency [77].</li> <li>Reduces the overall process duration [78].</li> <li>Results in lower energy loss compared with conventional heating.</li> </ul>	<ul style="list-style-type: none"> <li>Variable performance: Different catalysts react variably, with mixed results [77].</li> <li>High energy consumption: Consumes significant amounts of electricity.</li> <li>Technical challenges: Industrial-scale reactors are costly, complex, and difficult to design.</li> <li>Radiation penetration: Limited ability to infiltrate large volume reactors [79].</li> <li>Flow system issues: Not suitable for solutions with solids, heterogeneous mixtures, or high-viscosity fluids [80].</li> </ul>
Ultrasonic reactor	Catalyst: CaO Reaction time: 39.84 min Reaction temperature: 60 °C Biodiesel yield: 98.62 % [55] Catalyst: H <sub>2</sub> SO <sub>4</sub> Reaction time: 108 min Reaction temperature: 60 °C Biodiesel yield: 90 % [81]	<ul style="list-style-type: none"> <li>Improves reaction rates and yields [82].</li> <li>Promotes better mixing and radical formation.</li> <li>Reduces reaction time [82,83] and enhances biodiesel yield [84].</li> <li>Eliminates need for external heating.</li> <li>Addresses issues with emulsification and mass transfer [85].</li> <li>Enhance the medium bulk temperature and facilitates chemical reaction [86].</li> <li>Eliminates the need for a catalyst, simplifying the process.</li> <li>Allows simultaneous esterification and transesterification, converting triglycerides into methyl esters quickly (&lt;30 min).</li> <li>Fewer steps in the production process lead to greater efficiency.</li> <li>More tolerant to FFAs and water content, reducing the need for pre-treatment.</li> <li>Easier post-production purification with only methanol and methyl esters needing separation, without the need for washing [89].</li> <li>Can be applied to a wide variety of feedstocks.</li> <li>The purification process is more environmentally friendly.</li> </ul>	<ul style="list-style-type: none"> <li>High initial set-up cost.</li> <li>Requires precise conditions for effective cavitation.</li> <li>Can cause equipment wear and tear [85].</li> <li>Needs ongoing monitoring and maintenance.</li> </ul>
Supercritical reactor	Reaction time: 7–15 min Reaction temperature: 350 °C Pressure: 12 MPa (FAME) Biodiesel yield: 92.2–93.0 % [57] Reaction time: 30 min Reaction temperature: 350 °C Pressure: 10 MPa Biodiesel yield: 91.0 % (FAEE) [57] Reaction time: 128 min Reaction temperature: 280 °C Pressure: 128 bar [87] Biodiesel yield: 97 % Reaction time: 17 min Reaction temperature: 254.7 °C Pressure: 110 bar Biodiesel yields (FAMEs): 99.2 % (methyl oleate), 99.3 % (methyl palmitate), 99.13 % (methyl stearate), and 99.05 % (methyl stearate) [88]	<ul style="list-style-type: none"> <li>Enhance the medium bulk temperature and facilitates chemical reaction [86].</li> <li>Eliminates the need for a catalyst, simplifying the process.</li> <li>Allows simultaneous esterification and transesterification, converting triglycerides into methyl esters quickly (&lt;30 min).</li> <li>Fewer steps in the production process lead to greater efficiency.</li> <li>More tolerant to FFAs and water content, reducing the need for pre-treatment.</li> <li>Easier post-production purification with only methanol and methyl esters needing separation, without the need for washing [89].</li> <li>Can be applied to a wide variety of feedstocks.</li> <li>The purification process is more environmentally friendly.</li> </ul>	<ul style="list-style-type: none"> <li>Requires high temperatures (~250–350 °C) and pressures (5–130 atm), increasing energy consumption.</li> <li>Needs a high alcohol/oil ratio [90,91], which can be costly.</li> <li>Needs more materials such as co-solvents to reduce the critical temperature and pressure [92].</li> <li>Requires specialised equipment to handle supercritical conditions.</li> <li>Efficient recovery of methanol from the supercritical process can be challenging.</li> <li>Adding catalyst can increase yield, but more effort is required for the purification process [93,93].</li> </ul>
Advanced-Flow™ Reactor (AFR)	Catalyst: H <sub>2</sub> SO <sub>4</sub> Reaction temperature: 80 °C Biodiesel yield: 93 % [94]	<ul style="list-style-type: none"> <li>Reduces reaction time and energy consumption.</li> <li>Space-efficient.</li> <li>Minimal waste generation.</li> <li>Up to 1000 times higher heat transfer coefficient [95].</li> <li>Up to 93 % for waste oil and 99 % for fresh oil [96].</li> <li>Lower explosion risk due to efficient heat transfer [97].</li> </ul>	<ul style="list-style-type: none"> <li>Higher initial set-up costs.</li> <li>Requires specialised knowledge and training.</li> <li>May have limitations for very large production volumes.</li> </ul>
Centrifugal contact separator (CCS)	Reaction time: 120 min (maximum) Catalyst: SiO <sub>2</sub> @TiO <sub>2</sub> Reaction temperature: 65 °C Stirring speed: 500 rpm Biodiesel yield: 98 % [98]	<ul style="list-style-type: none"> <li>Integrated functionality, which combines reactor and separator in one unit [96].</li> <li>Exit stream recycling is unnecessary.</li> <li>Achieves up to 96 % biodiesel yield under optimal conditions.</li> <li>Potentially faster than conventional methods [99].</li> <li>Cost reduction: Methanol recycling reduces production costs.</li> <li>Enhanced removal of inhibitors: Multiple CCS units improve glycerol and inhibitor removal [100].</li> </ul>	<ul style="list-style-type: none"> <li>Temperature sensitivity: High temperatures can vaporise methanol.</li> <li>Excess catalyst can cause soap formation.</li> <li>Precise flow rate control is essential for efficiency.</li> <li>Extreme frequencies reduce the biodiesel yield [101].</li> <li>Requires adaptation for industrial-grade production due to scaling challenges.</li> <li>Costly multiple units: Single-pass systems are risky, whereas multiple units increase costs.</li> </ul>
Packed bed reactor	Catalyst: CaO Reaction temperature: 65 °C Flow rate: 5 mL/min Biodiesel yield: 98.40 % [102]	<ul style="list-style-type: none"> <li>Does not require feedstock with low FFA and high enzyme ratio to achieve good biodiesel yields.</li> <li>Capable of processing significant volumes of low concentration feedstock mixtures.</li> <li>Allows direct reuse of enzymes, which reduces costs.</li> <li>Prolongs enzyme life by avoiding mechanical stress from stirrers.</li> </ul>	<ul style="list-style-type: none"> <li>Glycerol production at the bottom of the reactor degrades catalytic efficiency by coating the immobilised lipase surfaces [106].</li> <li>Requires modifications, such as enhanced glycerol removal processes, to minimise</li> </ul>

(continued on next page)

Table 3 (continued)

Method	Parameters and Performance	Advantages	Disadvantages
Membrane reactor	Catalyst: KOH Reaction temperature: 61 °C Flow rate: 26 mL/min Biodiesel yield: 92.6 % [108] Catalyst: TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> Reaction temperature: 58.5 °C Flow rate: 18.78 mL/min Biodiesel yield: 94.03 % [108] Catalyst: Sulfonated polyphenylsulfone (S-PPS) acid Reaction temperature: 60 °C Flow rate: Static Biodiesel yield: 86 % [108]	<ul style="list-style-type: none"> <li>• Suitable for large-scale and industrial-scale biodiesel production [103,104].</li> <li>• Enhanced biodiesel purity and effective glycerol removal.</li> <li>• Magnetically fluidised bed reactors reduce pressure drop and improve mass transfer efficiencies.</li> <li>• Better solubility between oil and reagents benefits large-scale production [105].</li> <li>• Improves reaction efficiency by overcoming mass transfer limitations.</li> <li>• Enhances product purity by ensuring effective separation of oil and methanol [109].</li> <li>• Increases reaction rate by restricting reversibility of transesterification.</li> <li>• Simplifies downstream processes by reducing the complexity of final distillation [100].</li> <li>• Reduces the downstream methanol recovery cost, separates and purifies efficiently, and uses less water for washing [109].</li> </ul>	<ul style="list-style-type: none"> <li>• drawbacks and improve retention times [107].</li> <li>• Complex membrane selection: Requires careful choice of suitable membrane type [110,111].</li> <li>• Need more effort for regular maintenance to ensure optimal performance and effective operation because the membrane must be replaced regularly.</li> </ul>
Microtube reactor	Catalyst: H <sub>2</sub> SO <sub>4</sub> Reaction time: 5 s Reaction temperature: 65 °C Flow rate: 2.92 mL/min Biodiesel yield: 91.76 % [62] Catalyst: Acid catalyst Reaction time: 2 min Reaction temperature: 55 °C Oil flow rate: 0.7–0.1 mL/min Ethanol flow rate: 0.2–3.5 mL/min Biodiesel yield: 98 % [112] Catalyst: MgO and GO@MgO Reaction time: 176.39 s (MgO) and 174.2 s (GO@MgO) Reaction temperature: 63 °C Biodiesel yield: 93.84 % (MgO) and 99.23 % (GO@MgO) [113] Catalyst: Kettle limescale deposit Reaction time: 12.5 min Reaction temperature: 60 °C Biodiesel yield: 97.16 % [114]	<ul style="list-style-type: none"> <li>• The performance of a microtube reactor is far better than a conventional batch reactor in terms of conversion rate as it requires a shorter reaction time [62].</li> <li>• Enhanced heat and mass transfer.</li> <li>• Higher conversion rates and reduced reaction times [115].</li> <li>• Requires less energy and reactants, producing less waste [116].</li> <li>• Better temperature control due to the large surface area [117].</li> <li>• Feasible for industrial use with methods to scale up production [118,119]. Refers to the current application in chemical and pharmaceutical industries, food industry [120,121], and energy industry [122].</li> <li>• Low work hazards and safety risks [123].</li> </ul>	<ul style="list-style-type: none"> <li>• Pressure drop: Higher pressure drop with an increase in the number of units, which increases costs.</li> <li>• Size limitations: Not ideal for solid–liquid or viscous fluids.</li> <li>• Material brittleness: Channels (often glass) can be brittle.</li> <li>• High initial cost: Expensive to set up and implement.</li> </ul>
Cavitation reactor	Catalyst: KOH Reaction time: 60 s Reaction temperature: 60 °C Biodiesel yield: 90.45 % *Ultrasonic- hydrodynamic combined cavitation system [124] Catalyst: KOH Biodiesel yield: >98 % [125] Catalyst: KOH Reaction time: 15 min Reaction temperature: 60 °C Biodiesel yield: ≥96.5 % [126,127] Catalyst: KOH Reaction time: 20 min Reaction temperature: 45 °C Biodiesel yield: 93.6 % [128]	<ul style="list-style-type: none"> <li>• Energy-efficient by reducing the overall energy consumption [129].</li> <li>• Significantly faster reaction time than conventional methods.</li> <li>• High biodiesel yield, up to 90 %.</li> <li>• Enhanced mass transfer and miscibility between oil and methanol [130].</li> <li>• Straightforward separation process between biodiesel and methanol/glycerol.</li> <li>• Reduced formation of emulsions due to low catalyst concentration.</li> <li>• Environmentally friendly and cost-effective.</li> </ul>	<ul style="list-style-type: none"> <li>• Requires design alterations and recalculations for energy circulation.</li> <li>• Might require specific design components such as throttling valve, venturi tube, and orifice plate [130].</li> <li>• Initial set-up and design modifications can be complex.</li> <li>• Potential challenges in scaling up beyond 50L without further modifications.</li> </ul>
Oscillatory baffled reactor (OBR)	Catalyst: H <sub>2</sub> SO <sub>4</sub> (esterification) and KOH (transesterification) Reaction time: 60 s Reaction temperature: 65 °C Frequency: 3.75 Hz Amplitude: 8.0 mm Biodiesel yield: 99.7 % [131] Catalyst: Dolomite Reaction time: 40 min Reaction temperature: 333 K Frequency: 4.3 Hz Amplitude: 8.0 mm Biodiesel yield: 96 % [132] Catalyst: Dolomite Reaction time: 45 min Reaction temperature: 65 °C Frequency: 5.6 Hz Amplitude: 9.2 mm	<ul style="list-style-type: none"> <li>• Enhanced mixing and improved mass and heat transfer.</li> <li>• Longer and adjustable residence time compared with conventional batch reactors.</li> <li>• High biodiesel conversion efficiency (up to 99 %) within shorter reaction time (10 min at 60 °C).</li> <li>• Continuous methanol recycling, reducing the methanol/oil molar ratio needed.</li> <li>• Capable of handling heterogeneous catalysis and processing liquids, crystallisation products, or solid suspensions.</li> <li>• Suitable for other processes such as hydrolysis and esterification.</li> </ul>	<ul style="list-style-type: none"> <li>• Complexity of reactor design and operation.</li> <li>• Potentially higher initial set-up costs compared with conventional reactors.</li> <li>• Requires precise control and maintenance of oscillatory flow conditions.</li> </ul>

(continued on next page)

Table 3 (continued)

Method	Parameters and Performance	Advantages	Disadvantages
Static mixers and motionless inline devices	Biodiesel yield: 98.597 % [133] Catalyst: KOH Reaction time: 30 min Reaction temperature: 60 °C Rotating oscillatory speed: 60 rpm Biodiesel yield: 93.72 % [134]	<ul style="list-style-type: none"> <li>Improved reaction outcomes through efficient transverse flow [136].</li> <li>Lower power requirements compared with static mixers [137].</li> <li>Suitable for both continuous and batch production with adaptable residence times [138].</li> <li>Quicker reaction times (e.g., 15 min for glycerol-free products) [139].</li> <li>Continuous removal of esters and glycerol, eliminating the need for additional separation steps.</li> <li>Commercial devices are available in the market and adaptable for low-pressure drop in the reactor pipe [149,150].</li> </ul>	<ul style="list-style-type: none"> <li>Slight drop in conversion efficiency (e.g., from 99 % to 95 %) [140].</li> <li>Not suitable for heterogenic processes and solid-liquid handling [141].</li> <li>Vessel angle affects separation efficiency.</li> <li>Potential for larger glycerol droplets and may affect overall conversion quality.</li> </ul>
	Biocatalyst: Lipase from <i>Candida</i> sp. 99–125 Reaction time: 12 h Reaction temperature: 40 °C Flow rate: 0.28 m/s Biodiesel yield: >80 % [135]		
Reactive distillation	Catalyst: CaO/Al <sub>2</sub> O <sub>3</sub> Vapourisation temperature: 120 °C Feed stage temperature: 75–80 °C Mass flow rate: 1050 kg/h Biodiesel yield: 99.87 % (with heat exchanger), 99.42 % (extended spacing stage modification), and 98.71 % (pervaporation integration) [142] Catalyst: Not mentioned Reaction temperature: 60 °C Biodiesel yield: 99.98 % [143]	<ul style="list-style-type: none"> <li>Adaptable to various catalysts (homogeneous and heterogeneous catalysts, as well as without catalysts) and applicable for both esterification and transesterification reactions [144].</li> <li>Unused methanol can be recovered and recycled, reducing wastes [145].</li> <li>No additional processes needed: Eliminates the need for additional washing, neutralisation, and waste recovery steps [146].</li> <li>Enhances immiscibility for better separation of products, such as water from fatty acids [147].</li> <li>Tackle the problem of methanol/oil molar ratio requirement, which must be nearly perfect [148, 149].</li> <li>Handle excess methanol recovery [150].</li> </ul>	<ul style="list-style-type: none"> <li>High power consumption: Like traditional distillation processes, the reactive distillation method has high overall power consumption.</li> <li>Performance fluctuates due to difficulties in controlling the ration of the inlet feed [150].</li> </ul>
Electrolysis	Catalyst: KOH, zeolite, and chitosan Reaction time: 3 h Voltage: 40 V Stirring speed: 100 rpm Biodiesel yield: 93 % [67] Catalyst: NaOH and KOH Reaction time: 2 h Reaction temperature 25 °C (ambient) Voltage: 50 V Stirring speed: 300 rpm Biodiesel yield: 98 % [151] Catalyst: KOH Reaction time: 24 h Reaction temperature: 55–60 °C Voltage: 12 V Stirring speed: 50 rpm Biodiesel yield: 87 % (graphite electrode) and 90 % (platinum electrode) [152] Catalyst: Phosphomolybdic acid/clinoptilolite Reaction time: 4.1 h Reaction temperature: Room temperature Voltage: 20.34 V Biodiesel yield: 96.73 % [153] Catalyst: Phosphomolybdic acid/graphene oxide Reaction time: 15 h Reaction temperature: Room temperature Voltage: 60 V Stirring speed: 500 rpm Biodiesel yield: 91 % (FAME) [154]	<ul style="list-style-type: none"> <li>The electrolysis method can achieve high biodiesel yields of more than 80 %.</li> <li>The electrolysis process operates at room temperature, and therefore, extra energy is not needed for heating.</li> <li>Inhibits saponification during purification, making it more cost-effective and environmentally friendly.</li> <li>The use of polar co-solvents and higher voltages enhances the biodiesel yield and conversion efficiency.</li> <li>Contact glow discharge electrolysis (CGDE) hinders soap formation and produces oxygen and hydrogen gas [155].</li> <li>There are many electrode variants available such as graphite [156,157], platinum [158], tungsten, and stainless steel 316 [155].</li> </ul>	<ul style="list-style-type: none"> <li>Commercial application is not yet established.</li> <li>Various parameters, such as electrode distance, must be optimised.</li> <li>Requires specific conditions, such as catalyst type and concentration, voltage, and co-solvents, in order to achieve optimal results.</li> <li>The process is less efficient because it is time-consuming and requires significant amounts of electricity.</li> </ul>
Pilot-scale biodiesel production	Catalyst: Kettle limescale Reaction time: 15 min Reaction temperature: 61.7 °C Biodiesel yield: 93.41 % [68] Catalyst: KOH Reaction time: 90 min Reaction temperature: 75 °C Stirring speed: 350 rpm Biodiesel yield: 97 % [159] Catalyst: NaOH Reaction time: 60 min Reaction temperature: 60 ± 5 °C Stirring speed: 300 rpm	<ul style="list-style-type: none"> <li>Allows testing the viability and efficiency of the biodiesel production process before scaling up to commercial levels [163].</li> <li>Provides opportunities to refine and optimise the process parameters and technologies [164].</li> <li>Helps identify potential cost-saving measures and estimate production costs accurately.</li> <li>Reduces the financial risk associated with full-scale production by identifying and addressing issues early.</li> <li>Facilitates the collection of crucial data on yield, quality, and environmental impact [165].</li> </ul>	<ul style="list-style-type: none"> <li>Results and efficiencies may not always directly translate to larger, commercial-scale operations.</li> <li>Requires significant initial investment in equipment and set-up.</li> <li>Can be time-consuming to set up and run experiments.</li> <li>Managing and maintaining pilot-scale operations can be complex and require specialised knowledge.</li> <li>May require considerable resources, including raw materials and skilled personnel.</li> </ul>

(continued on next page)

Table 3 (continued)

Method	Parameters and Performance	Advantages	Disadvantages
	Biodiesel yield: $86.25 \pm 1.58$ % [160] Biocatalyst: <i>Rhizopus stolonifer</i> 1aNRC11 mutant F (1F) and <i>Aspergillus tamarii</i> NDA03a mutant G (3G) Reaction time: 48 h Reaction temperature: 30 °C Stirring speed: 250 rpm Biodiesel yield: 92.3 % [161] Biocatalyst: Kettle limescale deposits Reaction time: 12.5 min Reaction temperature: 60 °C Stirring speed: 250 rpm Biodiesel yield: 97.16 % [114] Catalyst: NaOH Reaction time: 60 min Reaction temperature: 50–60 °C Stirring speed: 250 rpm Biodiesel yield: 82 % [162]		

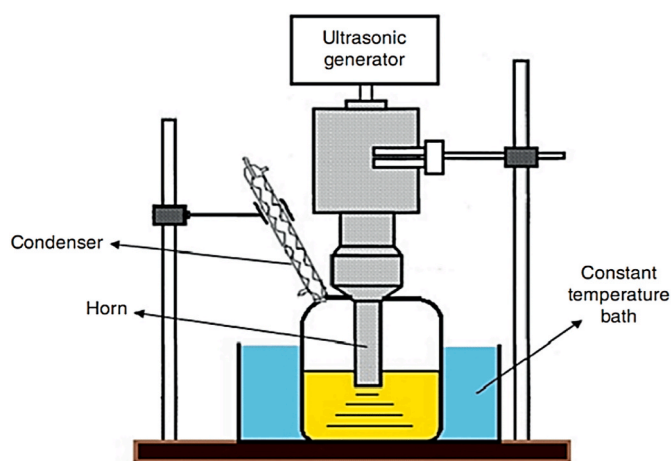


Fig. 8. Schematic ultrasonic reactor setup [55].

Supercritical transesterification avoids the use of catalysts through the use of methanol in supercritical conditions ( $>240$  °C and  $>8.1$  MPa). In this case, methanol plays two roles as a reactant and a solvent, thus

enhancing the fast hydrolysis of triglycerides to biodiesel, with the conversion rate being over 93 % within a period of 15 min [57]. The major limitation, however, lies in the huge energy demands necessary for achieving supercritical conditions. Fig. 9 shows the high-pressure chamber in addition to the procedure used for controlling reactor temperature. The Advanced-Flow™ Reactor (AFR) reactor employs heart-shaped microchannels to enhance turbulent mixing and heat transfer within a continuous flow process. This design reduces the residence time in the reactor to seconds, while at the same time attaining yields up to 95 %, thereby considerably reducing waste generation compared to batch reactors [58]. Fig. 10 illustrates the novel reactor geometry and the optimal fluid dynamics.

The continuous centrifugal contact separator (CCCS) enhances post-reaction purification by utilising rapid rotation of the oil-alcohol mixture, facilitating the separation of glycerol from biodiesel via centrifugal force. This approach enhances process efficiency by 20–30 % and minimises purification steps [59]. Fig. 11 illustrates the rotating drum and phase separation mechanism in detail. In a packed bed reactor (PBR), WCO and methanol are introduced to a fixed bed of solid catalyst, such as calcium oxide (CaO) or zeolite. This configuration facilitates conversion rates ranging from 85 % to 95 % by ensuring extended contact between the reactants and the catalyst. The continuous operation reduces catalyst deactivation and minimises operating expenses

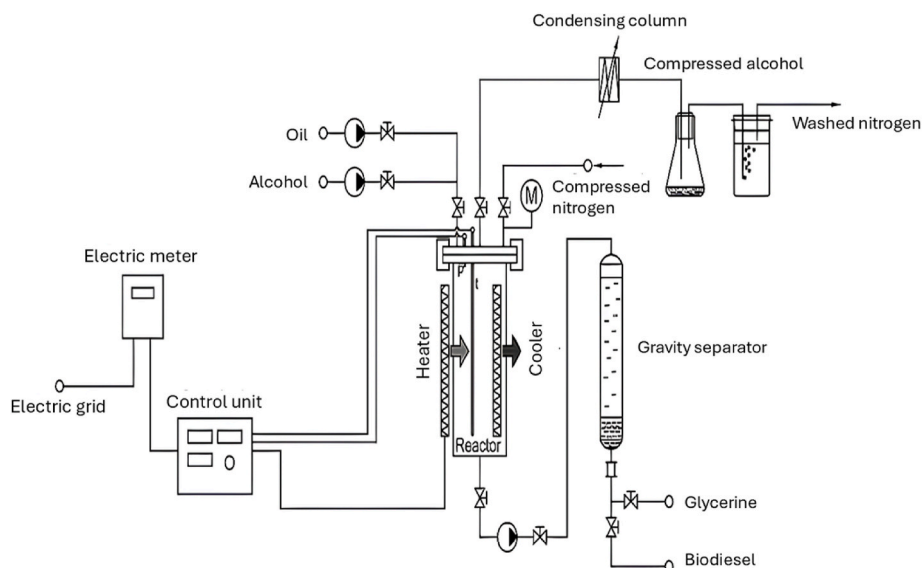


Fig. 9. Distribution schematic of supercritical batch reactor equipment [57].

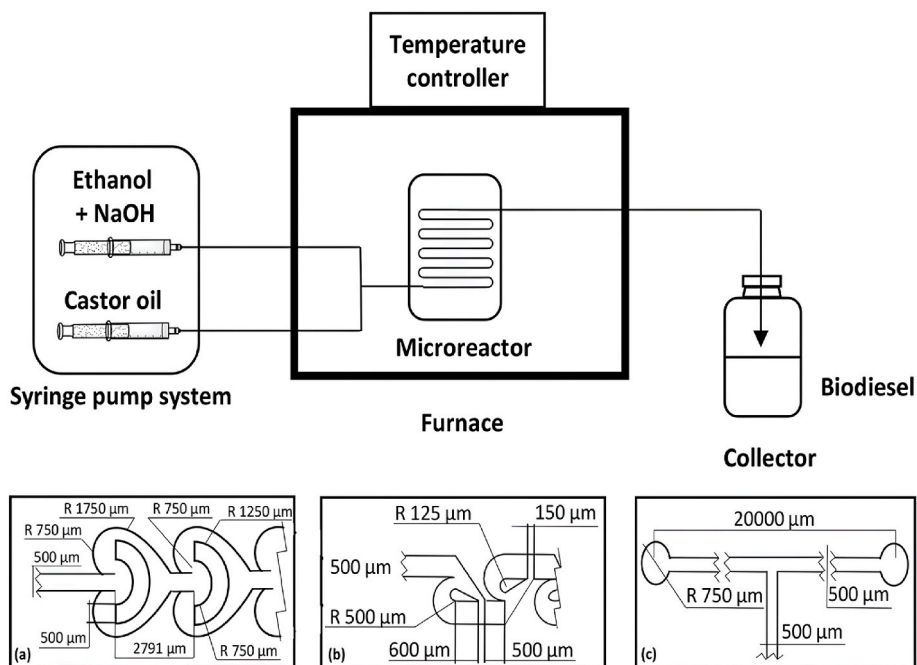


Fig. 10. Transesterification schematic with (a) omega-shaped, (b) Tesla-shaped, and (c) t-shaped microreactors [58].

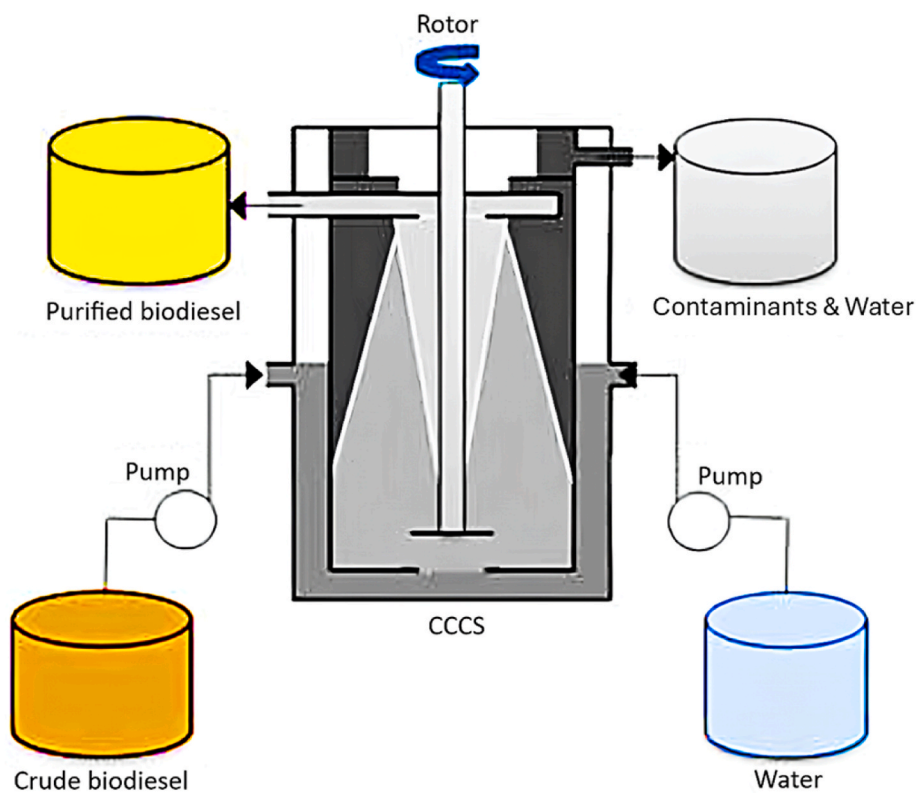


Fig. 11. Schematic of the CCCS device used for biodiesel purification [59].

[60]. Fig. 12 presents a vertical reactor design, with arrows denoting the flow of reactants through the catalyst bed.

The membrane reactor employs a semipermeable membrane for the direct separation of methanol and glycerol, facilitating the reaction equilibrium and resulting in a yield of 97%. This approach minimises the necessity for subsequent purification; however, it necessitates a membrane capable of enduring severe reaction conditions [61]. Fig. 13

illustrates the function of membranes in the phase separation process during biodiesel production. In addition, microtube reactors utilise narrow channels with a diameter of less than 1 mm to optimise the surface area to volume ratio. This design facilitates a conversion rate of 91% within a time frame of 5–20 s, achieved through improved laminar flow mixing. Scalability is constrained by the possibility of clogging [62]. Fig. 14 illustrates a cross-sectional view of the microtube array.

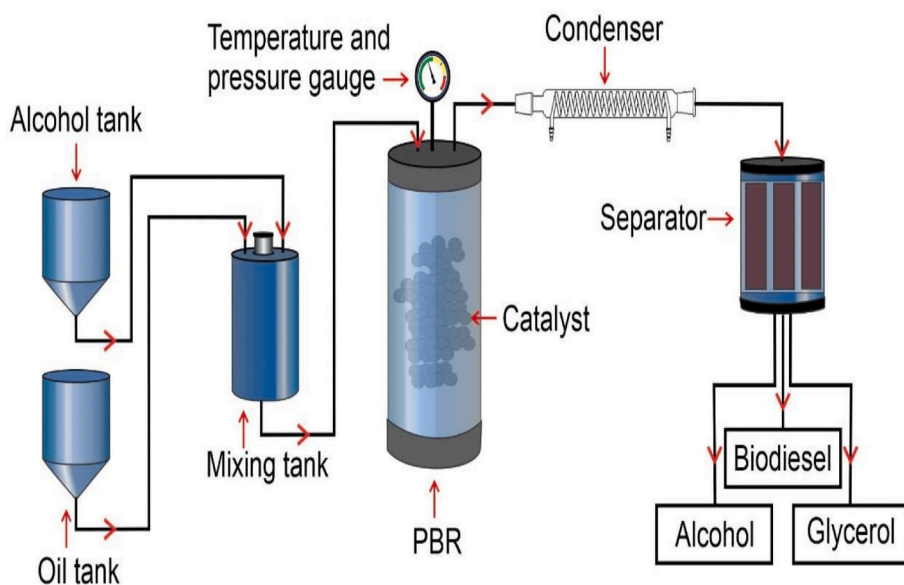


Fig. 12. Schematic of a packed bed reactor [60].

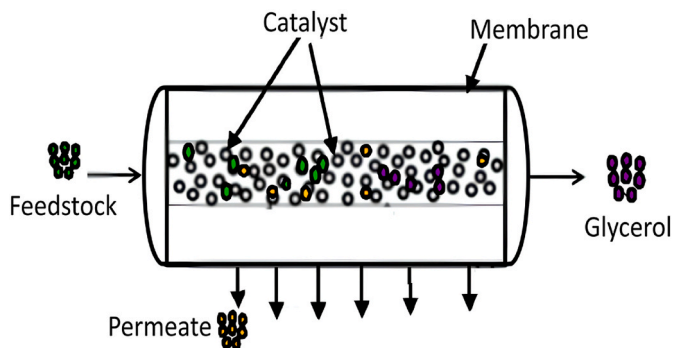


Fig. 13. Schematic diagram illustrating the raw materials and interactive surfaces of the membrane catalyst [61].

Cavitation reactors produce hydrodynamic or acoustic cavitation, resulting in the implosion of vapour bubbles that generates micro-turbulence. This process disrupts the oil-methanol interface and

enhances the reaction kinetics. The rotor-stator design demonstrates a yield of 95 % while minimising energy consumption [63], as illustrated in Fig. 15. The oscillating baffle reactor (OBR) employs an oscillating baffle to create a laminar flow vortex, which decreases the molar ratio of methanol to oil from 9:1 to 6:1, while attaining a conversion rate of 90 % within 30 min [64]. Fig. 16 illustrates the baffle plate along with the oscillating flow pattern.

Static mixers and motionless inline devices that do not utilise motion employ helical elements to create turbulence without the need for moving parts. This design can decrease reaction time by as much as 50 %, facilitating continuous production at an industrial scale [65]. Fig. 17 illustrates the internal geometry of the mixer. (Abbreviations utilized in the figure: T1 represents the refined palm oil (RPO) tank. H denotes the immersed heater. TC indicates the temperature controller. P1 refers to the RPO dosing pump. T2 signifies the CH<sub>3</sub>KO tank. P2 is the CH<sub>3</sub>KO dosing pump. S0 to S5 are the sampling ports located at 0–5 m. SM stands for the static mixer. L is the length, and D represents the diameter of the mixing element). Reactive distillation (RD) combines transesterification and product separation within a single column. In this

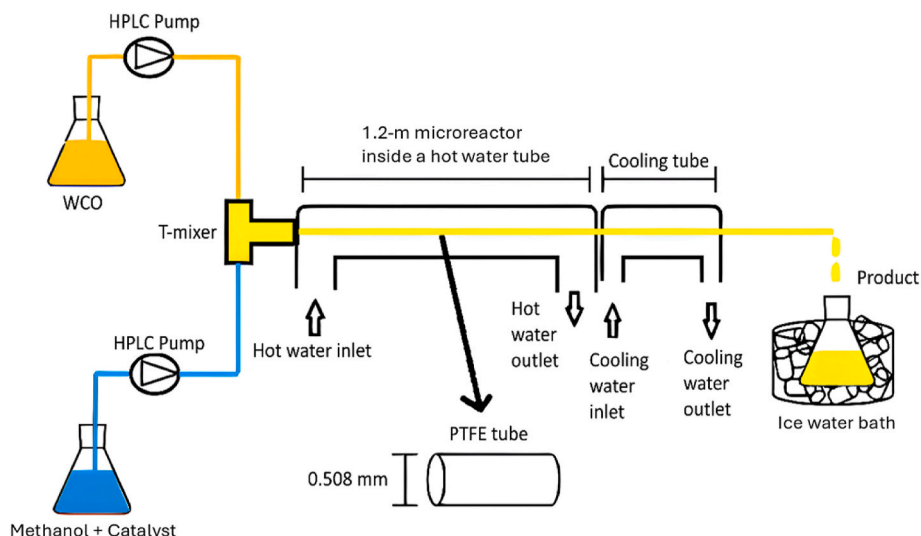


Fig. 14. Microtube reactor experiment equipment [62].

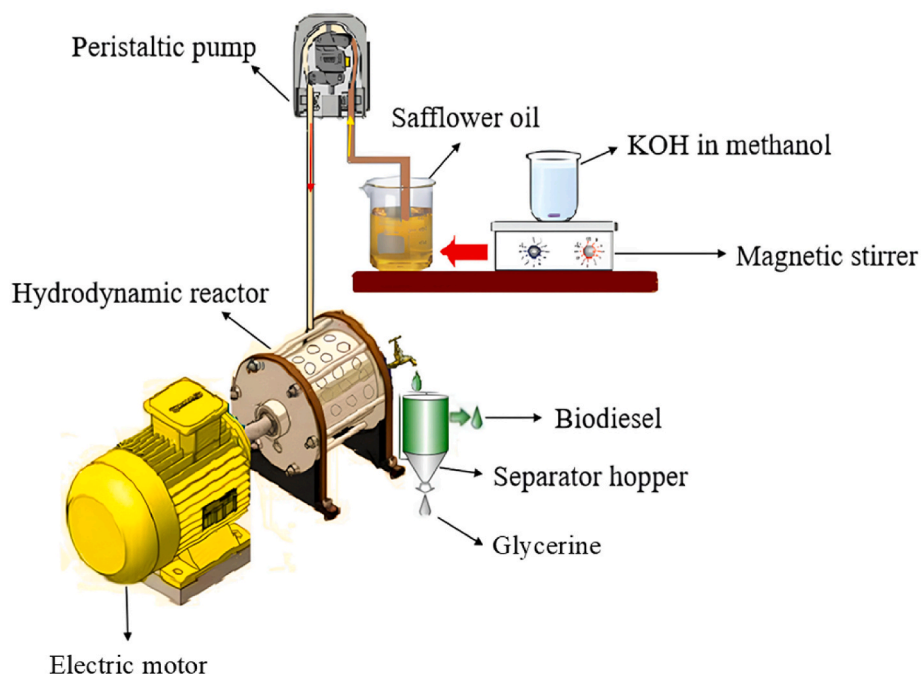


Fig. 15. Schematic of the hydrodynamic reactor system [63].

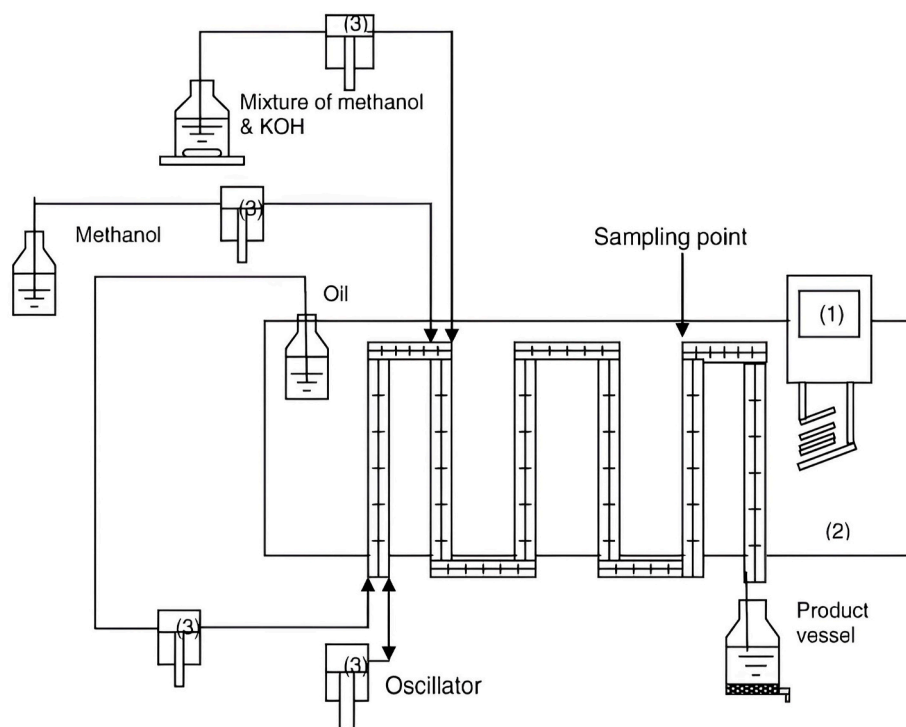


Fig. 16. Schematic representation of the experimental setup for continuous biodiesel production, including the following components: (1) temperature controller, (2) water bath, and (3) injection pump.

process, methanol vapour continuously extracts glycerol, thereby shifting the reaction equilibrium. Conversions exceed 98 %, while energy demand continues to be elevated [66]. Fig. 18 illustrates the reaction zones and separations within the distillation column.

Electrolysis-assisted transesterification generates  $H^+$  and  $OH^-$  ions, effectively inhibiting soap formation and achieving a yield of 93 % with minimal catalyst loading. The configuration of this method comprises electrodes and ion migration pathways, as illustrated in Fig. 19 [67].

Finally, pilot-scale production system is implemented to replicate industrial conditions, allowing for the optimisation of parameters including temperature and catalyst loading. A recent study utilising heterogeneous catalysts, such as kettle scale, indicated a yield above 93 % under 15 min reaction time, with potential for improved feasibility [68]. Fig. 20 depicts the control system of the pilot reactor along with the associated monitoring sensors.

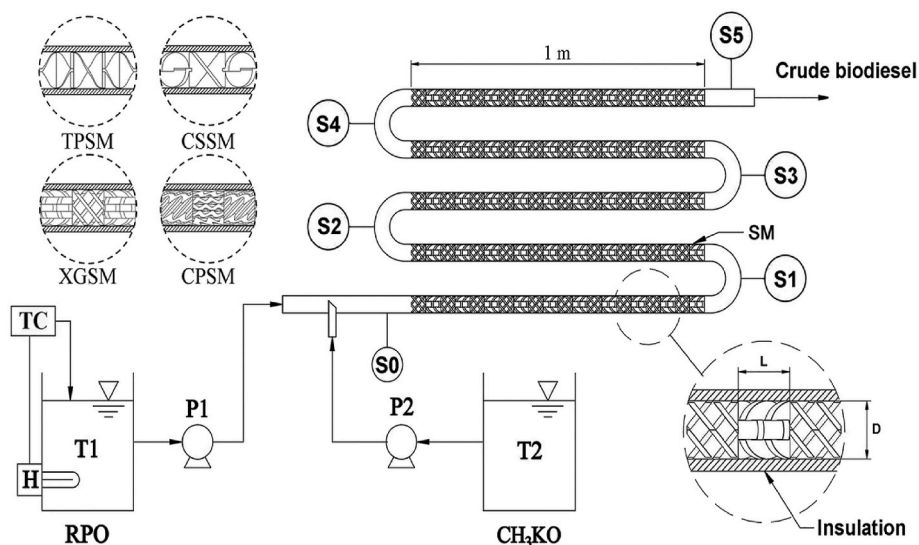


Fig. 17. Schematic representation of sustainable biodiesel production utilizing a 3D printed static mixer [65].

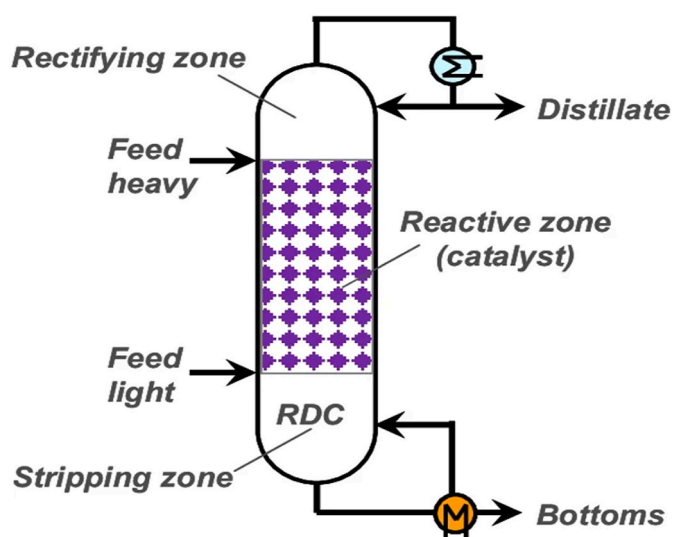


Fig. 18. Configuration of the reactive distillation process [66].

## 5. Types of catalysts

The FFA content must be restricted to allowable levels to prevent soap formation. Soap formation usually occurs during transesterification and results in the formation of non-reversible emulsions, which will reduce the biodiesel conversion rate. The recommended FFA content based on the literature survey will be discussed below. Acid pretreatment is suggested whenever the FFA content is above the recommended level. However, this will increase the overall operation cost. The benefits and drawbacks of homogeneous, heterogeneous, and bifunctional heterogeneous catalysts are discussed in the following sections.

### 5.1. Homogeneous catalysts

Homogeneous catalyst is a soluble catalyst with reactants, usually in the liquid phase [166]. Homogeneous catalysts are typically used in biodiesel production and homogeneous catalysts have been widely used in esterification and transesterification processes. These catalysts provide high catalytic efficiency and high reaction rate [167]. The limitations of homogeneous catalysts are the difficulties in separating the

products from the catalyst and the purification method. The homogeneous alkaline catalysts commonly used are sodium hydroxide, sodium methoxide, potassium hydroxide, and potassium methoxide.

In contrast, the homogeneous acidic catalysts used are sulphuric acid, hydrochloric acid, and super phosphoric acid [168]. The homogeneous catalyst used during the esterification and transesterification processes will cause inaccuracies when determining the physicochemical properties of the biodiesel [37]. In addition, soap formation as a result of excess alkaline catalysts may require more washing processes, leading to emulsion formation and high production costs for biodiesel production [169]. Lin et al. [46] conducted various experiments to investigate the effect of varying the ionic liquid concentration of 4-allyl-4-methylmorpholin-4-ium-bromine, NaOH, and combination of ionic liquid with NaOH as a catalyst on the biodiesel yield. The catalyst was formed from allyl bromide added dropwise into a solution of N-methylmorpholine. The mixture was refluxed under argon atmosphere for 24 h at 50 °C and cooled to form a purified ionic liquid. The ionic liquid can be recycled, and it is easily separated from the biodiesel by decantation. The reuse of ionic liquid is highly recommended since the ionic liquid can be used for seven times and result in a biodiesel yield of ~98 %. After seven times, the ionic liquid deteriorates as the removal of glycerol in the ionic liquid has not been investigated yet. The comparison of the transesterification process using various feedstock with different parameters using homogeneous catalysts are shown in Table 4.

In general, a catalyst is defined as any material or substance that accelerates the chemical reaction rate by reducing the activation energy. Catalyst is required in tiny amounts compared with the quantity of the reactants to initiate the esterification or transesterification process, and therefore, it is called an initiator. The catalyst is not consumed during a chemical process, but in some cases, the conversion process consumes the catalyst, which will delay the chemical reaction. Therefore, selecting an appropriate catalyst is vital to the chemical reaction, since some catalysts are hazardous to human health and the environment. Selecting a catalyst that produces few toxic by-products will make the reaction more environmentally friendly and commercially feasible. The homogeneous catalysts used in biodiesel production present some disadvantages since it is difficult to separate the catalysts from the reactants. Both catalyst and reactants work in the same phase in a reaction mixture, which makes it challenging to separate the catalyst from the unused reactant or biodiesel. In addition, the miscibility between the catalyst and reactant or between the catalyst and biodiesel increases the difficulties of the purification process, raising economic and environmental concerns. Therefore, the use of heterogeneous catalysts is proposed for

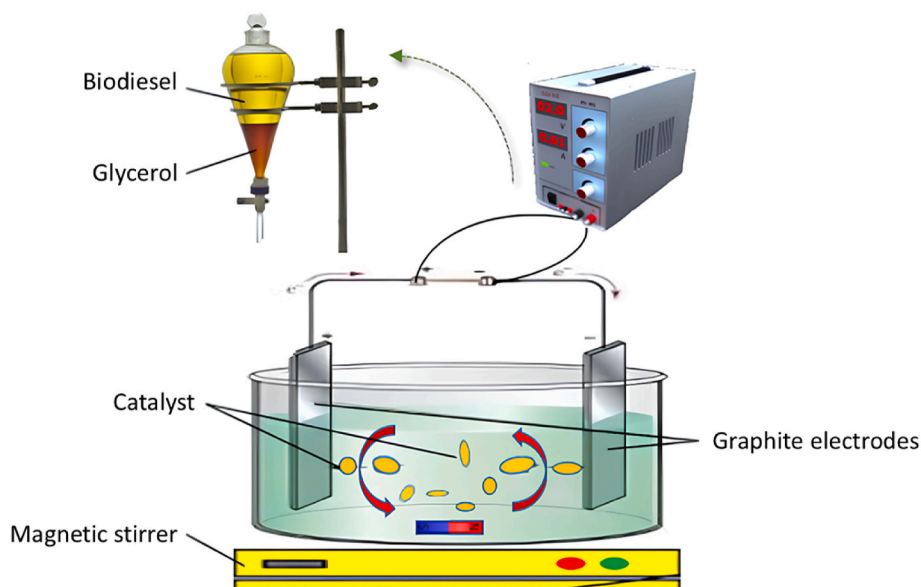


Fig. 19. The schematic of an electrolysis cell [67].

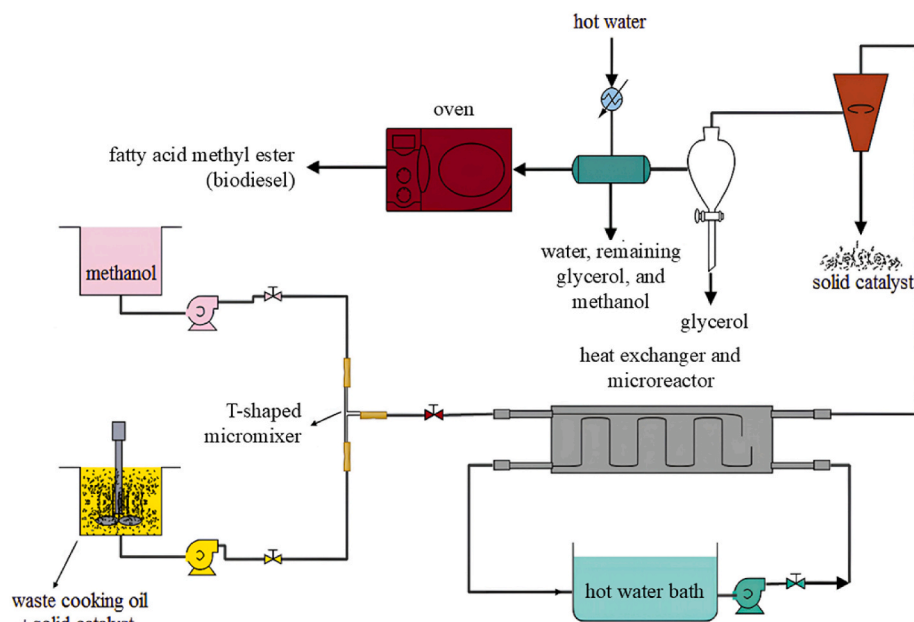


Fig. 20. Schematic representation of a semi-industrial microreactor utilized to produce biodiesel [68].

the esterification or transesterification process to synthesise the biodiesel because scholars found that heterogeneous catalysts eliminate some steps required by homogeneous catalysts. Green heterogeneous catalysts can simplify the catalyst separation process, facilitate purification, reduce soap formation, increase water tolerance, and increase the reusability of the catalyst.

## 5.2. Heterogeneous catalysts

Heterogeneous catalysts are catalysts that work in a different phase from that of the targeted medium. In biodiesel production, both the feedstock and alcohol are in the liquid phase whereas the heterogeneous catalyst is in the solid phase [182]. Heterogeneous catalysts have garnered much attention from the scientific community and biodiesel industry in recent years due to their lower costs, environmental

friendliness, reusability, and less purification hassle than homogeneous catalysts. Heterogeneous catalysts are easily separated from the mixture medium via filtration or centrifugation.

The heterogeneous catalysts involved in biodiesel production include mixed metal oxides (MgO, CaO, BaO, and  $\text{CoFe}_2\text{O}_4$ , SrO), alkaline metal oxides, transition metal oxides (ZnO, PbOx, and  $\text{ZrO}_2$ ), carbonates and oxides, lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ), ion-exchange resins, sulphated oxides, and immobilised enzymes [186,187]. Heterogeneous catalysts can be alkaline or acidic, and it is dependent on the scholar to select the suitable type of catalyst. Heterogeneous acidic catalysts such as ferric sulphate [188], sulfonated carbon [33,189], Cs-doped heteropolyacid [190], and magnetic acid ( $\text{MoO}_3/\text{SrFe}_2\text{O}_4$ ) [191] can be used to esterify the oil and reduce the FFA content. Heterogeneous alkaline catalysts are more widely used than acidic catalysts. Heterogeneous alkaline catalysts are used for the transesterification process, which converts

**Table 4**  
Comparative analysis of homogeneous, heterogeneous, and enzymatic catalysts for transesterification process.

Catalyst type	Feedstock	Catalyst concentration	Equipment	Operating conditions	Biodiesel yield (%)	Reference
Homogeneous Alkaline	<i>Chrysophyllum albidum</i> oil	KOH (1 % w/w)	Open-system reactor	Reaction time = 40 min Reaction temperature = 65 °C Methanol/oil molar ratio = 9:1 Stirring speed = 500 rpm	99.20	[53]
Homogeneous Alkaline	<i>Solanum nigrum</i> L. oil	KOH (1 % w/w)	Three-neck flat bottom flask	Reaction time = 35 min Reaction temperature = 65 °C Methanol/oil molar ratio = 9:1 Stirring speed = On	99.67	[170]
Homogeneous Alkaline	Black mustard ( <i>Brassica nigra</i> L.) seed oil	KOH (0.838 % w/w)	Three-neck round bottom flask	Reaction time = 56 min Reaction temperature = 35.4 °C Ethanol = 45.12 % (v/v) Stirring speed = 600 rpm	96.22	[171]
Homogeneous Alkaline	Black mustard ( <i>Brassica nigra</i> L.) seed oil	NaOH (0.504 % w/w)	Three-neck round bottom flask	Reaction time = 60.5 min Reaction temperature = 59.5 °C Methanol = 21.5 % (v/v) Stirring speed = 600 rpm	96.87	[171]
Homogeneous Alkaline	Flaxseed oil	KOH (0.51 % w/w)	Three-neck glass reactor	Reaction time = 33 min Reaction temperature = 59 °C Methanol/oil molar ratio = 5.9:1 Stirring speed = On	98	[26]
Homogeneous Alkaline	Castor oil	KOH (1 % w/w)	Batch reactor	Reaction time = 30 min Reaction temperature = 60 °C Methanol/oil molar ratio = 9:1 Stirring speed = 400 rpm	95	[172]
Homogeneous Alkaline	WCO + <i>Calophyllum inophyllum</i> oil	KOH (0.52 % w/w)	Double jacket reactor	Reaction time = 65.8 min Reaction temperature = 61 °C Methanol = 68 % (v/v) Stirring speed = 1000 rpm	94.12	[27]
Homogeneous Alkaline	WCO + <i>Calophyllum inophyllum</i> oil	KOH (0.77 % w/w)	Microwave reactor	Reaction time = 7.15 min Reaction temperature = 100 °C Methanol = 59.6 % (v/v) Stirring speed = 600 rpm	97.65	[173]
Homogeneous Alkaline	WCO	CH <sub>3</sub> ONa (0.75 % w/w)	Microwave reactor	Reaction time = 3 min Microwave power = 750 W Methanol/oil molar ratio = 6:1 Stirring speed = 600 rpm	97.90	[174]
Homogeneous Alkaline	Waste cottonseed oil	KOH (0.46 % w/w)	Ultrasound reactor	Reaction time = Not stated Reaction temperature = 53.2 °C Methanol/oil molar ratio = 6.1:1	97.76	[175]
Homogeneous Alkaline	Waste cottonseed oil	KOH (0.65 % w/w)	Microwave reactor	Reaction time = 9.6 min Reaction temperature = 50 °C	96.55	[176]

(continued on next page)

Table 4 (continued)

Catalyst type	Feedstock	Catalyst concentration	Equipment	Operating conditions	Biodiesel yield (%)	Reference
Homogeneous Alkaline	WCO	KOH (1.16 % w/w)	Microreactor	Methanol/oil molar ratio = 7:1 Stirring speed = 400 rpm Reaction time = 2 min Reaction temperature = 62.4 °C	98.26	[177]
Homogeneous Alkaline	WCO	NaOH (1 % w/w)	Oscillatory flow reactor	Methanol/oil molar ratio = 9.4:1 Reaction time = 30 min Reaction temperature = 60 °C	72.50	[178]
Homogeneous Alkaline	WCO	KOH (1 % w/w)	Ultrasound reactor	Methanol/oil molar ratio = 6:1 Reaction time = 10 min Reaction temperature = 60 °C	96.50	[179]
Homogeneous Alkaline	WCO	KOH (1 % w/w)	Microwave reactor	Methanol/oil molar ratio = 7.4:1 Reaction time = 6 min Microwave power = 500 W	96.50	[180]
Homogeneous Alkaline	<i>Ceiba pentandra</i> oil	KOH (0.84 % w/w)	Microwave reactor	Methanol/oil molar ratio = 8:1 Reaction time = 388 s Methanol = 60 % (v/v) Stirring speed = 800 rpm	95.42	[181]
Heterogeneous Alkaline	WCO	CaO (5 % w/w (derived from eggshell))	Fixed bed reactor	Reaction time = 6 h Reaction temperature = 65 °C Methanol/oil molar ratio = 12:1 Stirring speed = 500 rpm	86.7	[182]
Heterogeneous Acid	WCO-High FFA	SO <sub>4</sub> ZrO <sub>2</sub> (3 % w/w)	Reactor tank with stirrer	Reaction time = 10 min Reaction temperature = 140 °C Methanol/oil molar ratio = 1:10 Stirring speed = 500 rpm	96.38	[183]
Heterogeneous bifunctional	Palm oil	SrO-ZnO/Al <sub>2</sub> O <sub>3</sub> (10 % w/w)	Two necked glass reactors	Reaction time = 3 h Reaction temperature = 70 °C Methanol/oil molar ratio = 10:1	95.1	[184]
Heterogeneous	WCO	CaO (3 % w/w (derived from snail shells))	Hot plate with stirrer	Reaction time = 1 h Reaction temperature = 65 °C Methanol/oil molar ratio = 9:1 Stirring speed = 300 rpm	92.5	[54]
Enzymatic	WCO	<i>Candida</i> sp. 99-125 lipase (0.2 % and 0.4 % w/w)	Batch reactor	Reaction time = 24 h Reaction temperature = 40 °C Stepwise methanol addition Stirring speed = 220 rpm	N/A	[49]
Enzymatic	WCO	<i>Candida</i> sp. 99-125 lipase (5–30 % w/w)	Fixed bed reactor	Reaction time = 100 h Reaction temperature = 40 °C Lipase/oil molar ratio = 25:100 Stirring speed = 200 rpm	76.74	[185]

the oil with low FFA content into biodiesel. Heterogeneous alkaline catalysts such as MgO [192], CaO [193,194], CaO–MgO [195], MnFe<sub>2</sub>O<sub>4</sub>–graphite [196], Ba<sub>2</sub>TiO<sub>4</sub> [197], CaO–CoFe<sub>2</sub>O<sub>4</sub> [198], SrO [199], SrO–CaO–Al<sub>2</sub>O<sub>3</sub> [200], Fe(III)–ZnO [201,202], Kr–CaO [48], and Na<sub>2</sub>ZrO<sub>3</sub> [203] have been used by many scholars. The catalyst is

prepared via the wet impregnation method, which involves a few steps. The catalyst or oxides are doped with a transition metal in the form of an aqueous solution, or the catalyst is composed of alkaline metals and alkaline earth metals from Group I or Group II of the periodic table. After doping, the catalyst is dried, calcined, and cooled. Most scholars used

CaO as their heterogeneous catalyst as CaO can be obtained from natural resources such as limestone ( $\text{CaCO}_3$ ). However, limestone is not renewable. Scholars have also used sustainable natural resources to produce CaO, such as eggshells [182,204], crab shells [205], snail shells [54], mussel shells [206], oyster shells [194], and bones from poultry [207,208] or marine sources [209]. CaO has high basicity and low solubility, and is easy to handle, widely available, and inexpensive, and can be obtained from sustainable sources [183]. The characteristics of the produced heterogeneous catalyst are determined by X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). The efficiency of the heterogeneous catalyst is dependent on the specific surface area, total pore volume, and diameter. Larger pore diameters with larger interconnected pores are preferable as it will minimise the diffusion limitation of the reactant molecules, allowing reactants to diffuse into the interior of the catalyst, which boosts catalytic activity. Scholars have developed heterogeneous catalysts with bifunctional characteristics, where the catalysts have both acid and alkali active sites. The bifunctional heterogeneous catalysts are Sr/ZrO<sub>2</sub> [47], SnO<sub>2</sub>@Mn-ZIF [210], Co-N<sub>x</sub>-ZIF67 [211], LiNbO<sub>3</sub> [212], MFHAC-4 K<sub>2</sub>CO<sub>3</sub>/Cu [213], and SrO-ZnO/Al<sub>2</sub>O<sub>3</sub> [184]. The bifunctional heterogeneous catalysts assist both esterification and transesterification reactions simultaneously, achieving a biodiesel yield of more than 95 %. They have high catalytic activity on acid and alkali sites. Bifunctional catalysts can be reused up to five times. The bifunctional catalysts improve the biodiesel yield, minimise environmental problems, and require less hassle compared with acidic or alkaline heterogeneous catalysts. The stability of the catalysts makes them promising candidates for future biodiesel production. However, bifunctional catalysts still have many issues that need to be addressed before they can be commercialised, especially in terms of the processing technology.

In summary, heterogeneous catalysts will reduce the number of metal elements dissolved in the biodiesel, which generally comes from the catalyst. Even though heterogeneous catalysts perform well compared with homogeneous catalysts, they do have their disadvantages. First, the limitation of active catalytic sites of heterogeneous catalysts results in a large amount of catalyst used for the biodiesel conversion process (2–25 (w/w)%). Similarly, a catalyst with a different phase than the reaction mixture results in mass transfer resistance, which will reduce the reaction rate of the transesterification process. Moreover, heterogeneous catalysts require a preliminary process, which is very time-consuming, and they need to be calcined before the transesterification process. Exposing the catalyst to the surrounding air will reduce their active sites, which will reduce the efficiency of the heterogeneous catalyst. Heterogeneous catalysts are preferred as alternative catalysts to initiate the synthesis of biodiesel since they can be easily separated from the liquid mixture. Moreover, heterogeneous catalysts can be reused up to five times and have high catalytic activity, and therefore, they are more environmentally friendly than homogeneous catalysts. However, heterogeneous catalysts are limited by their low mass transfer as they are of a different phase from the reaction medium. In addition, the production cost of heterogeneous catalysts is higher than that of homogeneous catalysts. However, the prices of heterogeneous catalysts can be reduced after their growth trends are stabilised in the global market.

### 5.3. Enzymatic catalysts

Enzymatic catalysts, which are currently used in biodiesel production, are lipase enzymes which can be divided into three main groups: (1) plant lipase (papaya latex, rapeseed, and castor seed), (2) animal lipase (pancreas of cattle, sheep, hogs, and pigs), and (3) microbial lipase (bacteria, fungi, and yeast) [214]. Microbial lipases are widely used as they are more stable and cheaper compared with plant and animal lipases. Many scholars have stated that enzymatic conversion is very slow, and the biodiesel yields are lower than those obtained using

conventional catalysts. Many studies have been carried out to select the suitable enzyme for the right feedstock. The following factors will influence the results: (1) type and properties of the enzymatic catalyst, (2) enzyme pre-treatment, (3) enzyme production process, (4) biodiesel substrate, (5) type of solvent, and (6) operating conditions such as the reaction temperature. Enzymatic catalysts require a longer reaction time (>25 h) and a reaction temperature slightly above room temperature (35–45 °C) with step-wise addition of methanol to the medium. The common enzymatic catalyst used by scholars are *Candida* sp. 99–125 lipase [49,185], Novozym 435, and Lipozyme TLIM [215]. They obtained a biodiesel yield of 97 %, which is quite high for enzymatic catalyst reaction. The reaction time is crucial for enzymatic catalysts. If the reaction time is prolonged, this means that the addition of methanol into the medium will be increased. The toxicity of methanol inhibits lipase function or glycerol, which reduces the surface area of the immobilised lipase. Even though the use of enzymatic catalyst results in a slower conversion reaction, the enzymatic catalysts are advantageous since they will solve wastewater generation and promote more glycerol recovery, which are typically problems associated with conventional chemical catalysts. However, the use of enzymatic catalysts is not recommended for the biodiesel industry as the catalysts are very time-consuming and costly compared with other catalysts, and technical expertise is required to observe and study the activity of the enzymatic catalysts.

## 6. Optimisation of biodiesel production

In biodiesel production, the biodiesel yield is the main interest of scholars. The higher the number of controlled parameters, the more experimental trials must be carried out, in which not all the results are necessarily essential. Optimisation simplifies the experimental design by reducing the number of experimental trials based on a set of variables. There is various optimisation methods used to optimise the process parameters and maximise the biodiesel yield, which will be discussed in this section.

Response surface methodology (RSM) is an optimisation method commonly used to effectively examine the effect of independent and dependent variables. In optimising the transesterification process, the RSM is used to collect statistical data and develop mathematical models to optimise the process parameters and predict the biodiesel yield. Without RSM, many experiments need to be carried out to develop a mathematical model. Therefore, RSM coupled with Box–Behnken design (BBD) has greatly facilitated scholars in obtaining the optimal process parameters [216]. At the same time, the method significantly reduces the total number of experimental trials. Hence, RSM helps boost productivity while minimising the time, materials, and costs required for an optimisation study [217]. BBD ensures fitting of a quadratic model, and the estimation of variance is dependent on the factors. Scholars have used this method to optimise biodiesel production [218,219]. The investigated parameters were the type of technology, type of catalyst, catalyst concentration, alcohol/oil molar ratio, stirring speed, reaction temperature, and reaction time [220,221]. Optimisation studies assist scholars to obtain the optimal process parameters in order to achieve high biodiesel yields (>97 %).

Many scholars have claimed that RSM coupled with BBD have greatly reduced the total number of experiments while obtaining a mathematical model with a high coefficient of determination ( $R^2 > 0.9$ ), indicating that more than 90 % of the variability of dependent variable is explained by the variability of the independent variables in the model. Besides BBD, central composite design (CCD) has also been widely used by scholars to optimise biodiesel production, as described in the following section.

### 6.1. Optimisation using RSM coupled with CCD

CCDs contain twice as many star points as there are factors in the

design. The star points in the design represent the extreme value of the study parameters. There are three types of CCDs: (1) central composite circumscribed (CCC), central composite inscribed (CCI), and central composite face-centred (CCF). Fig. 21 shows the star points located for every CCD design. The original form of the CCD is the CCC design, where the star points show the extreme low and high values for all factors. CCI design is a scaled-down version of the CCC design, where each factor level of the CCC design is divided by  $\alpha$  to generate the CCI design, which also requires five levels for each factor. In the CCF design, the star points are at the centre of each face of the factorial space,  $\alpha = \pm 1$ . The CCF design requires three levels for each factor [222].

A crucial component is the rotational capacity, or iso-variance per rotation, indicating uniform prediction error from all sites equidistant from the centre point [223]. As shown in Fig. 21, the CCD model is always magnate with corner points, with black dots denoting the corner locations. The lateral edges (black dots) restrict the extraction spots from the centre. The star points establish new extremes for both low and high settings across all variables. This design exhibits circular, spherical, or hyperbolic symmetry and necessitates five levels for each factor. A factorial design with initial points enhances the current elements, facilitating the creation of a design. Scholars identify the CCC design as a rotational configuration [222]. The CCI design uses the arrangement of factors as star points and creates a factorial design within the boundary. In other words, the CCI design is a modified version of the CCC design. It divides the CCC design into a CCI model, which then forms a rotation model, as shown in the middle of Fig. 21. The design with a plane angle (CCF) (right of Fig. 21) cannot be rotated, and its star points serve as the centre points for each side of the factorial space. Therefore,  $\alpha = \pm 1$ . This design requires three levels for each factor [224].

Scholars have adopted CCD to perform enzymatic interesterification using immobilised mixed lipase of *B. subtilis* and *B. cepacian* (MTCC 1617) methyl acetate as an acyl acceptor to produce biodiesel [225]. RSM coupled with CCD based on four factors with five levels ( $2^4$  factorial design) has been adopted to investigate the effect of the independent factors such as biocatalyst loading, oil/methyl acetate molar ratio, reaction temperature, and reaction time with five levels [(-2) -(-1)-0-1-2]. RSM with CCD was found to predict the response within limits and produce a maximum biodiesel yield of 93.61 %. The CCD was also adopted in another study to optimise the extraction process and the results showed that the extraction time was reduced by 75 % compared with that obtained using the conventional method [226]. CCD was also used to study the interaction of process variables and to predict the optimal process conditions using a bifunctional catalyst [227]. The process variables were the methanol/oil molar ratio, catalyst concentration, reaction time, and reaction temperature. RSM has facilitated scholars in determining the relationships between the process parameters with a minimum number of experimental trials. CCD has been widely adopted for biodiesel synthesis and the error between predicted and actual experimental results is less than 10 % [228]. CCD is a useful experimental design to optimise biodiesel production process parameters and estimate the maximum biodiesel yield. In CCD, the effects of independent factors and their interaction effects are studied. CCD is capable of predicting the response variable effectively by varying the

process parameters simultaneously.

## 6.2. Optimisation using Taguchi method

The Taguchi method is another statistical tool used to reduce the variation in a process through robust experimental design. The Taguchi method evaluates the parameters that affect the mean and variance of the performance characteristics of a process. The Taguchi method involves using orthogonal arrays to organise the parameters affecting the process and the levels at which they should be varied, rather than testing all of the possible combinations, which is the case for full factorial design. The Taguchi method only tests pairs of combinations, which results in fewer experimental trials than BBD and CCD. Analysis of variance (ANOVA), bin yield, and Fisher's exact test, and chi-squared test are used to test the statistical significance. The Taguchi method requires fewer number of experiments to determine the optimal process parameters. The results are then analysed by referring to the signal-to-noise (S/N) ratio and the effects of the factors on the response are evaluated. Here, S indicates the desirable value whereas N indicates the undesirable value. The larger the S/N ratio, the better criterion is applied to maximise the biodiesel yield. Some scholars performed biodiesel production optimisation studies using two methods such as RSM and Taguchi method [229]. The optimal process parameters obtained from the RSM and Taguchi method were compared and the results were close to one another. The error between the two methods was less than 2 %. Scholars suggest that RSM is more reliable in predicting the non-linear relationship between the variables and response. The Taguchi method is more suitable for linear interactions due to fewer experimental data in the analysis. The Taguchi method has also been coupled with grey relational analysis (GRA) to optimise the transesterification process [230]. The GRA analysis resulted in an accuracy of 0.9687, indicating the reliability of the developed model in predicting the biodiesel yield. The common parameters optimised for biodiesel production are the methanol/oil molar ratio, type of catalyst, catalyst concentration, reaction temperature, stirring speed, and reaction time [231]. The Taguchi method was also used to study the production of heterogeneous catalyst by varying the catalyst calcination temperature, catalyst calcination time, catalyst loading, alcohol/oil molar ratio, reaction temperature, and reaction time [232]. The error between the experimental and predicted biodiesel yields was less than 1 %, which makes the Taguchi method one of the reliable methods to optimise the biodiesel production process parameters.

## 6.3. Optimisation using full factorial design

In full factorial design, one can manipulate the controllable factors (independent variables or inputs) at different levels to observe the effect of these factors on the response variable (dependent variable or output). The experimental design has input factors set at two levels, each called 'high' and 'low' or '+1' and '-1', respectively. A design with all possible high and low combinations of input factors is called a two-level full factorial design. If there are  $k$  factors, each with two levels, the full factorial design has  $2^k$  experimental runs. The experimental design is

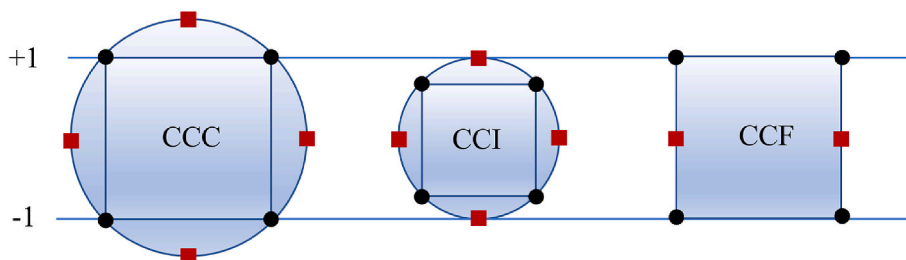


Fig. 21. Comparison of three types of CCD [222].

represented by a full factorial design matrix. Optimisation study has been carried out using full factorial design recently [233]. The investigated factors were the methanol/oil molar ratio, reaction temperature, catalyst concentration, reaction time, and stirring speed and the targeted responses were the FAME purity and yield [221]. ANOVA can be used to develop an accurate FAME model based on the factors and their interactions at the 95 % confidence level. The  $R^2$  value represents the variability of the dependent variable explained by the independent variables in the model. Full factorial designs are not recommended for more than five factors as the total number of experimental trials will be large, which is not cost-effective.

#### 6.4. Optimisation using multi-objective optimisation

Multi-objective optimisation is a decision solver that helps to make conflicting decisions that often exist in biodiesel production. Biodiesel production typically involves a few issues: economic, environmental (ecology issue), and social issues [234]. Multi-objective optimisation not only deals with biodiesel yields but also decisions involving environmental and sustainability issues. From the economic perspective, studies are often focused on the optimal operation of the plant and annual biodiesel production to maximise the net profit. Environmental impact is another objective that needs to be considered, and it is crucial to minimise the environmental impact and cost simultaneously. Minimising costs and environmental impact are usually contradictory objectives, since using environmentally friendly technologies implies higher costs. In terms of social objectives, increasing the chemical operators' job is considered to be an unrealistic approach. Most industrial companies expect to reduce their costs and maximise profit, while reducing their environmental footprint. However, there is no information about how the company aims to increase the number of operators' jobs as this will affect the production cost. The main operating cost for a biochemical industry is material cost (86.19 %), facility-dependent cost (9.36 %), utility cost (2.25 %), and labour cost (2.23 %). Hence, labour cost only constitutes a small portion of biodiesel production [235].

Woinaroschy [235] performed multi-objective optimisation of biodiesel production using soya bean oil with focus on sustainability. The objectives of their study involved economic, environmental, and social aspects. They performed simulations using SuperPro Designer software and optimisation using MATLAB's genetic algorithm based on COM technology. The objective functions are listed as follows:

Economic objective,  $f_1$  : maximising the net profit  $\left(\frac{\$}{\text{year}}\right)$

Ecological objective,  $f_2$  : minimising the volatile organic compound (VOC) emissions  $\left(\frac{\text{kg}}{\text{h}}\right)$

Social objective,  $f_3$  : maximising number of chemical operators' jobs

This case study presented a first attempt of a multi-objective optimisation problem (MOOP) with three objectives under one function vector that generally only deals with two objectives. The results showed that soya bean oil was the main drawback due to the high cost of the raw material. Hence, a low-cost and sustainable feedstock, such as WCO, should be applied to reduce the total biodiesel production cost.

Principal component analysis (PCA) has been used to simplify environmental engineering problems and reduce the number of environmental objectives in multi-objective optimisation [236]. PCA coupled with multi-objective optimisation (MOO) helps to solve multi-objective (>3 objectives) problems in environmental engineering. Two cases were used to validate the usefulness of this approach, and the results revealed this method can overcome the numerical difficulties that typically arise when there are many environmental objectives. Moreover, multi-objective optimisation can be used to minimise the

energy cost and environmental impact (CO<sub>2</sub> emissions) based on a distributed energy resource system (DER) [234]. Multi-objective optimisation has also been applied to optimise the esterification and transesterification processes based on economic and environmental objectives using WCO [237]. Aspen Plus simulator was used to perform simulations, considering palm oil constituents and detailed kinetics for both processes. Following this, both processes were optimised by considering the profit, heat duty, and organic wastes. The organic wastes in this study were methanol, glycerol, and tri/di/monoglycerides. At the same time, profit was calculated by subtracting the cost of manufacture from the revenue obtained by selling the products (biodiesel and glycerol). Based on this analysis, profit was improved by increasing the heat duty and forming organic wastes. As expected, esterification had lower organic wastes (32 %), lower heat duty requirement (39 %) and a slightly higher profit (1.6 %) than transesterification. Multi-objective optimisation has also been carried out for integrated transesterification process and separation system using orthogonal collocation on finite elements (OCFE) [238]. Every process involving biodiesel production such as reaction, methanol separation, methyl ester washing, decantation, and unreacted oil separation, and biodiesel purification was considered in order to optimise the overall productivity and cost-effectiveness. Firstly, the biodiesel production in the final batch time was maximised, and dynamic optimisation was then converted into a non-linear programming problem. The results showed that 7.31 % savings in the reactor energy cost was achieved compared with the baseline case. Moreover, by multi-objective optimisation, the FAME concentration increased by ~11 % by increasing the reactor energy cost by 212.8 %. This indicates that high-purity biodiesel requires a higher reactor energy cost. Therefore, increasing the FAME concentration by 11 % has shown positive results by enhancing the overall heat by 44.86 %, which improves the profit by ~20 %.

## 7. Effects of biodiesel production process parameters

### 7.1. Effect of methanol/oil molar ratio

Statistical methods discussed in the previous section involve designing, collecting data, and analysing the results. Following this, statistical analysis is performed to test the hypothesis, summarise, interpret, and present the collected data so that they can be understood by the layperson. After optimisation, scholars interpret the effect of each independent process parameter and the interaction effect of the parameters. A surface plot is plotted to examine the interaction effect of the parameters. In biodiesel production, the methanol/oil molar ratio is one of the major parameters affecting the biodiesel yield. Based on the stoichiometry of the transesterification process, 1 mol of triglycerides required 3 mol of methanol to produce 3 mol of methyl ester and glycerol. However, a high methanol/oil molar ratio than the stoichiometric methanol/oil molar ratio results in a higher biodiesel yield [48, 239]. The transesterification process is a reversible reaction that sometimes reverses to the undesired path. Therefore, scholars suggest a higher methanol/oil molar ratio should be used to push the reaction forwards. However, after the biodiesel yield reaches the maximum value, the excess methanol will decrease the biodiesel yield [240]. The reason for the decrease in the biodiesel yield after the biodiesel yield reaches its maximum value is that the excess methanol in the transesterification process will increase the solubility of the glycerol and complicates the purification process [27]. To the best of our knowledge, the methanol/oil molar ratio should be within a range of 3:1–30:1. Furthermore, it is found that long-chain alcohol does not promote the transesterification process; rather, it reduces or hinders the biodiesel conversion process. For this reason, most scholars prefer to use methanol in biodiesel production. Moreover, the water content in the alcohol determines the biodiesel yield. During the transesterification process, a high amount of water content will cause hydrolysis of triglycerides to FFA, leading to soap formation and lower biodiesel yields [241]. The

illustration interaction between the ratio of methanol and temperature is depicted in Fig. 22.

### 7.2. Effect of catalyst concentration

The effect of catalyst concentration is also similar to the effect of the methanol/oil molar ratio. Both parameters are found to have a pronounced effect on the biodiesel yield. The hydrolysis reaction of triglycerides into biodiesel requires a catalyst, and it has been shown that increasing the catalyst concentration will increase the biodiesel yield. However, a higher catalyst concentration complicates the biodiesel recovery (purification). The catalyst requirement for the transesterification process differs depending on the type of catalyst, operating temperature and pressure, and the use of advanced equipment. Based on the previous section, all of these criteria influence the biodiesel yield. Therefore, for a homogeneous catalyst, Kasirajan [53] revealed that increasing the KOH catalyst concentration from 0.25 (w/w)% to 1 (w/w)% increased the biodiesel yield from 20 % to 81 %. However, when the catalyst concentration reached 1.25 (w/w) %, the biodiesel yield reduced to 70 %. Hence, the amount of catalyst should be restricted because a high catalyst concentration will inhibit the conversion of triglyceride molecules into FAME due to saponification. Saponification initiates the formation of emulsion when the biodiesel is washed with water. Most scholars found that a homogeneous catalyst concentration of less than 1 (w/w) % is essential to optimise the conversion of oil into biodiesel. The amount of catalyst is dependent on the nature of the oil used for biodiesel production. NaOH has similar catalytic behaviour as KOH. Even though NaOH has better efficiency than KOH, NaOH produces more emulsions, which complicates the separation process [242]. NaOH in ethanol produces more saponification than NaOH in methanol due to the higher number of hydroxide ions in ethanol [171]. The use of heterogeneous catalysts such as alkali metals also results in a high biodiesel yield. Heterogeneous catalysts require a higher catalyst concentration (>2(w/w) %) than homogeneous catalysts. The performance of heterogeneous catalysts is dependent on the surface area and the active sites available for transesterification reaction. Heterogeneous catalysts are insoluble in water, which facilitates the separation of catalyst from the biodiesel during the purification process, resulting in a high biodiesel yield (>98 %). The yield of optimisation for the use of KOH, CaO, and NaOH catalysts is shown in Fig. 23.

### 7.3. Effect of reaction temperature

Transesterification is an endothermic reaction, and thus, a high temperature is favourable to move the reaction forwards. The reaction

temperature is crucial in biodiesel production as temperature provides the minimum energy required for the catalyst to accelerate the transesterification process. By increasing the reaction temperature, the kinetic energy of molecules increases and eases mass transfer between phases. In addition, the oil viscosity will be reduced at high reaction temperatures, which permits the solubility of oil and alcohol, and accelerates the transesterification process [243,244]. However, increasing the reaction temperature may result in a reverse reaction, which reduces the biodiesel yield. For example, increasing the reaction temperature from 40 °C to 60 °C increased the biodiesel yield from 82.5 % to 90 %. However, when the reaction temperature was increased from 70 °C to 80 °C, the biodiesel yield decreased from 77.5 % to 65 % [245]. For an open reactor, a higher reaction temperature that exceeds the methanol boiling point of 65 °C will cause evaporation of methanol, thus minimising the interaction of fatty acids and catalyst, and eventually reduces the biodiesel yield. In another study, a microwave reactor was used for the transesterification reaction, and the reaction temperature could be increased up to 100 °C. Since the microwave reactor is a closed system, there is no evaporation of methanol. Furthermore, high reaction temperatures have been shown to reduce the reaction time [173]. The influence of temperature and time on the amount of biodiesel produced is depicted in Fig. 24.

### 7.4. Effect of reaction time

The reaction time is an important parameter in biodiesel production, particularly for commercialisation. In biodiesel production, extending the reaction time after the system has achieved equilibrium will not boost the biodiesel yield. Still, a higher reaction time can result in reverse transesterification. Hence, after the maximum biodiesel yield is attained, the process should be terminated immediately, and the biodiesel should be subjected to the separation and purification processes. The average reaction time of a transesterification process is 1–2 h using homogeneous catalysts [53,171]. In contrast, heterogeneous catalysts require a longer reaction time (1–24 h) [246]. Significant improvement for WCO was achieved using microwave irradiation as reported by Khatun et al. [242]. The biodiesel yield was 90 % within 4 min and became 99.5 % in 6 min [74,242]. Microwave irradiation is much more efficient compared with the conventional method due to rapid heating at the molecular scale. At this scale, the molecules move very fast, which means that the molecules have less time to relax and generate more energy. The results also indicate localised superheating, resulting in a higher reaction rate [247]. The influence of reaction time and temperature on the amount of biodiesel produced is illustrated in Fig. 25.

### 7.5. Effect of stirring speed

Stirring speed is another important factor in biodiesel production as it promotes homogeneity of the catalyst, methanol, and oil during the transesterification process. The stirring speed increases mixing of the reactants, which accelerates the biodiesel conversion process. If there is no agitation in the mixture, there will be two phases, and only the interface between two impermissible layers will experience a slight transesterification process [248]. The absence of stirring speed will result in a sluggish reaction rate, which impedes the biodiesel conversion process. As long as the stirring speed ensures homogeneous mixing between the oil, methanol, and catalyst, the transesterification process will be accelerated. A stirring speed of ~600 rpm ensures uniform temperature distribution through mixing and promotes mass transfer. Increasing the stirring speed beyond 600 rpm has no significant effect on the biodiesel yield [249,250]. The link between the speed of stirring and the reaction time pertains to the amount of biodiesel that is produced, as shown in Fig. 26.

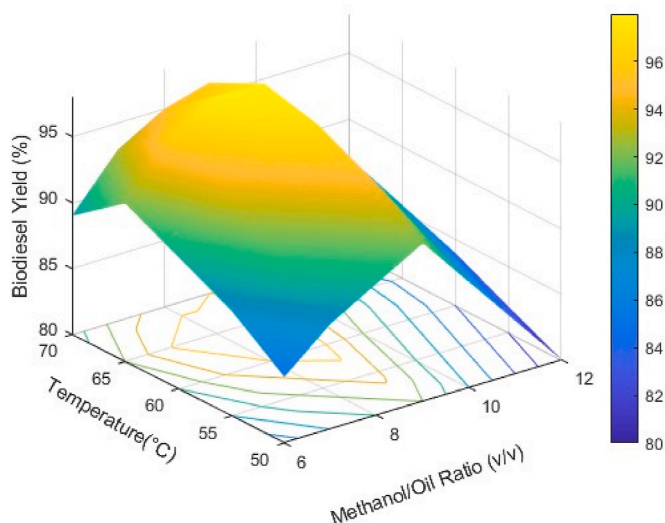


Fig. 22. Interaction between methanol ratio and temperature.

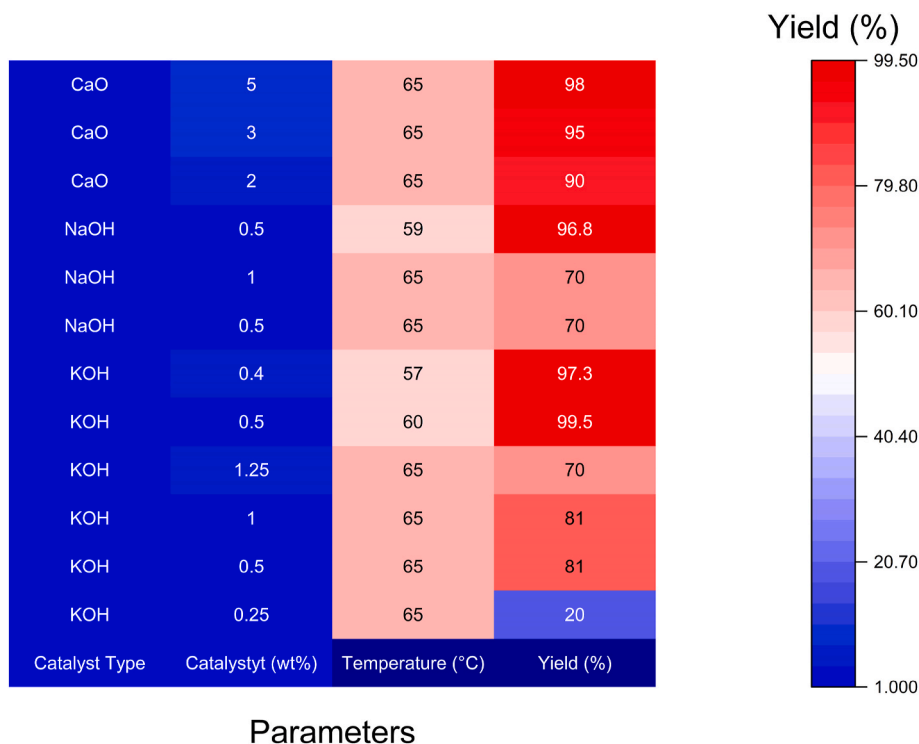


Fig. 23. Yield of optimisation using KOH, CaO and NaOH catalyst.

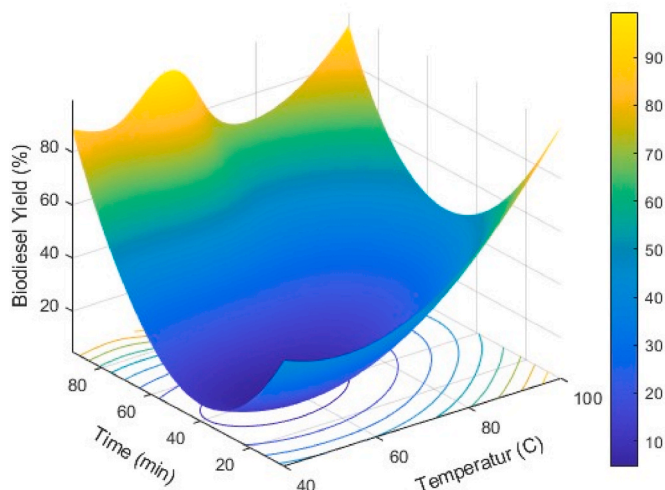


Fig. 24. Interaction between temperature and time on biodiesel yield.

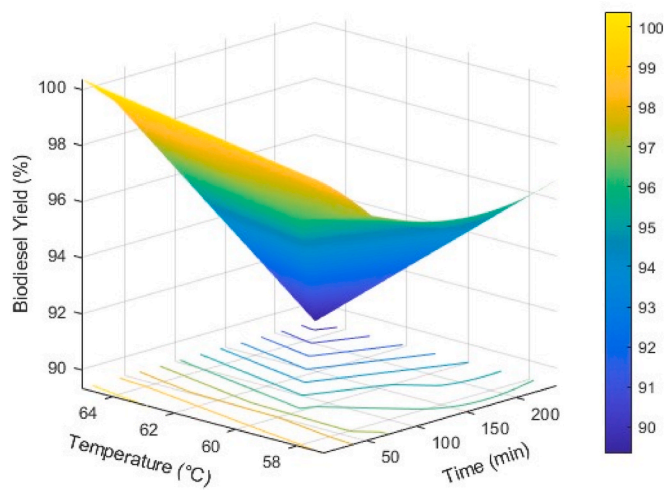


Fig. 25. Interaction between reaction time and temperature on biodiesel yield.

### 8. Kinetics, thermodynamics, and energy consumption of the transesterification reaction

Thermodynamics and kinetics are crucial to comprehend a particular reaction, such as the biodiesel conversion process. Thermodynamics determines the extent to which a reaction occurs, whereas kinetics describes the rate of reaction. The transesterification reaction is a process of converting 1 mol of triglycerides (TGs) with 1 mol of methanol to form diglycerides (DGs) and methyl ester (ME). Following this, in a similar manner, the diglycerides form monoglycerides, and lastly form glycerol. Therefore, 1 mol of TGs forms 3 mol of ME with 1 mol of glycerol. Each TG requires three successive steps to form ME. The TGs are the key to measure the rate of reaction, whereas methanol is usually oversupplied to drive the transesterification reaction forwards. Therefore, transesterification reaction is considered as pseudo first-order

reaction, which is given by Eq. (1). By integrating Eq. (2) with a limit of zero to  $t$  min, a straight line is obtained, which is expressed as Eq. (3), where  $x$  is considered to be the fractional conversion of biodiesel [98]. [74].

$$\text{Rate of reaction (Rr)} = -\frac{d(\text{Triglycerides})}{dt} = -\frac{d(TG)}{dt} = k[TG] \quad (1)$$

$$\ln[TG_t] = -kt + \ln[TG_0] \quad (2)$$

$$\ln(1 - x) = -kt \quad (3)$$

$$\ln k = -\frac{Ea}{R} \left(\frac{1}{T}\right) + \ln(A) \quad (4)$$

The above equation represents the first-order kinetics of the

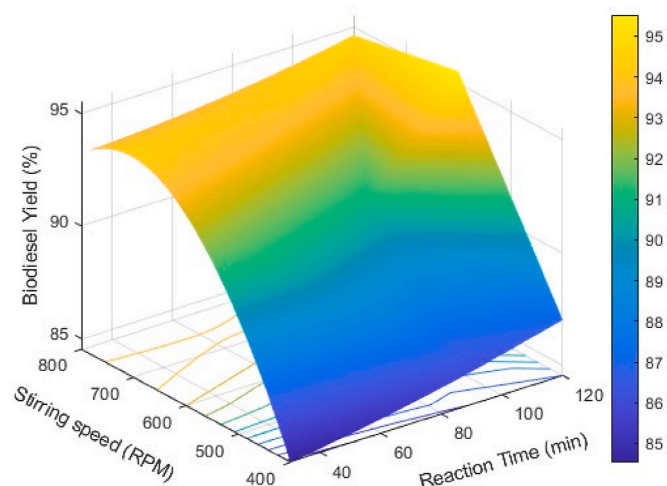


Fig. 26. Illustrates the relationship between stirring speed and reaction time concerning biodiesel yield.

transesterification reaction. In Eq. (4), the terms  $A$  and  $R$  represent the Arrhenius constant and universal gas constant (8.314 J/mol·K), respectively. The  $E_a$  can be obtained from Eq. (4). Then, the rate constants can be determined by plotting  $-\ln(1-x)$  versus time at various temperatures. The kinetic energy is different due to the biodiesel production process, equipment used, type of catalyst, reagent concentration, reaction temperature, and pressure [251,252]. It is important to study the kinetics of the transesterification process based on the biodiesel yield and fuel characteristics when WCO is used as the feedstock [253]. The activation energy of transesterification reaction of WCO using NaOH catalyst was 27.24 kJ/mol. Heterogeneous catalyst (Na-SiO<sub>2</sub>@TiO<sub>2</sub>) was used for transesterification of WCO and the  $E_a$  was determined to be 21.65 kJ/mol. Enzymatic catalyst (Novozym 435) was used to produce WCO biodiesel and the  $E_a$  was reduced to 18.96 kJ/mol [74]. Hydrodynamic cavitation used to assist the conversion of WCO biodiesel was shown to reduce the  $E_a$  (89.7 kJ/mol) compared with mechanical stirring ( $E_a = 92.7$  kJ/mol) [126].

Thermodynamic parameters such as standard Gibbs free energy change ( $\Delta G$ ), standard change in enthalpy ( $\Delta H$ ), and standard change in entropy ( $\Delta S$ ) are used to study the adsorption behaviour. The adsorption behaviour can be determined spontaneously ( $\Delta G < 0$ ) or non-spontaneously ( $\Delta G > 0$ ) under a specific mixture temperature. The change in enthalpy can be used to determine whether the adsorption process is exothermic ( $\Delta H < 0$ ) or endothermic ( $\Delta H > 0$ ), and the magnitude of the change in enthalpy is used to determine whether the process is physisorption ( $\leq 60$  kJ/mol) or chemisorption ( $\geq 200$  kJ/mol). Normally, the thermodynamic parameters ( $\Delta H$  and  $\Delta S$ ) are calculated based on the linear form of the Van't Hoff equation by combining the first and second laws of thermodynamics. The thermodynamic parameters differ mostly due to the equipment and catalyst used to produce the biodiesel. Conventional heating has a  $\Delta H$  value of 55 kJ/mol when alkaline catalyst is used for the biodiesel conversion process. Using heterogeneous catalyst will reduce the  $\Delta H$  value up to 16%. Moreover, a high  $\Delta H$  value (3.1–3.5 MJ/kg) is obtained when pyrolysis is used because high thermal energy is needed to promote endothermic cracking of the WCO.

The energy consumption of the transesterification process is an important factor as energy consumption is always associated with environmental side effects. The energy consumption of conventional heating mantle is higher than cost-effective energy efficiency biodiesel technologies such as microwave reactor [74,173], hydrodynamic cavitation [127], and ultrasonic reactor [175]. All of these advanced intensification systems have shortened the reaction time, which boosts the efficiency of the transesterification reaction. Hydrodynamic

cavitation reactor speeds up the rate constant by seven-fold compared with conventional reactor and is four times more efficient [126].

## 9. Exergy and energy analysis

Energy and exergy analysis is crucial to identify the inefficiencies within a thermal system, including the location and sources of these inefficiencies. For simplicity, the exergy is the maximum amount of work that can be obtained by reversibly bringing the reaction into thermodynamic equilibrium. In addition, energy and exergy analysis can identify the thermodynamic losses and help to boost the process efficiency. Although exergy analysis is important, less than 15% of the chemical industry is focused on this area. Based on the literature survey, a simulator has been combined with exergy analysis tools such as Dudgeon and Olexan. Thermo-economic analysis has also been conducted using Thermo-economic Analysis of Energy Systems (TAESS) software to determine the exergy cost. Other scholars have used Aspen HYSYS chemical process simulator or a combination of Aspen Plus and Microsoft Excel. Energy and exergy analysis can be performed for the whole biodiesel production process, such as the cultivation/plantation of the seeds, dehydration process of the seeds, extraction of the oil, transesterification process, by-product processing, and lastly, the application of the produced biodiesel (engine testing). Energy and exergy analysis is extensive, and most scholars will judiciously select the biodiesel production process. This section presents the details of the energy and exergy analysis in biodiesel production.

Antonova et al. [254] performed exergy analysis of biodiesel production from canola oil based on the classic model of the environment. The exergy analysis results are dependent on the methodology, taking into account all stages of biodiesel production from planting of canola seeds to biodiesel production to the sale of the biodiesel. Even the weather conditions in Belarus were used in the exergy analysis. The initial exergy inputs for the transesterification process used to produce methyl ester and ethyl ester were 30.97 and 33.28 GJ/ha/yr, respectively. The output chemical exergies for methyl ester and ethyl ester were 27.82 and 29.19 GJ/ha/yr, respectively. Based on their results, the biggest consumer of exergy was the canola cultivation stage (constituting 66% of the total exergy). The high amount of exergy was due to fertiliser utilisation and chemicals used on the plant. By comparing ethyl ester and methyl ester production, the ethyl ester required a higher operating temperature for the conversion process, resulting in a 7% higher exergy cost than methyl ester. However, this high exergy can be improved by suitable waste utilisation. First, canola straw can be used to produce solid fuel or serve as feedstock for biogas production. In contrast, the glycerine produced after transesterification can be sold, and potassium phosphates can be returned to the cultivation stages to be used as mineral fertilisers.

The comparison of exergy and energy analyses in industrial biodiesel production was recently reported by Amelio et al. [255]. The simulations using Aspen Plus process simulation software revealed that the reaction condition is the main energy loss. Meanwhile, the energy analysis confirmed that biodiesel purification through three distillation columns is a major loss, as shown in Fig. 27. Grassman diagrams visualised the observation of exergy flows. The loss of work can be minimised by making irreversible reactions and pre-heating of low-pressure steam. Thus, the exergy analysis gives benefits by designing a reactor with higher profit and reducing environmental impact. By optimising the energy and exergy, the energy consumption was reduced by 46%, whereas the reduction in exergy was slightly lower (45.7%). Exergy analysis on the esterification and transesterification processes facilitates in reducing the materials used and energy consumption [256]. Thermodynamic analysis is performed to obtain the exergy input and output of the experiment. The purification process is essential in determining the exergy loss, economic efficiency, and environmental sustainability. Reducing energy consumption and wastage will improve the exergy and economic efficiency of biodiesel

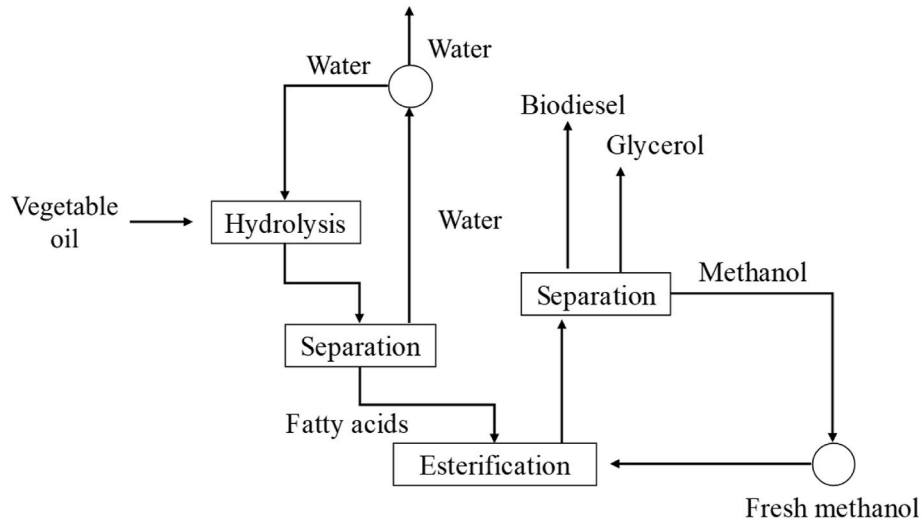


Fig. 27. Flow path of biodiesel production.

production.

Madheshiya and Vedrtnam [257] recently reported the energy and exergy analysis of biodiesel from WCO and mustard oil. This biodiesel was evaluated in a multi-cylinder diesel engine using NaOH as a catalyst. They confirmed that the system requires a coolant inlet, thermocouple, and cooling water flow to minimise energy losses. The energy losses can be determined using Eqs. (5)–(8) [257].

$$Q_f = m_f \text{ LHV} \quad (5)$$

$$Q_w = m_w C_{p,w} (T_{w1} - T_{w2}) \quad (\text{kW}) \quad (6)$$

$$Q_{\text{ex}} = \frac{m_{\text{gw}} C_{p,w} (T_{w2} - T_{w1})}{(T_{e2} - T_{e3})} \cdot (T_{e1} - T_0) \quad (\text{kW}) \quad (7)$$

$$Q_l = Q_f (\text{BSFC} \times \text{BP} + Q_w + Q_{\text{ex}}) \quad (\text{kW}) \quad (8)$$

In these equations,  $Q_f$ ,  $Q_w$ ,  $Q_{\text{ex}}$ , and  $Q_l$  denote the fuel energy supply rate, cooling water loss, heat loss through the exhaust, and other losses, respectively. The mass flow rate of the fuel and lower heating value is denoted as  $m_f$  and LHV, respectively.  $C_{p,w}$  is the specific heat capacity of the calorimeter.  $T_{w1}$  and  $T_{w2}$  are the cooling waters at the inlet and outlet, respectively.  $T_{e2}$  and  $T_{e3}$  are the exhaust gas temperatures for the inlet and outlet to the calorimeter, respectively.  $T_{e1}$  is the exhaust temperature and  $T_0$  is the ambient temperature. Lastly, BSFC and BP are the brake specific fuel consumption and brake power, respectively. This study verified that the amount of energy loss for cooling water increased with an increase in the percentage of biodiesel in the blend and the energy loss was higher than that for conventional diesel. The biodiesel resulted in better combustion characteristics due to oxygen. From an energy perspective, WCO is competitive to diesel with controlled heat losses. The exergy return on investment (ExROI) of WCO is more maintainable compared with other vegetable oils.

## 10. Physicochemical properties of WCO biodiesel

During transesterification, the polymers are converted into monomeric and dimeric fatty acids. The oligomers reduce the oil volatility and increase the molecular weight. Thus, different vegetable oils with different fatty acid content produce distinct combustion characteristics. Hence, standards are developed by the American Society of Testing and Materials (ASTM) and European Standard (EN) to assess the physicochemical properties of biodiesels. The biodiesels produced need to satisfy the fuel specifications stipulated in ASTM D6751 and EN 14214 standards [173,258]. Gas chromatography analysis is used to determine

the FAME content, linolenic acid methyl ester content, glycerol content, mono/di/triglyceride content, and methanol content. These standards provide the ranges of various physicochemical properties of the fuel so that the engine can work efficiently. The physicochemical properties are density ( $\text{kg}/\text{m}^3$ ), acid number ( $\text{mg KOH}/\text{g oil}$ ), ash content (%), oxidation stability (h), kinematic viscosity ( $\text{mm}^2/\text{s}$ ), flash point ( $^{\circ}\text{C}$ ), cloud point ( $^{\circ}\text{C}$ ), pour point ( $^{\circ}\text{C}$ ), cetane number, copper strip corrosion, sulphur content, and glycerine ( $(\text{w}/\text{w})\%$ ) [259,260].

### 10.1. Density

Density is crucial to estimate the appropriate quantity of fuel to be injected in order to achieve proper combustion. The fuel density affects the injector nozzle design and fuel atomisation, which shows a direct relation to the fuel efficiency since it affects the energy consumption due to the air/fuel mass ratio. The density plays a significant role in the extensive use of biodiesels. Many national standards set the density of the fuel within a range of  $860\text{--}900 \text{ kg}/\text{m}^3$ . The densities of most third-generation feedstocks are within this range, indicating their suitability in terms of their alkyl ester nature and content. The biodiesel produced from cottonseed oil has a density of  $929 \text{ kg}/\text{m}^3$  [261] and linseed methyl ester has a density of  $921 \text{ kg}/\text{m}^3$  [262], which exceed the density specification given in the EN ISO 3675/12185 standard. In contrast, jojoba methyl has a density of  $833 \text{ kg}/\text{m}^3$  [263], coconut methyl ester has a density of  $856 \text{ kg}/\text{m}^3$  [264], and chicken feather biodiesel has a density of  $810 \text{ kg}/\text{m}^3$  [265], which are below the density requirement of the EN ISO 3675/12185 standard. The WCO biodiesel has a density within a range of  $865.5\text{--}879 \text{ kg}/\text{m}^3$  [258,266], which satisfies the limits stated by European legislation. The difference in the density of the WCO biodiesel is less than  $15 \text{ kg}/\text{m}^3$ . Blending WCO with *Calophyllum inophyllum* oil resulted in a biodiesel with a density of  $862 \text{ kg}/\text{m}^3$  and altered the properties of the fuel blend to meet the requirements stipulated in the EN 14214 standard.

### 10.2. Kinematic viscosity

Kinematic viscosity is another crucial fuel property that plays a significant role in spray penetration. The kinematic viscosity of biodiesels is 10–15 times higher than that of conventional diesel due to the complexity in the chemical structure and higher molecular mass of biodiesels. The oxidation and triglyceride polymerisation during the heating process of WCO also contributes to higher kinematic viscosity, producing biodiesel with a slightly higher kinematic viscosity than pure oils (palm oil, sunflower oil, and soya bean oil). The kinematic viscosity

of biodiesels must be less than 5 and 6 mm<sup>2</sup>/s, as stipulated in the EN ISO 3104 and D445 standards, respectively, to achieve complete combustion with minimum coke deposits in the engine. A low kinematic viscosity is preferable as it affects the flow in fuel lines, pumps, and injectors, and improves fuel atomisation, which results in a more complete combustion. The overall kinematic viscosity is also dependent on the degree of purification, where free glycerol is sometimes present in the FAME. A low kinematic viscosity produces finer fuel droplets, enabling the fuel pumps to push the fuel into the combustion chamber. However, an overly low kinematic viscosity will cause deterioration of the fuel injection system, causing the fuel to spill out to different parts of the diesel engine [267]. *Spirulina platensis* microalgae has a kinematic viscosity of 5.45 mm<sup>2</sup>/s [268], while chicken fat methyl ester has a kinematic viscosity of 4.94–6.84 mm<sup>2</sup>/s [269]. WCO biodiesel has a kinematic viscosity of 4–5 mm<sup>2</sup>/s, while biodiesel produced from a blend of WCO with *Calophyllum inophyllum* oil has a kinematic viscosity within a range of 4.7–5.2 mm<sup>2</sup>/s. Most of the biodiesels fulfil the kinematic viscosity requirement stipulated in the ASTM D445 standard, but not the EN ISO 3104 standard. However, intensification process using a microwave reactor is promising to reduce the kinematic viscosity of the fuel blend [173].

### 10.3. Cloud point, pour point, and cold filter plugging point

The minimum temperature that results in a cloud-like appearance of the fuel is defined as the cloud point (CP). At this temperature, the wax crystallises, and it is generally acceptable to use this property as a benchmark to use the fuel at low temperatures. The CP of biodiesels is dependent on the fatty acid composition. The lowest and highest CPs of the biodiesel are –4 and 19 °C, respectively [270,271]. The CP of pure WCO biodiesel is 7–10 °C, while WCO–*Calophyllum inophyllum* biodiesel has a CP of 2–3 °C. A fuel can lose its flow characteristics at certain temperatures, which is defined as the pour point (PP). To work efficiently, the engine operation should be higher than PP. In general, biodiesel exhibits higher CP and PP than petroleum diesel. The highest and lowest reported PPs are –18 and 15.5 °C, respectively. The PP of pure WCO biodiesel is 5–8 °C. Blending WCO biodiesel results in a reduction in the PP of ~5 °C. The cold filter plugging point (CFPP) is the lowest temperature at which the fuel would gush through a standard filter. CFPP is the filterability limit of which the fuel can still be used. In general, the CFPP of biodiesel is higher than that of petroleum diesel due to the existence of polymerised ester. Cold flow properties of biodiesels are essential if the engine is to be operated at lower temperatures, indicating that the biodiesels can be used in cold-climate countries. Based on the ASTM D6371 standard, the highest CFPP of 18 °C is obtained for *Moringa* and *Jatropha* biodiesels whereas the lowest CFPP of –1 °C is obtained for *Ceiba pentandra*–*Nigella sativa* biodiesel. The CFPP of pure WCO biodiesel is 6 °C whereas the lowest CFPP is 1 °C for WCO biodiesel blend. Blending WCO with non-edible oil results in a biodiesel with lower cold flow properties than using pure WCO biodiesel. Blending WCO is another option to improve the cold flow properties of the WCO biodiesel.

### 10.4. Flash point

Flash point (FP) is defined as the minimum temperature at which the fuel starts to ignite. The FP of biodiesels is typically higher than 150 °C, compared with conventional diesel, which has an FP within a range of 50–65 °C. A few biodiesels have an FP lower than 150 °C such as *Juliflora* biodiesel (128 °C) [272], *Calophyllum inophyllum* biodiesel (123.5 °C), *Ceiba pentandra* biodiesel (125.5 °C), and *Calophyllum inophyllum*–*Ceiba pentandra* biodiesel (122.5 °C) [259]. This indicates that biodiesels are generally safer than petroleum diesel, which makes it easier to store and transport biodiesels. A higher FP is preferable since it will reduce the risk of fire hazards when the fuel is exposed to ignition sources. The FP is determined based on the EN ISO 3679 and ASTM D93 standards. Based

on the literature survey, the lowest and highest FPs are 30 and 189 °C, respectively, which are obtained from inedible animal tallow and microalgae. The FPs of the pure WCO biodiesel and WCO biodiesel blends are within a range of 154–171 °C [258,273] and 160–165 °C [173], respectively, which are slightly lower than that of palm oil biodiesel (182.5 °C) [270], but higher than that of *Calophyllum inophyllum* biodiesel (123.5 °C) [259]. The reported FPs are still within the range stipulated in the EN ISO 3679 and ASTM D93 standards.

### 10.5. Cetane number

Cetane number (CN) is highly correlated with ignition delay. The ignition delay is the time between fuel injection and ignition. The higher the CN, the faster the ignition delay. The CN is higher for fuels with long-chain saturated fatty acids. A low CN can lead to engine knocking, noise, excessive solid deposits in the engine, and more harmful emissions. Biodiesels have a higher CN due to their rich oxygen content, which improves combustion efficiency. The CN is determined according to the EN ISO 5165 and ASTM D613 standards. Cottonseed biodiesel has a lower CN of 46.8 [274], whereas palm oil biodiesel has the highest CN of 59 [270]. The WCO (sunflower oil) biodiesel has a CN of 51.33 [98], which is slightly lower than that of palm oil biodiesel.

### 10.6. Calorific value

Calorific value (CV) or heating value is expressed to the amount of energy that is released during fuel combustion. Thus, a high CV is preferable to achieve more efficient internal combustion. Based on the EN 14213 standard, the CV should be higher than 35 MJ/kg. In general, biodiesels have 10 % lower energy than conventional diesel due to their oxygen content [260]. One study on microwave irradiation-assisted transesterification showed that the CV of WCO biodiesel (38.59 MJ/kg) was higher than that of *Calophyllum inophyllum* biodiesel (37.16 MJ/kg) [173]. The biodiesel produced from hydrotreated waste cooking oil (HVO) has a higher CV than other biodiesels; however, the CV is still lower than that of diesel [275]. Furthermore, waste cooking oil methyl ester (WB) and waste pyrolysis oil (WPO) have a higher CV than WCO; however, the CV is still lower than that of diesel [276]. The CV can be improved by blending biodiesel with diesel [277]. Although WCO has a lower CV than diesel, it still fulfils the minimum CV required for fuels specified in the EN 14213 and ASTM D6751 standards (35 MJ/kg).

### 10.7. Sulphur content

The growing concern on environmental sustainability made policy-makers strictly limit the sulphur content of fuels. Sulphur emissions can cause acid rain, which is harmful to organisms. Fortunately, vegetable oils have a low sulphur content. The sulphur content of vegetable oils is ~10–15 ppm, which is significantly lower than that of diesel. However, there are few reports on the sulphur content for plant-derived biodiesels. The sulphur content of WCO–*Calophyllum inophyllum* biodiesel is 3.32–3.55 ppm, which is markedly lower than that of diesel (450 ppm).

### 10.8. Acid number

Acid number (AN) describes the concentration of FFAs in the sample, expressed as mg KOH/g oil. The higher the AN, the more engine components are susceptible to corrosion. The maximum AN of biodiesel is 0.5 mg KOH/g according to the EN 14104 and ASTM D664 standards. Based on the literature survey, WCO has a low AN of 0.113 mg KOH/g, whereas non-edible oils such as *Calophyllum inophyllum* and *Ceiba pentandra* oils have an near the borderline, with a value of 0.41 and 0.38 mg KOH/g, respectively. The AN of WCO blended with *Calophyllum inophyllum* oil is 0.46 mg KOH/g. A feedstock with a low AN will produce biodiesel with a low AN. WCO can be blended with other feedstocks; however, pre-treatment needs to be carried out to reduce the high AN of

WCO. Pre-treatment (esterification) is typically used to reduce the FFA content of non-edible oils [27]. A low AN is favourable for direct transesterification reaction, which can be performed without a catalyst, or with a heterogeneous catalyst or enzymatic catalyst. Moreover, a low AN will boost the biodiesel yield, preventing saponification during biodiesel purification.

### 10.9. Iodine value

Iodine value (IV) denotes the iodine mass adsorbed in the unsaturated carbon chain per 100 g of fuel. IV describes the tendency of the fuel to oxidise when the sample is placed in an open area. IV correlates with the kinematic viscosity, CN, and CFFP. The IV of biodiesels is 120 g I<sub>2</sub>/100 g according to the EN 14111 and ASTM D6751 standards. Linseed biodiesel has an IV of 184 g I<sub>2</sub>/100 g, while cottonseed oil has a lower IV of 116.5 g I<sub>2</sub>/100 g [262,274]. There are no results reported regarding the IVs of palm oil, WCO, and WCO–*Calophyllum inophyllum* biodiesels.

### 10.10. Oxidation stability

Oxidation stability (OS) is a crucial indicator in estimating the reactivity of the fuel in air and the tendency of the fuel to oxidise. OS also indicates the fuel degradation rate, which plays a vital role in the storage, handling, and transportation of the fuel. OS is dependent on the number of bis-allylic sites in the unsaturated compounds of fatty acids. Thus, the higher the unsaturated chain of fatty acids, the lower the OS. The oxidation process is initiated with peroxides, forming volatile organic compounds such as aldehydes and ketones. Then, these small molecules are converted into waste sludge that can clog the fuel injection system of the engine. The OS indicates the degradation of the physicochemical properties of the fuel. Oxidation may occur during the handling process, forming insoluble sediment and resin due to polymerisation. These solids can lead to filter problems in the engine, causing other deposits to form on the engine parts. Since the deposits are insoluble in diesel, this will lead to pumping and injection problems. The oxidation process can cause severe corrosion since biodiesel is acidic, and oxidation forms hydroperoxides, which will increase the AN of the biodiesel [278]. Oxidation stability is an essential property since it influences the storage conditions and time management for biodiesel usage. The OS of biodiesel is dependent on light, oxygen (air) exposure, temperature, pollutants, and water. All of these can oxidise the biodiesel and cause a harmful reaction [279]. Harmful pollutants and changes in the fuel properties cause the biodiesel to become a non-standard product that cannot be sold in the market. Oxidised biodiesel will have a higher kinematic viscosity and density. In the long term, oxidised biodiesel will deteriorate the fuel pump as the fuel pump needs more energy to increase the fuel flow to the engine parts, leading to fuel injection problems [280]. The minimum induction time according to the EN 14112 standard is 3 h. WCO biodiesel has an OS of 4.7 h [273], which is superior to the OS of *Ceiba pentandra*–*Nigella sativa* biodiesel (3.27 h) [281]. Biodiesel produced from a mixture of WCO and *Calophyllum inophyllum* oil has superior OS of 22.4 h [27].

### 10.11. Water and sediment content

The cleanliness of biodiesel can be assessed based on the water and sediment content. These properties can be expressed in dissolved form and water droplets. The existence of water in biodiesel can corrode the engine components and reduce the calorific value of the biodiesel. In addition, excessive water content can stimulate a reverse reaction of the biodiesel, forming FFAs. The sediment may comprise dirt particles and rust that can clog the fuel track. Based on the EN ISO 12937 and ASTM D2709 standards, camel fat has zero sediment and water content.

### 10.12. Fatty acid methyl ester (FAME) content

FAME content and linolenic acid methyl ester content are determined according to the EN 14103:2011 standard test method. The FAME content of biodiesel is determined by measuring the methyl esters from C6 to C24, whereas the linolenic acid methyl ester content is determined by measuring C18:3. The FAME content indicates the purity of the biodiesel. Based on the standard test method, the FAME content should be greater than 90 (w/w) %, while the linolenic acid methyl ester content should be within a range of 1–15 (w/w) %. Linseed biodiesel contains a very high amount of linolenic acid (51.12 (w/w) %). The FAME contents of pure WCO and WCO–*Calophyllum inophyllum* biodiesels are 98.85 and 98.67–98.94 (w/w) %, respectively. Most of the biodiesels produced from edible and non-edible feedstocks have FAME content within the range stipulated in the EN 14214 method. The saturated FAME content for WCO biodiesel is 25–39 (w/w) %, whereas the unsaturated FAME content is 60–73 (w/w) %. The saturated FAME content of WCO biodiesel is slightly higher than that of biodiesels produced from edible oils (<15 (w/w) %). Biodiesels produced from non-edible feedstocks have a saturated FAME content within a range of 29–41 (w/w) %.

### 10.13. Glycerol, monoglyceride, diglyceride, and triglyceride contents

The glycerol, monoglyceride, diglyceride, and triglyceride contents of biodiesels must fulfil the specifications given in the EN14214 standard. The efficiency of the transesterification process can be evaluated by determining the value of monoglycerides, diglycerides, and triglycerides in the biodiesel. A lower value of these glycerides indicates that most of the glycerides have been successfully converted into biodiesel. Glycerol is the by-product of the transesterification process, where it separates from the methyl ester during the separation and purification processes. Glycerol will be washed off from the methyl ester, and therefore, the glycerol content indicates the purity of the biodiesel. The monoglyceride, diglyceride, and triglyceride contents should be less than 0.8, 0.2, and 0.2 (w/w) %, respectively, and the glycerol content should be less than 0.25 (w/w) %. The triglyceride content of WCO and WCO–*Calophyllum inophyllum* biodiesels are 0.2 and 0.016–0.024 (w/w) %, respectively.

### 10.14. Methanol content

Similar to glycerol, after transesterification, the methyl ester, methanol, and glycerol are separated using a separating funnel during the separation phase. Therefore, the methanol content also indicates the efficiency of the purification process of the biodiesel. The methanol content should be less than 0.2 (w/w) % for biodiesels. The WCO–*Calophyllum inophyllum* biodiesel has a methanol content of 0.03–0.045 (w/w)% [27,173]. However, there are no reports on the methanol content of other biodiesels.

## 11. Engine performance, exhaust emissions, and biodiesel compatibility

The physicochemical properties of the biodiesel will affect the performance and emissions of the diesel engine. Scholars have found that the degree of saturation, molecular bonds (*trans* or *cis*), and molecular chain length directly correlate with the engine performance. The combustion characteristics are dependent on the cylinder pressure, ignition delay, heat release rate, compression ratio, air/fuel ratio, and combustion duration. Biodiesels and their blends can be used as fuel in compression ignition (CI) engines without modifications. The performance of the fuel blend can be determined by observing the performance characteristics such as brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), brake specific energy consumption (BSEC), and exhaust emissions. The exhaust emissions such as unburned hydrocarbons (UHC), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>),

nitrogen oxide (NO<sub>x</sub>), particulate matter (PM), and smoke indicates the quality of the fuel blend.

### 11.1. Engine performance

#### 11.1.1. Brake specific fuel consumption

Brake-specific fuel consumption (BSFC) is defined as the ratio of total fuel consumption to the brake power generated by the engine. BSFC is one of the parameters used to measure the performance of the engine. The BSFC is calculated using Eq. (9) [282].

$$BSFC = \frac{30 \times q}{\pi \times n \times T_{eq}} \times 10^6 \quad (9)$$

where  $q$  is the fuel consumption of the biodiesel blend (kg/h),  $T_{eq}$  is the engine torque (N-m), and  $n$  is the engine speed (rpm).

The effects of methanol–diesel (M5–M10) and ethanol–diesel (E5–E10) fuel blends on a single-cylinder four-stroke, direct injection diesel engine was studied in Ref. [282]. The addition of methanol and ethanol was found to improve the BSFC and increase the NO<sub>x</sub> emissions at an engine speed between 1000 and 1800 rpm. Pure waste mustard oil biodiesel (B100) resulted in the highest NO<sub>x</sub> emissions compared with other fuel blends [283]. B10 and B20 resulted in higher BSFC than pure diesel (B0); however, increasing the engine load decreased the overall BSFC. The oxygen content of the biodiesel also influences the BSFC, where a higher oxygen content results in higher BSFC. The BSFC of diesel was found to be the lowest, whereas adding biodiesel into diesel increased the BSFC [284]. The addition of WCO biodiesel into diesel improved the BSFC, with the highest BSFC attained for the B20 blend [285]. However, the addition of butanol with B20 decreased the BSFC. The addition of biodiesel and alcohol increased the oxygen content of the fuel blend; however, the addition of butanol resulted in low-temperature combustion behaviour that eventually slightly decreased the BSFC [285]. The BSFC values of the B10, B20, B40 and B50 fuel blends using trout oil biodiesel were 0.45, 1.04, 1.1, and 1.47, respectively, which were higher than that of diesel [286]. The fuel consumption rate is caused by the lower calorific value [286]. There are a few cases where scholars reported the addition of WCO biodiesel reduced the BSFC [287,288].

#### 11.1.2. Brake thermal efficiency

Brake thermal efficiency (BTE) is defined as the ratio of brake power obtained in the crankshaft to the fuel power supplied to the engine and is given by Eq. (10) [289].

$$BTE = \frac{120 \times \pi \times n \times T_{eq} \times 10^{-6}}{q \times [k_b \times LVH_b + (1 - k_b) \times LVH_m]} \times 100\% \quad (10)$$

Here,  $LVH_b$  and  $LVH_m$  are the lower heating values of the biodiesel (MJ/kg) and  $k_b$  is the mass fraction of biodiesel in the fuel blend. Jayaprabakar et al. [290] performed a study on a single-cylinder, direct injection diesel engine using rice bran and *Gracelaria verrucosa* biodiesel blend at a constant speed. The results showed that the BTE was dependent on the calorific value and specific gravity. The calorific values of rice bran and algae biodiesels were 8850 and 7945 kcal/kg, respectively. The BTE of pure diesel was slightly higher than that of rice bran biodiesel and algae biodiesel blend, and the rice bran biodiesel was superior to the algae biodiesel due to its higher calorific value. Scholars have studied the effects of blending alcohols (propanol, butanol, and pentanol) with WCO biodiesel on the performance of NWK22 direct injection engine [291]. The BTE of pure biodiesel was 1.89 % higher than that of diesel. However, the addition of diesel and biodiesel in a 50:50 ratio reduced the BTE by 0.24 %. The addition of 20 % of butanol resulted in the highest BTE, where the BTE was 5.58 % higher than that of the 50 % butanol–biodiesel blend and pentanol blend. Alcohol contains more oxygen molecules, and it is shown that adding alcohol into biodiesel increases the oxygen content of the biodiesel, which results in a more

complete combustion with low heat loss compared with diesel. In addition, blending 10 % of waste mustard oil biodiesel with diesel decreased the BTE [283]. The same trend was observed by blending 20 % of waste mustard oil biodiesel with diesel. Blending WCO biodiesel (up to 60 %) with diesel reduced the BTE by 1.5 % [292]. The BTE increased for all WCO biodiesel–diesel blends, and the BTE of the B20 blend was close to that of diesel. The BTE slightly increased when the percentage of WCO biodiesel was increased from 5 % to 20 %, whereas the BTE decreased when the percentage of WCO biodiesel increased from 20 % to 100 % [289]. The reduction in BTE is caused by the higher kinematic viscosity and density of biodiesel, which causes poor fuel atomisation in the combustion chamber. Moreover, some scholars blended WCO biodiesel with pentanol. The addition of 10 % of pentanol improved the BTE, but a further increase in the concentration of pentanol (20–30 %) reduced the BTE [293]. The addition of butanol–WCO biodiesel–diesel at ratio of 1:1:8 resulted in the highest BTE [285]. However, the addition of 20 % of butanol degraded the BTE. Based on the literature survey, the addition of WCO biodiesel or alcohol reduced the BTE compared with neat diesel. However, a small percentage of biodiesel or alcohol increased the BTE, whereas higher concentrations of biodiesel or alcohol decreased the BTE. The B20 blend (20 % WCO biodiesel + 80 % diesel) is recommended because it results in a BTE that mimics the BTE of diesel. Many found that the BTE is highly correlated with the heating value, density, and kinematic viscosity, which influence the fuel atomisation and combustion efficiency.

### 11.2. Combustion characteristics

Biodiesels typically have a higher density and kinematic viscosity and lower calorific value than diesel. Therefore, these properties need to be tailored to enhance the combustion characteristics and minimise exhaust emissions. The combustion characteristics are assessed based on the following parameters: cylinder pressure, ignition delay, heat release rate, compression ratio, and combustion duration. The engine load plays an important role in the performance and consumption of biodiesel in CI engines. By increasing the engine load, the maximum in-cylinder pressure increases, which is likely because more of the fuel molecules are combusted as the engine load increases [294,295].

### 11.3. Exhaust emissions

The engine exhaust emissions comprise carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), unburned hydrocarbons (UHC), nitrogen oxide (NO<sub>x</sub>), and particulate matter (PM). The emission legislations are becoming more stringent worldwide and therefore, there is a need to minimise the exhaust emissions of CI engines. Biodiesels generally have lower UHC, CO, and PM emissions than diesel, but most biodiesels have higher NO<sub>x</sub> emissions. The emissions of biodiesel-fuelled engines vary depending on the feedstock due to differences in the physicochemical properties, particularly the carbon chain length of the alkyl esters. A brief description of the exhaust emissions is provided in the following sub-sections.

#### 11.3.1. CO emissions

Poor combustion with ineffective fuel/air mixing results in fuel-rich zones in the combustion chamber, which in turn, affects the CO emissions. Moreover, inaccuracies in ignition time and oxygen concentration cause a delay in the oxidation of CO into CO<sub>2</sub>, which also results in CO emissions. Sanli et al. [296] found that biodiesel produced less CO emissions than petroleum diesel. However, CO emissions were the highest at low engine speed (1100 rpm) due to poor fuel atomisation and large fuel droplets in the combustion chamber, causing locally fuel-rich zones. In addition, volumetric efficiency was low because the oxygen concentration in the combustion chamber decreased, which adversely affected combustion. This can be overcome by increasing the engine speed, where the volumetric efficiency, turbulence, and fuel atomisation

greatly improve. Ogunkunle and Ahmed [297] found that CO emissions were low when the engine was operated at low and medium loads. The CO emissions increased at high engine loads. However, biodiesels generally produced lower CO emissions compared with diesel. The WCO biodiesel reduced CO emissions up to 87 % [298], which was significantly higher than other biodiesels (60 % reduction) [299]. Some claimed that the CO emissions produced from CI engines are not significant. In general, WCO biodiesel generates lower CO emissions than diesel.

### 11.3.2. UHC emissions

Incomplete combustion in the combustion chamber results in UHC emissions. UHC are present when there is a rich fuel/air mixture in the combustion chamber, which increases fuel consumption. Pradhan et al. [283] found that 10 % of waste mustard oil biodiesel blended with diesel enhanced combustion and considerably reduced UHC emissions among the tested fuels. Zare et al. [284] found that WCO biodiesel produced lower UHC emissions compared with neat diesel. They found that the high cetane number and oxygen content of the biodiesel correlated with the UHC emissions. The addition of triacetin additive increased the UHC emissions since triacetin reduced the cetane number of the fuel and increased the ignition delay. Zhu et al. [293] added pentanol into WCO biodiesel blend and found that pentanol increased the UHC emissions of the diesel engine. Pentanol reduced the cetane number of the fuel, which resulted in a lean fuel/air mixture. Similar trends were observed when butanol was added into WCO, resulting in higher UHC emissions [285]. Sanli et al. [296] found that the UHC emissions were the highest at an engine speed of 1700 rpm for neat diesel (38 ppm) and methyl ester (25 ppm), which were higher than those for ethyl ester (21 ppm). Buyukkaya et al. [286] used trout oil biodiesel and they discovered that this biodiesel reduced UHC emissions by 45 % owing to the higher cetane number and gas temperature of the fuel. Pure WCO biodiesel was shown to produce lower UHC emissions (~7.89 %) than B20 [296]. In general, biodiesels reduce UHC emissions, but the addition of additives will increase the UHC emissions.

### 11.3.3. NO<sub>x</sub> emissions

The formation of NO<sub>x</sub> in the exhaust of CI engines is affected by the cylinder temperature, air/fuel ratio, fuel spray characteristics, duration of high temperature in the combustion cycle, chemical structure of the fuel, amount of oxygen in high-temperature zones, and engine technology. The addition of biodiesel, additives, alcohol, or oil will affect the temperature at the combustion chamber, oxygen concentration, and chemical composition of the burning compound. Engine load also influences NO<sub>x</sub> emissions. When the engine load is increased, the fuel input increases, which will increase the combustion temperature in the engine. Most scholars found that the addition of biodiesel into diesel increased the NO<sub>x</sub> emissions of unmodified diesel engines. Sanli et al. [296] found that the NO<sub>x</sub> formation was due to the deficiency of oxygen molecules and lower in-cylinder temperature for the fuel-rich and fuel-lean mixtures. Blending methyl ester and ethyl ester with diesel in a ratio of 20:80 significantly reduced the NO<sub>x</sub> emissions. Ethyl ester resulted in a better emission profile than methyl ester. Atmanli [291] analysed the emission characteristics of WCO biodiesel and B50 blend and found that NO<sub>x</sub> emissions of the B100 and B50 fuels were 1.68 and 9.74 % lower than diesel. Some reported that WCO biodiesel increased the NO<sub>x</sub> emissions [300]. The highest NO<sub>x</sub> emissions (22.13 %) were observed for pure biodiesel produced from waste palm oil [298]. Blending biodiesel with diesel reduces the cetane number and ignition delay that forces hot gases to remain in the combustion chamber under high temperature, reducing the formation of NO<sub>x</sub>. The effect of the addition of alcohol has also been investigated and the results showed that the addition of alcohol reduced the NO<sub>x</sub> emissions by 15.05 % (propanol), 19.27 % (butanol), and 27.44 % (pentanol). Similar results were obtained by other scholars who stated that the addition of alcohol into the fuel blend reduced the NO<sub>x</sub> emissions [301,302]. However, the

addition of triacetin additive increased the NO<sub>x</sub> emissions [284].

### 11.3.4. CO<sub>2</sub> emissions

CO<sub>2</sub> emissions indicate complete fuel combustion as well as efficiency of the combustion process. Zare et al. [284] examined the effect of adding triacetin as an additive into WCO biodiesel and investigated the emission characteristics of the fuel. By increasing the engine load or decreasing the engine speed, the CO<sub>2</sub> concentration increased. Oxygenated fuel has the lowest CO<sub>2</sub> concentration due to the lower burning rate of the oxygenated fuel. Hence, the WCO biodiesel had the lowest CO<sub>2</sub> emissions. Paulo et al. [289] found that WCO biodiesel blended with diesel (B75) produced the highest CO<sub>2</sub> emissions compared with other tested fuels. Sanli et al. [296] observed that methyl ester produced more CO<sub>2</sub> emissions than ethyl ester and diesel by 2.08 and 1.86 %, respectively. The CO<sub>2</sub> emissions increased after the addition of biodiesel in the blend, owing to the higher oxygen content of the fuel, resulting in a more complete combustion compared with neat diesel. Ozsezen et al. [298] observed that CO<sub>2</sub> formation is correlated with the carbon/hydrogen ratio of the fuel, and the CO<sub>2</sub> emissions can be reduced by reducing the carbon content of the fuel. They found that canola biodiesel produced 1.74 % more CO<sub>2</sub> emissions whereas WCO biodiesel produced 1.74 % lower CO<sub>2</sub> emissions than neat diesel. Pradhan et al. [283] found that CO<sub>2</sub> emissions varied linearly with the engine load for all tested fuels (B0, B10, B20, and B100) produced from waste mustard oil.

### 11.3.5. Smoke opacity and PM emissions

The presence of smoke signifies incomplete combustion of biodiesel in the diesel engine. To date, there is no information regarding the formation of smoke. Smoke can be reduced by increasing the engine load to the maximum level. In addition, poor fuel atomisation in fuel-rich zones in the combustion chamber and high kinematic viscosity of the biodiesel will result in smoke formation. Most biodiesels tested in the diesel engine have very low smoke opacity due to the enhanced combustion characteristics of the biodiesel in the fuel blend, which reduces the formation of smoke. However, WCO biodiesel produced more PM emissions (24 %) [303] and had higher smoke opacity (20–24 %) [295]. Some biodiesel blends significantly reduced the smoke opacity and PM emissions in the diesel engine such as those fuelled with canola biodiesel [298] and waste palm oil biodiesel [300].

### 11.4. Engine wear and durability

Biodiesels have physicochemical properties that are comparable to those of diesel. However, the direct use of biodiesels in modern CI engines is not recommended since they result in fuel filter clogging, injector coking, formation of carbon deposits on the engine parts, piston ring deterioration, lubrication oil emulsification, and excessive engine wear [304,305]. In addition, Veza et al. [306] found that higher biodiesel concentrations reduces the mechanical properties of rubber elastomers, which causes swelling. To overcome this, they suggested other materials such as Viton and Teflon. Aydin and Sayin [307] have modified the piston, exhaust, and intake valves by coating them with a layer of ceramic material (100 μm of NiCrAl) and another layer composed of 88 % ZrO<sub>2</sub>, 4 % MgO, and 8 % Al<sub>2</sub>O<sub>3</sub>. They found that the coated engine components had better engine performance and reduced exhaust emissions, except for NO<sub>x</sub> emissions. Pillai et al. [308] coated the engine exhaust valve with Ni-based alloys using an aluminide coating process, which is a cost-effective method to improve the oxidation resistance.

Several studies showed that biodiesels had better performance in terms of engine wear and durability. Milano et al. [309] found that biodiesel produced from WCO mixed with *Calophyllum inophyllum* oil had better lubricity and could be used as an additive for petroleum-based lubricants. Furthermore, Amriya Tasneem et al. [310] showed lower wear debris detection in the case of karanja biodiesel and

biolubricant combination due to better the lubrication of vegetable oils compared with petroleum-derived oils.

### 11.5. Carbon deposits on engine components

Cetinkaya et al. [311] used WCO biodiesel to run a Renault Megane four-stroke, four-cylinder diesel engine with 75 kW in winter conditions for a 7500-km road test. They found that the environmental conditions led to incomplete combustion, and carbonisation in the injectors was observed due to biodiesel usage even though the cylinders and piston heads were clean. Dorado et al. [312] performed a 500-h test run using a three-cylinder, direct injection, 2.5-L Diter diesel engine fuelled with 10 % WCO blended and 90 % diesel. They found that the carbon deposits and wear were similar to those when the diesel engine was fuelled with diesel. The test run should be prolonged to obtain a significant difference between the fuel blend and diesel. Peterson et al. [313] performed a 1000-h test run on three Yanmar 3TN75E-S 15-kW diesel engines using pure soya ethyl ester, 50 % soya ethyl ester and 50 % diesel, and 25 % soya ethyl ester and 75 % diesel. Out of the three fuel blends, the blend composed of 25 % soya ethyl ester with 75 % diesel resulted in the most visible soot on the oil pan and valve cover, whereas the pure soya ethyl ester had the lowest soot formation. Complete combustion was obtained for the pure soya ethyl ester. The formation of deposits at the fuel injector hole will change the spray characteristics (fuel atomisation), which will deteriorate the engine performance and result in higher undesirable exhaust emissions.

## 12. Life cycle analysis

Life cycle analysis (LCA) refers to the systematic procedure for assessing the environmental impacts of a process or a product throughout its life, from the acquisition of the raw materials to the final disposal at the point where it has reached the end of life. LCA differs with respect to budgeting techniques in that it deals with the quantification of environmental loads, that is, the emissions of the greenhouse gases, depletion of the natural resource, and environmental toxicity. Life Cycle Cost Analysis (LCCA) refers to the analysis with respect to economic viability as well as environmental consequences. Clearly differentiate the LCCA with respect to the Life Cycle Assessment (LCA). In the production of biodiesel, the Life Cycle Assessment (LCA) deals with various issues, that is, environmental indicator values with respect to the global warming potential (GWP), acidification, eutrophication, and toxicity with respect to humans. Resource efficiency analysis deals with the consumption of fossil fuel, water, and land conversion. Energy balance analysis deals with the relation of renewable output and non-renewable input to the necessary power. Biodiesel production with higher agricultural yields and extensive use of co-products in its life cycle offers the best environmental results. The impact categories encompass a wide range and require comprehensive research. The impact categories are environmental performance, environmental impact, global warming potential, life cycle energy efficiency, fossil energy ratio, abiotic depletion potential, ozone depletion potential, economic analysis, acidification potential, freshwater aquatic ecotoxicity, land conversion, climate change, resource depletion, particulate matter, and human toxicity. LCA is performed based on the scholars' aims and concepts. Scholars have performed energy and cost analyses on biodiesel production using WCO [314]. The energy inputs were the WCO, methanol, catalyst, human labour, electricity, and machinery. The energy outputs were biodiesel, glycerol, waste methanol, water, soap, monoglycerides, and diglycerides. The economic inputs comprised the expenses of human labour, WCO, alcohol, electricity, machinery, and rant land, and the economic outputs were biodiesel, glycerol, and waste alcohol. Based on their study, the total energy input and output were 30.05 and 44.91 MJ/L, respectively. Based on the energy distribution used in biodiesel production, WCO (77.08 %) and alcohol (19.44 %) had the highest share of energy input. The methanol used for biodiesel production is

considered as non-renewable energy from the total energy input. The share of renewable energy can be increased by using biomethanol in place of methanol for the transesterification process. Moreover, the WCO constituted ~55 % of the total cost, followed by the labour cost (28 %). The net return and productivity of biodiesel production were 1.298 \$/L and 0.946 kg/\$, respectively. These returns can be improved by implementing more advanced technologies to accelerate the transesterification reaction instead of using conventional methods. LCA was also performed for biodiesel production from WCO using both homogeneous and heterogeneous catalysts [315]. The WCO had lesser environmental impact than other non-edible oils. The KOH catalyst (homogeneous catalyst) required more post-reaction procedures (purification and neutralisation) than CaO (heterogeneous catalyst). KOH had a higher environmental impact than CaO since it pollutes water. Soluble catalyst influences the marine aquatic ecotoxicity as heavy metals are released to the ocean/freshwater and contributes to climate change.

Moreover, LCA was carried out to compare biodiesel production from WCO and microalgae in Greece, Europe [316]. The scholars studied the environmental impact, including the energy inputs that drove the conversion process. The other input parameters were methanol and potassium methoxide (CH<sub>3</sub>KO). The co-products were glycerol and potassium sulphate. Valorisation of biodiesel production using WCO has a positive environmental impact as recycling WCO will solve the illegal disposal of WCO into the sewage system. The environmental footprints of the biodiesels produced were found to be 3 times lower than the environmental footprint of petroleum diesel. Therefore, WCO biodiesel is an alternative fuel for decarbonising the transportation sector and attain energy security. LCA and life cycle cost (LCC) were performed to study the feasibility of WCO for biodiesel production in China [317]. Resource depletion is lower when WCO is used (391.4 kg oil eq.) compared with that when conventional diesel is used (1270 kg oil eq.). However, the transesterification of WCO to produce 1 tonne of WCO biodiesel significantly contributes to climate change (934.95 kg CO<sub>2</sub> eq.), particulate matter formation (2.19 kg PM<sub>2.5</sub> eq.), photochemical oxidant formation (3.15 kg NO<sub>x</sub> eq.), human toxicity (332.36 kg 1,4-DB eq.), and mineral resource depletion (8.74 kg Fe eq.) compared with diesel.

In addition, scholars have used LCA to model a medium-sized biodiesel production plant with a capacity of 138 Mtonne/day, which serves as a start-up reference [318]. The cost of the equipment for biodiesel production was one-third of the total expenditure, and the greatest contributor was the cost of feedstock, accounting for ~88 % of the total estimated production cost. By selling the by-product of the transesterification process, namely glycerol, the production cost was reduced by 6 %. Purification of biodiesels is costly, and some countries encountered difficulties in acquiring freshwater and controlling the wastewater disposal system. Wash water microfiltration based on a recycling strategy using 30 % wash water and 70 % freshwater for biodiesel purification has been proposed to solve water source problems [319]. The average price of WCO biodiesel is 0.611 USD/L [320], which is lower than the global average price of 0.86 USD/L in Iran. Iran is a diesel-exporting country, where the price of diesel is very low; however, the use of renewable energy is encouraged due to environmental legislations. WCOs are one of the most affordable liquid feedstocks due to their low price, which is half of the virgin oil price in Iran. The Government of Iran has systematically established a waste oil collection service that can collect ~3 million tonnes of oil. Based on their model, the cost of feedstocks accounted for 85 % of the total cost for biodiesel production. Therefore, they found that WCO biodiesel can be exported to diesel-importing countries such as Turkey and China to sustain their diesel industry.

Based on the literature survey, the price of WCO is the main factor that determines the price of the biodiesel. The price of the feedstock accounts for 70–80 % of the price of biodiesel. WCOs obtained from food processing companies, restaurants, slaughterhouses, and residences can

be directly transported to biodiesel plants, local collecting agents, or recycling companies [320]. The prices of the WCOs vary due to the cost of transportation of delivering the oil from a remote market to the refinery. In addition, the physicochemical properties of the biodiesel along with their sulphur and aromatic contents play a role in determining the feasibility of biodiesel production. Based on the LCA, biodiesel production from first-generation feedstocks is more expensive than the production of diesel. The cost of biodiesel can be reduced if WCO is used as an alternative feedstock. The food industries worldwide discard WCO on a daily basis, amounting to billions of tonnes per year. Recycling programmes of WCOs have many benefits such as educating the public on the detrimental impact of disposing WCOs into the sewage system. The use of WCOs helps reduce the cost of biodiesel, minimise soil and water pollution, reduce clogging and drainage complications, boost electricity savings in the degreasing process by the wastewater plant, and minimise the volatility of the prices of edible oils. Many scholars have employed LCA to evaluate the feasibility of WCO biodiesel production. Table 5 provides a summary of the environmental impacts of WCO biodiesel and diesel throughout their life cycle.

### 13. Global warming potential

Biodiesels reduce pollution compared with petroleum diesel. However, biodiesel production still has many drawbacks, such as the presence of catalyst residue, free glycerine, residual triglycerides, and other undesired chemicals during the reaction. Biodiesel purification consists of unreacted methanol separation, glycerol purification, and final drying. Thus, the unreacted methanol is recycled to the transesterification unit directly. The glycerol residue is obtained after soap formation, and the remaining water is recycled to the glycerol purification unit. Following this, in the biodiesel drying section, the separated methanol is recirculated to the rectification column and subsequent transesterification is performed. In addition, 20 kg of water is consumed during purification to produce 1 tonne of biodiesel [100]. Water consumption is considered high and requires extensive treatment before it is discharged to the environment. Pacific Biodiesel introduced a waterless refining process by reacting methanol with a hydroxide catalyst in two stages. The glycerol is circulated, and the excess methanol is removed by vacuum distillation to obtain crude biodiesel. This biodiesel is then

refined to remove free glycerine, catalyst residue, and other impurities. This technique results in a high-quality biodiesel without the use of water. They also used three-stage recovery to minimise methanol consumption to reduce the overall biodiesel production cost [100]. Meanwhile, Axens' Esterfip-H evaporate excess methanol in two fixed bed reactors, and the excess methanol is recycled and mixed with fresh methanol. Then, a settler is used to separate glycerol from the biodiesel. Pure biodiesel is obtained using an adsorber to remove the remaining glycerol. Although this method uses non-toxic chemicals with minimum waste, it requires higher temperature and pressure than that of conventional biodiesel production. However, the actual conditions for Axens' Esterfip-H process are not clearly stated in the literature. In general, the overall production cost is more expensive than the commercial process [326]. Axens' technologies [327] convert any feedstocks with a FFA content less than 0.25 %, and the water content in the oil has to be limited to less than 1000 ppm. The transesterification process only involves a heterogeneous catalyst derived from a mixed oxide of two metals. The biodiesel produced has high purity (>99 %), without hassle for the purification process. The excess methanol is removed by partial evaporation and then recycled for the following transesterification process. Next, glycerine is removed using an absorber, producing biodiesel with high purity (at least 98 %). No hazardous chemicals are used, and the amount of wastes is greatly minimised. Table 6 summarises the findings of various studies regarding the kg CO<sub>2eq</sub> emissions associated

**Table 6**  
Summary of environmental impact assessment.

Biodiesel production processes	Biodiesel (kg CO <sub>2eq</sub> /t)	Case study and reference
Esterification and transesterification	550	Industrial-scale production, Greece [316]
Transesterification	843	Use of biodiesels in internal combustion engines [328]
Esterification and transesterification	1383	Biodiesel production plants, China [317]
Transesterification	383	Industrial-scale production, Brazil [329]
<sup>a</sup> Transesterification	328	Biodiesel production [330]

<sup>a</sup> Fish waste oil.

**Table 5**  
Summary of LCA and environmental impact of WCO biodiesel.

Ref.	Final products	Processes	Environmental Impact Indicator			
			Impact category	Indicator	WCO biodiesel	Comparison
[321]	Airborne emissions, glycerol, potassium sulphate, wastewater, distillate residue, biodiesel (1 tonne of biodiesel)	WCO transportation/collection, production facility, pre-treatment, acid-catalysed esterification process, alkaline-catalysed transesterification process, biodiesel refining.	Global Warming Potential (GWP). Environmental Footprint Reduction	Kg CO <sub>2</sub> eq. per MJ energy. % reduction vs. 1st generation of biodiesel	0.09 40 %	Diesel: 0.30 3rd generation of biodiesel >100 %
[322]	Glycerol, wastewater, heterogeneous catalyst, biodiesel	WCO collection and transportation, pre-treatment (esterification process), biodiesel production (transesterification process), biodiesel separation and purification.	Climate change impact	Kg CO <sub>2</sub> eq. per tonne biodiesel (CaO catalyst)	$2.72 \times 10^2$	KOH catalyst: Higher
[323]	Glycerine, free fatty acids, mono and dipotassium phosphates, wastewater, biodiesel	WCO pre-treatment, transesterification, decantation, methanol recovery, neutralisation of crude glycerol, biodiesel washing, biodiesel dehydration.	Exergy Efficiency	MJ exergy content per MJ produced	$1.68 \times 10^{-1}$	N/A
[324]	Fatty acid methyl ester (biodiesel), glycerol, solid waste, wastewater (1 tonne of WCO)	Collection of WCO from food industry and households, washing and pre-treatment of WCO, delivery of WCO, biodiesel production (transesterification).	Catalyst performance	Optimal environmental solution	Alkaline (NaOH)	Acidic catalyst: Lower environmental impact
[325]	Glycerol, wastewater, biodiesel, other products	WCO collection and transportation, feedstock extraction, pre-treatment, biodiesel production, and combustion.	Emission reduction B5 blend (50 % WCO biodiesel)	% reduction in exhaust emissions	Significant reduction	Diesel-baseline
[317]	Waste water, smoke, ash, sludge, glycerol, and biodiesel	WCO collection, WCO pretreatment, esterification and transesterification, purification and transportation.	Economic feasibility	Cost increase vs. diesel	31 %	Diesel-baseline

with the production of 1 tonne of WCO biodiesel. The consumption phase is not considered. Variations in the production methods, reaction conditions, assumptions, and other factors impede an accurate comparison of kg CO<sub>2eq</sub> emissions. Nonetheless, the critical areas in the biodiesel transesterification process may be identified.

#### 14. Value-added products from WCO

Biodiesel production converts triglycerides into methyl ester and glycerol through the transesterification process. Glycerol is always assumed to be a co-product of this process. Most plants will resell the glycerol to reduce the production cost, and glycerol is assumed to be an environmental liability for the biodiesel industry. Due to the advances in biodiesel production and increasing demand for biodiesels, the amount of glycerol produced has doubled, though the demand for glycerol remains constant. Hence, the excess in glycerol supplied and the limited demand for raw glycerol causes the price of glycerol to remain low. The by-product of biodiesel production (glycerol) needs to be converted into value-added products to ease the oversupply of glycerol.

There are a few processes required to produce pure glycerol from the raw glycerol obtained from the biodiesel plant: filtration, chemical addition, and fractional vacuum distillation. These processes are expensive and unfeasible for a small- or medium-sized biodiesel plant. Therefore, glycerol is treated as a waste product or low-demand product in the biodiesel industry. To prevent disposal or wastage of glycerol, alternative ways are needed to convert glycerol into value-added products [331]. Scholars have found that glycerol has a similar function as other products derived from the petrochemical industry, making it a valuable resource when converted into a high value-added product. These high-value products can be synthesised through chemical reactions. Hence, high value-added products can improve the biodiesel industry's economic sustainability and reduce glycerol waste disposal [332]. Glycerol is generally used in manufacturing cosmetics, soaps, resins, foods, drinks, esters, polymers, and other products. Chemical alteration of glycerol such as oxidation or reduction process will produce other chemicals such as 1,2-propanediol, propanol, isopropanol, n-butanol, 2,3-butanediol, allyl alcohol, acetone, docosahexaenoic acid (DHA), eicosapentaenoic acid (EPA), citric acid, lipids, poly-hydroxyalkanoates (PHA), dihydroxyacetone, mesoxalic acid, glyceraldehyde, glyceric acid, malonic acid, hydroxypyruvic acid, lactic acid, pyruvic acid, propylene glycol, propionic acid, glycidol, acrylic acid, acetone, propylene oxide, propionaldehyde, acrolein, acetol, and glycerol carbonate using microorganisms such as bacteria, fungi, and microalgae via anaerobic fermentation, and microaerobic fermentation [332,333]. Díaz-Álvarez and Cadierno [334] found that glycerol with potassium permanganate oxidation produces tartronic acid and glyceric acid. Miran et al. [335] synthesised alkyd resins through the

alcoholysis–polyesterification method using glycerol produced from biodiesel production. The alkyd resin was used to produce resin films. Besides producing other products, glycerol also works as a solvent for synthesising bioactive unsaturated ketones [336]. Even though glycerol is assumed to be a waste product from the transesterification reaction, this low-value product can be converted into a high-value product using different strategies and approaches. The new opportunities of converting glycerol have shown its value in the global market. The summaries for value-added products emphasise their market value or potential market value derived from biodiesel byproducts, as presented in Table 7.

#### 15. Regulatory trends and industrial outlook on biodiesel production from waste cooking oil (WCO)

##### 15.1. Industrial outlook on biodiesel production from WCO

###### 15.1.1. WCO to biodiesel on an industrial scale conversion

The use of used cooking oil as a biodiesel feedstock continues to grow with various technological innovations to improve production efficiency and industry sustainability. One of the latest approaches is the use of a nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>)-based magnetic acid catalyst impregnated with molybdenum oxide (MoO<sub>3</sub>), which enables methyl transesterification reactions with conversion rates of up to 95.4 % under optimal conditions. This catalyst showed high stability after seven reaction cycles, with ester conversions remaining above 90.3 %, making it a promising solution for the biodiesel industry in processing used cooking oil more efficiently and sustainably [337]. In addition, the combination of used cooking oil with waste plastic in the form of a ternary fuel blend (B20P20D60) has been tested in a diesel engine and showed an increase in thermal efficiency of up to 1.71 % and a reduction in exhaust emissions compared to conventional diesel, making it a viable alternative for the transportation sector [338]. Furthermore, pyrolysis of used cooking oil with low-density polyethylene (LDPE) has shown potential to produce biofuel with characteristics similar to Grade No. 2 and No. 4 diesel, with economic feasibility analysis indicating a payback period of less than 14 months [339].

From an economic and energy perspective, the efficiency of biodiesel production from used cooking oil is greatly influenced by process optimisation and production scale. A study in Japan showed that around 92 % of biodiesel plants have low production efficiency levels, both in terms of technical and production scale, which hinders production cost reduction. Therefore, increasing the production scale and improving the quality of used cooking oil are key strategies in increasing the competitiveness of the biodiesel industry [340]. Furthermore, the integration of hydrodeoxygenation-hydrosiommerization methods in the production of second-generation biodiesel has shown significant potential in increasing purity to 99.99 %, although with a slight compromise on

**Table 7**  
Summaries of value-added product from biodiesel byproduct.

Products	Application	Market Value/Potential	Ref
Alkyd resins	Paints, coating, and adhesives	High value polymer market: replace petroleum-based resins	[335]
Bioactive unsaturated ketones	Agrochemicals and pharmaceuticals	Specialised market exhibiting significant value in pharmaceutical synthesis	[336]
Glycerol Polyhydroxyalkanoates (PHA)	Biodegradable plastics (packaging, medical devices)	Growing market due to global shift toward eco-friendly plastics	[332]
Citric Acid	Pharmaceutical, food preservatives, beverages, and detergents	High demand food industry: market value ~\$3.49 (USD) billion (2023)	[332]
Lactic Acid	Bioplastics, food additives, curing agent, flavouring agent, and medicines	Rapid growth in bioplastics sector market: projected >\$8.6 billion by 2030	[332]
Aceton	Solvent, nail polish removers, medications	Stable market with ~\$6.5 (USD) billion in 2024 and predicted to reach ~\$12.4 (USD) billion by 2033 global value	[332]
Docosahexaenoic Acid (DHA)	Infant formula, nutraceuticals, vitamins	High-value health industry; yearly market >\$4.51 (USD) billion 2024	[332]
Propylene Glycol	Cosmetics, medicines, antifreeze	Established market; yearly global demand more than \$4 billion	[332, 333]
Soaps and cosmetics	Personal care products	Established market; glycerol enhances sustainability of formulations	[331, 332]
Tartronic Acid and Glyceric Acid	Biodegradable plastic, food industry	Emerging demand in green chemistry and sustainable materials	[333]

production yield. With an energy optimisation strategy, production efficiency can be increased to 18.92 %, thereby reducing production costs and increasing the profitability of the used cooking oil-based biodiesel industry [341]. In addition, carbon life cycle analysis shows that waste cooking oil-based biodiesel produces much lower carbon emissions compared to fossil-based diesel, which is only about 11.61 % of the total carbon emissions of conventional diesel [342]. Micro flow reactor technology has also been developed to improve the efficiency of the waste cooking oil epoxidation process, which allows conversions of up to 86 % with selectivity to oxirane groups of more than 80 %, providing new opportunities for value-added products from this waste [343]. Finally, the utilisation of magnetic biochar-based catalysts from corn processing industry waste has shown biodiesel yields of up to 93.6 %, with simulation studies showing economic feasibility and lower environmental impacts compared to conventional methods [344]. Thus, the development of a biodiesel industry from waste cooking oil not only provides economic benefits, but also contributes to reducing carbon emissions and supporting the transition to cleaner and more sustainable energy.

#### 15.1.2. Use of WCO in non-biodiesel products

WCO has great potential as a raw material for various industrial products other than biodiesel. One of the main uses of WCO is in the production of biosurfactants used in the food, cosmetics, pharmaceuticals, and bioremediation industries [345]. Biosurfactants produced from WCO have the advantages of high biodegradability and efficiency in reducing surface tension, so they can replace petrochemical-based surfactants [346]. In addition, research also shows that WCO can be used as a base material for bio-lubricants, which are an environmentally friendly alternative to petroleum-based lubricants [347]. Biolubricants produced from WCO show better oxidative stability, viscosity suitable for industrial applications, and tribological properties that support efficient engine use [348]. Molecular distillation technology has been applied to improve the quality of bio-lubricants from WCO, producing lubricants with better lubricating properties and thermal stability than raw WCO [349].

In addition to lubricants and biosurfactants, WCO has also been applied in industrial waste processing. Recent studies have shown that WCO can be used as a flotation collector in the separation of carbon ash from coal gasification waste [350]. This technology utilizes the fatty acid content in WCO to improve the efficiency of carbon separation in solid waste, thereby reducing the environmental impact of the coal gasification process [351]. In other sectors, WCO has been processed into green solvents that can replace petrochemical-based solvents in various industrial applications, including the production of paints, inks, and cleaning agents [352]. WCO-based green solvents have lower toxicity and smaller environmental impacts than conventional solvents [353]. Several studies have also proposed the use of WCO in the manufacture of industrial waxes and soaps, although the main challenges in this application are the stability of the final product and the potential for contaminants in the raw materials [354].

Further development of WCO for industrial applications still faces several challenges, especially in terms of regulation and efficiency of the production process. The main obstacle in the use of WCO is the variability of its chemical composition, which can affect the quality of the final product [355]. Therefore, stricter processing standards are needed to ensure the consistency and safety of WCO-based products [350]. In addition, government policy support and investment in research and development of WCO recycling technologies are essential to increase industry adoption of this raw material. With the right strategy, WCO utilisation can provide a sustainable solution for industry while reducing the environmental impact of unmanaged waste cooking oil disposal.

## 15.2. Government regulations and policies in recycling WCO

### 15.2.1. Global policies in recycling used cooking oil

The trend of government regulation in recycling used cooking oil is growing rapidly in various countries, especially in the European Union (EU), the United States (US), and Asia. The European Union has implemented a strict policy on the use of used cooking oil for biodiesel through the Renewable Energy Directive (RED), which requires at least 14 % of transportation energy to come from renewable sources by 2030 [356]. This policy also provides incentives for industries that use used cooking oil as a raw material for biodiesel to reduce dependence on fossil fuels and reduce carbon emissions [357]. Meanwhile, in the United States, the Environmental Protection Agency (EPA) through the Renewable Fuel Standard (RFS) program has encouraged the use of used cooking oil as an alternative fuel source, by providing Renewable Identification Numbers (RINs) as trade credits for producers of waste oil-based biodiesel [358]. Various studies have shown that this policy is effective in increasing the production of used cooking oil-based biodiesel, while reducing its negative impact on the environment [359].

In Asia, regulations regarding the recycling of used cooking oil still vary from country to country. In China, government policies are becoming stricter, imposing economic and criminal sanctions on restaurants that illegally dispose of used cooking oil, while introducing a credit reporting system to monitor the food industry's compliance in recycling used cooking oil [360]. Meanwhile, Singapore has begun to utilise used cooking oil as biodiesel through tax incentive policies and mandating the use of biodiesel in the transportation sector to reduce carbon emissions from motor vehicles [361]. Taiwan is also implementing strict regulations through a used cooking oil conversion program to biodiesel, which not only reduces pollution but also contributes to national energy diversification [362]. These regulatory trends indicate a global shift towards a circular economy-based approach to used cooking oil management, which not only reduces waste but also creates new economic opportunities in the sustainable energy sector.

### 15.2.2. Subsidy schemes and tax incentives for the biodiesel industry

In recent years, various countries have begun to strengthen regulations related to used cooking oil recycling as part of sustainable energy transition efforts. The implementation of subsidy schemes and tax incentives for the used cooking oil-based biodiesel industry has become a major strategy to increase the competitiveness of biofuels and reduce dependence on fossil fuels [363]. Fossil fuel subsidy reforms in various countries have shown that the elimination of fossil fuel subsidies can increase the competitiveness of biofuels, including used cooking oil-based biodiesel, and generate significant fiscal benefits [364]. In addition, countries with more comprehensive and balanced biofuel policies tend to have more developed biofuel sectors [28]. In Indonesia, for example, the palm oil-based biodiesel policy has had a significant economic impact, although there are still challenges in managing subsidies and land expansion [365]. The Computable General Equilibrium (CGE) dynamic model also shows that the elimination of biofuel subsidies without a supporting strategy can cause economic contraction, so a more targeted policy is needed [366].

In addition to the economic aspect, the use of used cooking oil for biodiesel production also provides environmental and health benefits. The use of used cooking oil as a raw material for biodiesel not only reduces soil and water pollution but also prevents the risk of used cooking oil entering the food supply chain, which can be harmful to public health [367]. From an automotive energy perspective, converting used cooking oil into biodiesel is more economically profitable than using it in coal-fired power plants [367]. Therefore, to ensure the sustainability and effectiveness of this policy, synergy is needed between government regulations, fiscal incentives, and support for research and development of used cooking oil-based biodiesel technology.

### 15.2.3. Future regulatory trends with circular economy for sustainability

In recent years, the trend of government regulation on WCO recycling has increasingly moved towards the implementation of a circular economy to support a sustainable economic system. This concept aims to reduce waste, increase resource efficiency, and reduce carbon emissions through policies that encourage the reuse of waste, including used cooking oil as a raw material for biofuel [337]. A study in Brazil showed that the application of a circular economy to the production of used cooking oil-based biofuels can improve the sustainability of the energy industry, with a positive impact on reducing water pollution and CO<sub>2</sub> emissions [368]. In Indonesia, the implementation of a circular economy in the urban food system also revealed that strong regulations and the involvement of various actors are essential in creating an ecosystem that supports the recycling of waste oil and other organic waste [369]. Policies that enable cross-regional cooperation and incentives for industry and local communities are key factors in the success of this system.

In addition, the application of circular economy principles in various industries has been shown to increase resource efficiency and reduce environmental impacts. A study on the circular economy in the palm oil sector showed that incentive policies, such as subsidies for green technology and carbon prices, can accelerate the transition to more sustainable practices, including the use of waste oil for energy [370]. Similar approaches are also applied in plastic waste management through plastic tax schemes and extended producer responsibility (EPR), which can be adapted for WCO recycling regulations [338]. Furthermore, research on food waste management in Europe shows that regulations that support systematic waste classification and processing can increase the economic value of organic waste [371]. In Spain, the successful implementation of a circular economy in the food industry shows that partnerships between the public and private sectors, together with research and development, are essential in building a more sustainable system [372]. As regulations related to the circular economy develop, governments in various countries can adopt more adaptive and innovative policies to support sustainability in WCO management.

## 16. Limitations and challenges

Even though biodiesel production from WCO offers significant environmental and economic benefits, it also faces several challenges that require attention to make it a more viable and scalable alternative to fossil fuels. Studies have shown that implementing and scaling up biodiesel production from WCO requires addressing several key challenges and limitations.

WCO, depending on its various sources (e.g., households, restaurants, or food processing industry), presents inconsistent quality and availability of WCO feedstock. This poses challenges in maintaining a stable and reliable supply chain for large-scale biodiesel production. WCO distribution and collection can be logistically challenging, and the cost of setting up collection infrastructure (e.g., transportation and storage) may offset some of the economic benefits of using WCO as a feedstock. Pre-treatment processes such as acid-catalysed esterification before transesterification reduce the FFA content of WCOs, while drying or adsorption techniques reduce the water content, which complicates the processing of WCO and increases the production cost of WCO biodiesel. Most of the time, homogeneous alkaline catalysts such as NaOH and KOH are used in the transesterification process. These catalysts are very sensitive to the amount of water and FFA content of the WCO and can lead to side reactions such as soap formation. Despite being effective homogeneous catalysts, these catalysts are difficult to recover for reuse, leading to wastes and high costs for catalyst replacement. Heterogeneous catalysts are advantageous owing to their reusability, but they require high reaction conditions (e.g., higher temperature and pressure), which also limit their economic feasibility.

Furthermore, the biodiesel refining process often requires a large amount of water for refining and washing, which poses environmental challenges related to water consumption and wastewater production

after this process. Although WCO is a renewable fuel, WCO biodiesel production requires large amounts of energy, especially in the pre-processing, transesterification, and refining processes. Optimising the energy input and reducing energy consumption are the main challenges. In addition, WCO biodiesel has a higher oxygen content, producing higher NO<sub>x</sub> emissions compared with petroleum diesel. NO<sub>x</sub> emissions contribute to air pollution, which need to be minimised for diesel engines. WCO biodiesel has a higher kinematic viscosity and lower energy content than petroleum diesel, which can lead to poor fuel atomisation, reduced engine efficiency, and low power output. Many scholars have suggested that blending biodiesel with petroleum diesel may be necessary to achieve optimal performance, given these limitations.

Changes in fossil fuel prices greatly influence the volatility of biodiesel prices. Low oil prices can make biodiesels less competitive, necessitating government incentives or subsidies to maintain their economic viability. Furthermore, there is a lack of public knowledge regarding the advantages of utilising leftover cooking oil for biodiesel production, which can impact the availability of WCO raw materials and the acceptance of biodiesel as a sustainable fuel. Therefore, the

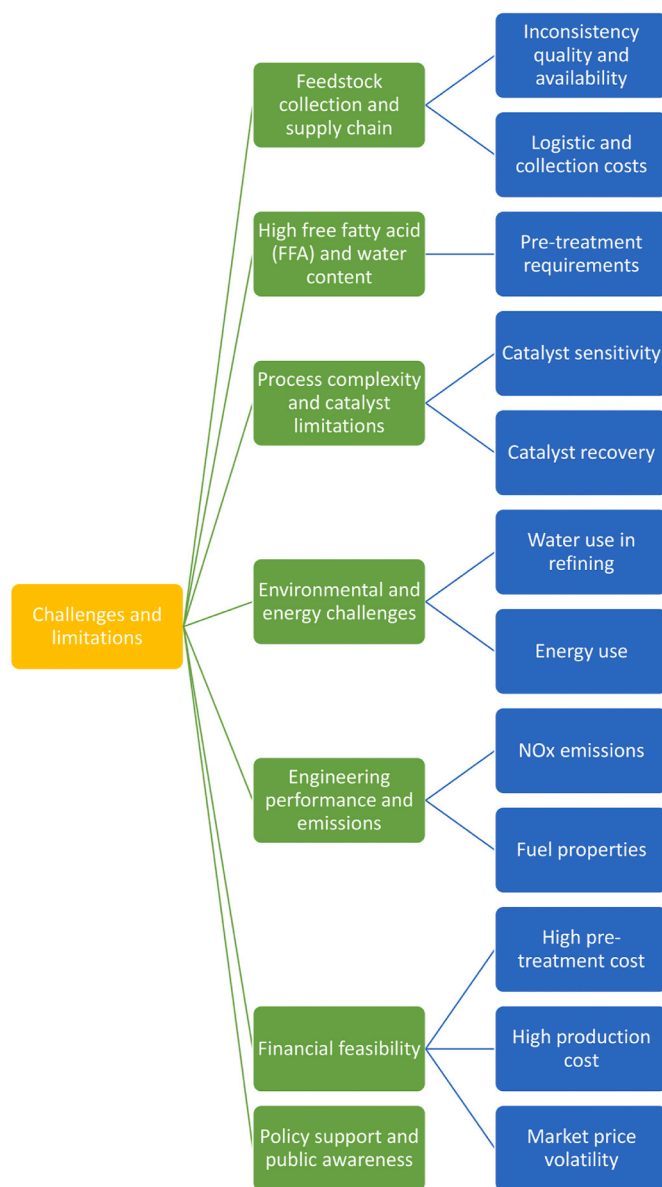


Fig. 28. Limitations and challenges of the biodiesel production process from WCO.

government must play a crucial role in promoting public awareness through campaigns and educational programmes. Fig. 28 summarises the principal challenges and limitations related to biodiesel production from WCO.

## 17. Conclusions

In this review, the potential of WCO as a biodiesel feedstock is analysed in detail, providing a scientific basis to support the results obtained from the review of biodiesels derived from WCO. This review discusses recent studies involving different conversion methods, catalyst types, process parameters (alcohol/oil molar ratio, catalyst concentration, reaction temperature, reaction time, and stirring speed), kinetics, thermodynamics, and energy consumption of the transesterification reaction, exergy and energy analysis, physicochemical properties of the biodiesel, engine performance, exhaust emissions, LCA, and an overall assessment of the environmental impact of WCO biodiesel. This review shows that the use of fresh cooking oil (e.g., palm oil and soya bean oil) for biodiesel production exacerbates global food security issues by diverting food resources to fuel production. Studies have shown that biodiesel production from pure cooking oil can cause price volatility and increased pressure on food supplies because it competes with agricultural food production. Edible crops are expensive to cultivate because of need of land, water, and agricultural fertilisers. This makes biodiesel from edible oil less competitive when compared directly with WCO, which is a waste by-product. According to the Global Subsidies Initiative and other reports, using inedible raw materials (such as WCO) for biodiesel reduces the risk of worsening global food prices and food shortages.

Pre-treatment of WCO is essential to remove impurities (e.g., high FFAs) to prevent soap formation during transesterification, as soap reduces the biodiesel yield. Methods such as microwave irradiation and ultrasonic transesterification improve mass transfer while reducing reaction time and energy consumption, resulting in a more efficient and sustainable biodiesel production. Homogeneous catalysts (e.g., NaOH and KOH) are inexpensive, efficient, and have high catalytic activity; however, they produce soap and require extensive purification. Heterogeneous catalysts are sustainable due to their reusable nature and minimal waste production. However, they require high operating conditions such as temperature and pressure. Enzymatic catalysts are environmentally friendly, but they are expensive and have long reaction times, making them less feasible for industrial-scale biodiesel production without further optimisation. RSM and other statistical techniques minimise the number of experimental trials while optimising the critical process parameters (e.g., methanol/oil molar ratio and reaction temperature). BBD and CCD provide multi-variable optimisation, enhancing conversion efficiency and biodiesel yields while accounting for economic and environmental factors. Optimising biodiesel production involves carefully balancing the methanol/oil molar ratio, catalyst concentration, reaction temperature, reaction time, and stirring speed, each of which significantly affects the yield and efficiency of the transesterification process. The transesterification reaction for biodiesel production involves first-order kinetics with varying activation energies by a catalyst, and advanced technologies such as hydrodynamic cavitation will improve efficiency and reduce energy consumption compared with conventional methods.

Hydrodynamic cavitation improves mass and heat transfer in the transesterification reaction, accelerating the reaction rate and decreasing energy consumption compared with conventional approaches. Studies indicate that this technique can decrease energy consumption by as much as 40 % relative to traditional mechanical stirring methods. The energy analysis quantifies the input–output energy, whereas energy evaluation assesses the quality of energy. The utilisation of WCO in biodiesel production enhances the process by detecting and reducing energy losses, thereby augmenting economic and environmental sustainability. Studies have shown that WCO biodiesel

blends reduce CO (87 %), UHC (~7.89 %), and PM emissions, resulting in cleaner combustion. However, the higher NO<sub>x</sub> emissions (22.13 %) due to higher oxygen content of biodiesels are still a major concern, requiring optimisation of the blend ratios and use of additives (e.g., antioxidants). LCA studies have shown that biodiesel derived from WCO has reduced environmental impact compared with diesel and first-generation biodiesels, particularly greenhouse gas emissions, energy consumption, and waste management. Advanced recycling methods boost these advantages. Although WCO biodiesel production is cleaner than the production of petroleum diesel, there are still challenges related to refining and water consumption of biodiesel production, which need to be addressed. However, advances such as waterless refining increases the efficiency and reduces the environmental impact of biodiesel production. The transformation of glycerol (a by-product of WCO biodiesel production) into high-value compounds such as propylene glycol and bio-based polymers enhances the economic value of glycerol, which aligns with circular economy principles.

## 18. Future research

Based on the literature survey and the conclusions presented above, there are some avenues for further research. There is a need to investigate non-edible feedstocks for biodiesel production (such as algae, microalgae, or agricultural residues) to prevent competition with food resources and assess their economic viability. In addition, there is a need to study the impacts of different government policies and support mechanisms on the scalability and sustainability of WCO biodiesel production. The following research topics are suggested here together with some future suggestions and possible studies to advanced biodiesel production from waste cooking oil (WCO) and complement world sustainability goals:

- Feedstocks diversification and sustainability involve the exploration of non-edible raw materials are investigated such as algae, microalgae, and agricultural residues such as rice husk or *Jatropha* to reduce competition for food fuels. Assess scalability, lipid yield and economic viability. Furthermore, WCO supply chain strategies need to be developed to increase the level of organized WCO collection in urban and rural areas by overcoming logistical and cost barriers.
- An integrated analysis of socio-economic policy and integration, with a focus on governmental incentives, is vital for assessing effects on biodiesel consumption due to carbon tax, subsidies, and mandating renewable fuel. Additionally, conducting a public outreach initiative is vital for designing and evaluating educational campaigns for enhancing consumer acceptance of biodiesel blends, especially from B10-B50.
- This development of catalytic strategies can be achieved through innovation in designing complex heterogeneous bifunctional catalysts, for example, SrO–ZnO/Al<sub>2</sub>O<sub>3</sub>, which catalysed esterification and transesterification simultaneously. Additionally, a new enzymatic catalytic system may also be developed through lipases engineered with increased tolerance for methanol, thus making them reusable and, as a result, lowering production costs of biodiesel through enzymatic routes.
- The direction of research on process efficiency and technology is to analyse energy or exergy that integrates real-time monitoring with thermodynamic modelling to minimise energy waste in transesterification reactors. Waterless purification also needs to be scaled purification technology based on microwaves or membranes to eliminate the washing step that requires a lot of water.
- Continuing the research in engine performance and emissions, such as the optimisation of the mixture to study the WCO (B10-B100) biodiesel mixture on engine durability, particles (PM<sub>2.5</sub>) and NO<sub>x</sub> emissions. In addition, it is necessary to develop additives to formulate antioxidants and increase the desired flow that is adjusted for high FFA feedstocks.

- Further research into utilisation of by-products. Recycling of glycerol by further analysing high-value products such as biodegradable plastics or pharmaceuticals to offset production costs. Waste-to-energy systems could explore anaerobic digestion of biodiesel by-products for biogas generation.
- Development of sustainability metrics. Conduct comprehensive LCA studies to expand life cycle assessment to include socio-economic and circular indicators. For example, job creation and closed-loop recycling. Further development of circular economy models by building a pilot industrial symbiotic network where WCO biodiesel plants exchange waste heat, glycerol and CO<sub>2</sub> with neighbouring industries.

### Declaration of competing interest

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

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### Data availability

The data that has been used is confidential.

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**Update**

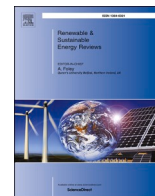
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## Corrigendum

### Corrigendum to ‘Status, developments, and sustainability of biowaste feedstock: A review of current progress’ [Renew Sustain Energy Rev Volume 217, July 2025, 115769]

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The authors regret < The authors regret that the CRediT authorship contribution statement was not included in the original publication. The statement is as follows:

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T.M.I. Riayatsyah, Alfian Sarifudin: Writing – review & editing,

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Abdi Hanra Sebayang: Methodology, Data curation.

Md. Abul Kalam, Oki Muraza, Nandy Setiadi Djaya Putra: Supervision.

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