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Reactor technologies for biodiesel production and processing: A review

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ABSTRACT

Diesel engines are preferred over spark ignition counterparts for heavy-duty applications and power generation plants because of their higher efficiency, durability, and productivity. Currently, the research interests have been propelled towards renewable and sustainable diesel fuels such as biodiesel in order to address the environmental and energy security challenges associated with these energy systems. However, the most challenging issue concerning large-scale production of biodiesel is its relatively high cost over fossil-based diesel owing to high feedstock and manufacturing costs. Therefore, cost-effective and eco-friendly biodiesel production technologies should be necessarily developed and continuously improved in order to make this biofuel more competitive *vs.* its petroleum counterpart. Accordingly, this paper comprehensively reviews biodiesel manufacturing techniques from natural oils and fats using conventional and advanced technologies with an in-depth state-of-the-art focus on the utmost important unit, *i.e.*, transesterification reactor. The effects of the main influential parameters on the transesterification process are first discussed in detail in order to better understand the mechanisms behind each reactor technology. Different transesterification reactors; *e.g.*, tubular/plug-flow reactors, rotating reactors, simultaneous reaction-separation reactors, cavitational reactors, and microwave reactors are then scrutinized from the scientific and practical viewpoints. Merits and limitations of each reactor technology for biodiesel production are highlighted to guide future R&D on this topic. At the end of the paper, the sustainability aspects of biodiesel production are comprehensively discussed by emphasizing on the biorefinery concept utilizing waste-oriented oils.

Abbreviations: ACC, Annular centrifugal contactor; ASTM, American society for testing and materials; BSTR, Batch stirred tank reactor; [BMIm][BF_4], 1-butyl-3-methylimidazolium tetrafluoroborate; [BMIm][PF_6], 1-butyl-3-methylimidazolium hexafluorophosphate; CFC^{TM}, Controlled flow cavitation; CSTR, Continuously stirred tank reactors; CTMAB, Cetyltrimethylammonium bromide; ECT, Electrical capacitance tomography; FAEE, Fatty acid ethyl ester; FAME, Fatty acid methyl ester; FBR, Fluidized bed reactor; FCI, Fixed capital investment; FFA, Free fatty acid; GHG, Greenhouse gas; JSR, Jet-stirred reactor; L/d_p, Length/diameter of particle; L/D, Length to diameter; LCA, Life cycle assessment; LLPTC, Liquid-liquid ptc; LUC, Land-use change; OFR, Oscillatory flow reactors; OBR, Oscillatory baffled reactor; PBR, Packed bed reactor; PFR, Plug flow reactor; PTC, Phase-transfer catalyst; RTD, Residence time distribution; RTR, Rotating tube reactor; RED, Renewable energy directive; RPBR, Rotating packed bed reactor; RSSDR, Rotor-stator spinning disc reactor; SCCD, Supercritical carbon dioxide; SCM, Supercritical methanol; SDR, Spinning disc reactor; SMCR®, Stacked multichannel reactors; SPR, Shockwave power reactor; STT, Spinning tube-in-tube; TBR, Trickle bed reactor; WAF, Waste animal fat; WCO, Waste cooking oil.

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Contents

1. Biodiesel production

Biodiesel (the most attractive biofuel types) as a biodegradable, sustainable, clean-burning, and nontoxic transportation fuel has gained a lot of interest in recent years [1–3]. In fact, this green fuel has gradually become more economical and widely used in many regions of the world due to the implementation of subsidiaries and tax exemptions. In order to further boost the economic benefits of biodiesel industry, glycerol as the main by-product of biodiesel production plants, which amounts to approx. 10 wt.% of the production volume, can be valorized into combustion improvers for diesel/biodiesel, such as solketal, solketalacetin, and acetins [4–6]. In spite of these efforts, the production cost of biodiesel has still remained a challenge toward its commercialization and industrialization phases as well as competition with fossil fuels [7]. Biodiesel highly resembles diesel fuel in terms of cetane number, density, and viscosity [7–9]. Chemically, biodiesel is an alkyl ester (mostly fatty acid methyl ester abbreviated as FAME) of long chain fatty acids (C14–C24) synthesized from various renewable lipid feedstocks such as vegetable oils and animal fats [10–12]. It is noteworthy that natural oils and fats can be used either in modified diesel engines in their neat form (direct use and blending as well as microemulsion; also known as physical approaches) or in existing diesel engines in chemically modified form (pyrolysis and transesterification; also known as chemical approaches) [13,14]. Table 1 compares these techniques with respect to their advantages and disadvantages.

1.1. Physical approaches

In physical methods, specific proportions of diesel fuel and other additives are employed to improve viscosity and volatility of natural oils. Since the chemical characteristics of natural oils remains unchanged, inherent problems of straight natural oil persist as discussed in the subsequent section.

Direct use and blending. The combustion of vegetable oils as diesel fuel was coined in 1893 when Rudolph Diesel, the German inventor of diesel engine, examined peanut oil in his compression engine [15]. Although the application of vegetable oils was completely boycotted due to higher availability and lower cost of petrol-diesel in 1920, researchers again suggested the possibilities of fueling diesel engines with natural oils in 1980. Brazilian researchers successfully powered pre-combustion chamber diesel engines with no adjustments using a diesel blend containing 10% sunflower oil. The application of up to 50% vegetable oil in diesel was tested by different scientists as well. In 1982, the first international conference on plant and vegetable oils as fuels was held to consider various aspects of using vegetable oil directly in diesel. These included oil production (oilseed processing and oil extraction) and fuel preparation methods to determine fuel cost, specifications, and impact on engine performance and durability. Additionally, waste cooking oil (WCO) was filtered and mixed with 5% diesel fuel to run a diesel fleet [16–18]. Although this cheap diesel fuel contained high thermal efficiency and no carbon build-up issue (coking), the blend required pre-heating for liquefaction

Table 1
Advantages and disadvantages of the four main biodiesel production processes.

Method	Advantage	Disadvantage
Direct use and blending	- Low capital and production costs - Simple production	- Solidification of blend at cold temperatures - Impractical and inappropriate for direct use in diesel engines - High viscosity - Gum formation - Lubricating oil thickening - Incomplete fuel combustion - Oil deterioration - High free fatty acid (FFA) - Low volatility - Unsaturated hydrocarbon chains reactivity - Injector nozzles plugging - Poor atomization - Engine durability reduction, - Higher air pollution emission - Higher engine maintenance costs - Higher engine wear
Microemulsion	- Biodiesel formation with lower viscosity and higher liquidity - Lower nitrogen oxide emissions - No by-product or waste formation - Clear, single phase, and thermodynamically stable colloidal equilibrium dispersion of biodiesel fluid	- Heavy deposition of carbon residue - Inadequate combustion - Lubricating oil thickening - Random injector needle sticking
Pyrolysis	- Suitable for areas with well-established hydro-processing industry - Generation of value-added by-products like syngas - Biofuel with satisfactory physical and chemical properties	- High production cost - Complex equipment requirement - Biofuel has no oxygenated value - Producing short chain molecules with more similarities to gasoline than diesel fuel
Transesterification	- The most common method for production of biodiesel - Unreacted feedstock can be recycled - The by-product (*i.e.*, glycerol) can be converted into value-added products	- Dry alcohol and oil must be used to increase biodiesel yield by avoiding saponification - Glycerol must be efficiently separated to avoid generation of hazardous gases (*i.e.*, acetaldehyde, formaldehyde) - Expertise requirement - Complex equipment requirement

at cold temperatures and also contaminated lubricating oil. The viscosity of lubricating oil was increased to the point of replacement after every 6440–7240 km because of the polymerization of polyunsaturated vegetable oils. Finally, it was concluded that some properties of vegetable oils including gum formation, high density, high FFA content, high viscosity, low volatility, lubricating oil thickening, and unsaturated hydrocarbon chains reactivity make direct application of pure vegetable in diesel engines inappropriate and impractical [19]. If engine remains unmodified, these drawbacks lead to inappropriate fuel combustion, injector nozzles plugging, poor atomization, engine durability reduction, higher air pollution emission, higher engine maintenance costs, and higher engine wear.

Microemulsion. The viscosity of vegetable oil and its low liquidity as well as high nitrogen oxide (NO_x) emissions of biodiesel can be improved through microemulsification without formation of by-product and waste. This method is classified into two groups, *i.e.*, water in oil and Winsor Type II and involves mixing microemulsions, solvents, or surfactants with animal fats and vegetable oils to produce a clear, single phase, and thermodynamically stable colloidal equilibrium dispersion of optically isotropic fluid with micro-structures (1–150 nm in size) and droplet diameter of 10–100 nm [18]. Different solvents including 1-butanol, 2-octanol, butanol, ethanol, hexanol, and methanol can be applied in preparation of microemulsions, with or without diesel fuel. A microemulsion comprising of soybean oil, 2-octanol, methanol, and cetane improver (52.7:33.3:13.3:1.0) has been already approved by 200 h Engine Manufacturers Association test [20]. Moreover, when short-term performance is considered, ionic and non-ionic microemulsions prepared by mixing ethanol with soybean oil have qualities close to No. 2 diesel fuel.

Nguyen et al. [21] extracted peanut oil (95% efficiency, 10 min, room temperature) using diesel-based reverse-micellar microemulsions to produce a peanut oil/diesel mixture that met the biodiesel fuel standards. Najjar and Heidari [22] formulated a nine-month stable, low viscosity microemulsions containing water droplets of 4.6 nm by blending 1-butanol as co-surfactant with diesel/colza oil (4:1 w/w), water, and Span 80 surfactant (47:44:5:4 wt.%). The addition of diethylene glycol ethyl ether and ethyl acetate improved the fuel properties while considerably lowered the emissions of CO and NO_x of microemulsion biofuels made from diesel/palm oil (1:1 v/v), ethanol, as well as some surfactants and co-surfactants [23]. An ecofriendly microemulsion biofuel with comparable fuel properties with biodiesel was generated by blending sorbitan monooleate (a sugar-based surfactant) and octanol (1:8 molar ratio) with palm oil [24]. A number of studies produced bio-oil *via* thermochemical liquefaction (250–350 °C, 5–10 MPa) of sludges and subsequently mixed it with various solvents (such as biodiesel, diesel, ethanol, methanol) and surfactants (such as rhamnolipid) to produce diesel fuel microemulsion, representing better cold flow properties, improved stability and solubility, reduced activation energy, satisfactory viscosity, and shorter ignition delay [25,26]. However, microemulsification of oils must be further improved to address heavy deposition of carbon residue, inadequate combustion, increased viscosity of lubricating oils, and random injector needle sticking.

1.2. Chemical approaches

These methods modify the chemical nature of natural oils and fats itself for its better exploitation in fuel industry.

Pyrolysis. This is a thermochemical process applying heat (300–700 °C or higher) to convert various feedstocks into value-added chemical species (such as energy carriers) under anoxic condition at atmospheric pressure [27]. More specifically, this technique allows the degradation of animal fat, methyl esters of fatty acids, or vegetable oil into a fuel resembling diesel fuels under a predefined process duration with or without catalyst. Pyrolysis of oils is particularly suitable for areas with well-established hydro-processing industry due to its similarity to conventional petroleum refining method [28,29]. A second generation biofuel was synthesized from pyrolysis-treated WCO (800 °C, 15 °C/min) to yield 80 wt.% bio-oil with a high heating value of 8843 kg/kcal. The by-products of this process, *i.e.,* syngas and biochar could also be conveniently consumed as energy source for the pyrolysis reactor and iron-rich fertilizer, respectively [30].

Abdelfattah et al. [31] synthesized castor-based diesel fuel *via* pyrolysis of crude castor oil in presence of 1% v/v NaOH and ZMS-5 as catalysts. The resultant diesel fuel showed satisfactory physical and chemical properties and was suitable as 5–10% blend in diesel to run single cylinder four stroke direct injection compression ignition engine. In another study, a high energy (42–49 MJ/kg), low nitrogen and oxygen, sulfur-free liquid oil with C13–C24 hydrocarbons was obtained through microwave co-pyrolysis of WCO and waste polyolefins under vacuum (20–25 °C/min, 62 wt.% yield) [32]. Despite the high versatility of pyrolysis technique, it is not highly appreciated due to high production cost as well as complex equipment requirement. Moreover, the generated biofuel has no oxygenated value and harsh reaction conditions lead to production of short chain molecules with more similarities to gasoline than diesel fuel.

Transesterification. The most widely employed chemical methods for converting natural oils and fats into diesel fuel is transesterification [33–35], in which, stoichiometrically, three moles of light alcohols (mainly methanol) react with one mole of triglyceride. This process is usually performed in the presence of a catalyst (60–70 °C, atmospheric pressure, 90 min) and results in the production of a mono-alkyl ester (mainly methyl ester) called biodiesel and glycerol as a by-product [36,37]. The unreacted alcohol can be recovered to some extent at the end of the process and glycerol can be sold to existing markets to reduce the production costs. The separation of glycerol is extremely important to enhance the quality of biodiesel and to prevent formation of hazardous gases, *i.e.,* acetaldehyde or formaldehyde during its combustion [38]. The application of dry alcohol and oil (with low concentration of FFA) is crucial for inhibiting the saponification and increasing biodiesel formation. The holding time is in inverse relation with temperature; however, temperature must be elevated above 60 °C in combination with pressure due to methanol boiling point (65 °C) as the most widely used alcohol. Alternatively, a higher temperature at ambient pressure can be applied when other alcohols such as butanol or ethanol is used. In contrast, lower cost of methanol as well as its chemical and physical features is highly preferable for transesterification though it develops a two-phase system.

Among different catalysts, *i.e.,* acids, alkalis, and lipases (enzymes), alkaline-catalyzed process is currently regarded as the most popular and commercial approach by accelerating the reaction up to 4000 times. Alkoxides such as sodium methoxide, hydroxides such as potassium or sodium hydroxides, and potassium and sodium carbonates are some common alkalis for this purpose. Despite the higher price, the best alkaline catalysts are alkaline metal alkoxides that provide up to 98% yields at low concentrations (0.5 mol%) after 30 min reaction time. At higher molar concentration of catalyst (1–2 mol%), alkoxides can be substituted by cheaper catalysts including potassium or sodium hydroxides. In contrast, acidic treatment, catalyzed by hydrochloric or sulfuric acids, is mostly applied as a pre-treatment process (esterification) for raw materials with high FFA contents. Although enzyme-catalyzed transesterification can be done in both aqueous and organic systems and it is chemically clean and specific reaction, the high cost of enzyme and long processing time render it economically unfeasible and hinder its commercial application [18,39,40].

The elementary reaction of a triglyceride with methanol is a three-step successive reversible reaction. First, methanol reacts with triglyceride producing a diglyceride, followed by the reaction of diglyceride with methanol producing a monoglyceride, and finally monoglyceride is reacted with methanol yielding glycerol. A mole of FAME is produced in each of the above-mentioned steps [41,42]. Thus, the overall reaction can be summarized as follows [43]:

$$\mathrm{TG} + 3\,\mathrm{MeOH} \xrightarrow{\text{catalyst}} \mathrm{Glycerol} + 3\,\mathrm{FAME} \tag{1}$$

These reactions proceed with different reaction rate constants (k_m) in both forward and reverse directions and can all be considered second order or pseudo-second order reactions [41]. The first reaction occurs at a slower rate compared with the second and the third reactions owing to the formation of diglyceride and mass transfer limitations imposed by the immiscibility of the oil-methanol combination [44–46]. The second reaction, however, is the fastest step of all because the produced methyl esters contribute to the development of a homogeneous phase by acting as a solvent or co-solvent in the reaction [47]. Unlike the first two steps, the third reaction tends to reverse because of the low amount of reactants remained [48].

1.3. Aim and scope

Currently, the high cost of biodiesel induced by high feedstock and process costs is the major obstacle hampering its widespread commercialization. Therefore, this paper is aimed at reviewing biodiesel production techniques from natural oils and fats using conventional and advanced reactors with an in-depth state-of-the-art focus on the transesterification process as the beating heart of biodiesel plants. The effects of the main influential parameters including quantity and type of catalyst, FFA content of feedstock, mixing intensity, alcohol/triglyceride molar ratio, reaction temperature, alcohol type, water content of feedstock, type of oil, and reaction time [19,39,48,49] on the transesterification process are first discussed in detail. Different transesterification reactors; *e.g.,* tubular/plug-flow reactors (packed bed reactors, fluidized bed reactors, trickle bed reactor, oscillatory flow reactors, micro-channel reactors), rotating reactors (stirred tank reactors, rotating/spinning tubes reactors, spinning disc reactors), simultaneous reaction-separation reactors (membrane reactors, reactive distillation reactors, annular centrifugal contactors), cavitational reactors (sonochemical/ultrasonic reactors, hydrodynamic cavitation reactors, shockwave power reactors), and microwave reactors are then scientifically and practically scrutinized. Advantages and disadvantages of each reactor technology are comprehensively described. Some of the challenging issues impeding commercialization of each reactor technology are also highlighted. In the final part of this paper, the sustainability aspects of biodiesel obtained through transesterification of various available feedstocks have been analyzed with respect to net GHGs emission, impacts on tropical forests and biodiversity, socioeconomic impacts, and food/water *vs.* fuel debate. The biorefinery concept utilizing waste-oriented oils is also elaborated as a potential strategy to further boost the economic viability and environmental sustainability of the biodiesel industry.

Overall, the present manuscript is very relevant to ongoing research on biodiesel production and processing while the detailed information provided will be very useful for researchers (*i.e.,* encouraging future R&D) in the field, industrial experts and policy makers.

2. Main parameters affecting transesterification reaction

2.1. Catalyst

2.1.1. Type of catalyst

2.1.1.1. Homogenous catalysts. Homogeneous catalysts have been conventionally used in transesterification reaction by the biodiesel industry. Homogeneous basic and acidic catalysts are inexpensive and effective, but both require excess amount of alcohol and relatively high energy to complete the conversion. Moreover, their application is usually limited to batch processes and a catalyst separation step is inevitable.

Homogeneous basic catalysts. Alkaline metal hydroxide and methoxides such as potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium methoxide (CH_3KO), and sodium methoxide (CH_3ONa) are the most commonly used homogeneous base catalysts in transesterification reaction [50]. Among them, NaOH and KOH are extensively used by the industry in transesterification process. Although catalysts containing sodium are preferable compared with potassium-based catalysts because of their lower molecular weight, potassium phosphate could be obtained after neutralization of KOH at the end of the process and used as fertilizer in agriculture [51]. Alkaline-catalyzed biodiesel production follows a simple mechanism through which a tetrahedral intermediate is initially formed as a result of the interactions between the negative species of the incorporated alcohol (such as CH_3O^-) and the carbonyl groups of the oily feedstock. Afterwards, new O–H bonds are formed by the departure of R_1COOCH_3. Reformation of carbonyl groups will continue for two more identical cycles so that a methyl ester is formed (Fig. 1).

A study conducted by Dias et al. [52] revealed that sodium-based catalysts like NaOH and CH_3ONa have higher activities in comparison with KOH for conversion of sunflower oil, WCO, and soybean oil. Notably, some investigations have documented that alkali methoxides are more desirable in the industry than alkali hydroxides because they do not generate water in reaction system. Application of homogeneous alkali catalysts in the industry has advantages such as high catalytic activity, low cost, wide availability, and short reaction time. However, it is accompanied with some unfavorable issues as well. For example, homogeneous basic catalysis is limited to batch process, which needs high amount of energy and high product cost. Moreover, water production, and subsequently saponification could lower the final yield of methyl esters. Importantly, alkali catalysts are sensitive to high content of FFA in feedstock. Therefore, substrate containing more than 3 wt.% of FFA must be pre-treated using acid catalysts to decrease the acid value before alkali catalyzed-transesterification [53].

Homogeneous acid catalysts. Acid catalysts are used less commonly than their basic counterparts in transesterification reaction mainly due to their slow reaction rate and corrosive nature. In addition, higher alcohol requirement, compared with that of the homogeneous basic catalysts is another major shortcoming associated with the application of acidic catalysts [54]. In contrast to alkali catalysts, acid catalysts can be used for conversion of low cost feedstocks into biodiesel due to their insensitivity to the high amount of FFA in oils. Moreover, saponification never occurs during acidic catalysis. The most common acid catalysts applied in esterification reaction are sulfuric acid, phosphoric acid, hydrochloric acid, and sulfonic acid. During the acid-catalyzed biodiesel production process, tetrahedral species are resulted from the interaction of positively-charged hydrogen ions and carbonyl groups by the nucleophilic attraction of alcohol. In the next step, $H^+$is mobilized and the process is carried out for two more cycles so that a methyl ester is formed (Fig. 2).

Trifluoroacetic acid (0.2 M) was used for acid catalysis of soybean oil at 80 °C using methanol-to-oil molar ratio of 20:1 for the production of biodiesel with 98.4% yield [55]. Su [56] tested three homogeneous acid catalysts including hydrochloric acid, nitric acid, and sulfuric acid to convert soybean oil into biodiesel. All these acids showed high catalytic activities; however, hydrochloric acid was the only recoverable acid and could be reused for up to five cycles. After optimization of the process, a conversion of 98.1% was obtained at 76.6 °C and methanol-to-oil molar ratio of 7.9:1.

2.1.1.2. Heterogeneous catalysts. The biodiesel production cost can be discounted by applying heterogeneous catalysts [57,58], offering several advantages such as easy recovery from the end products (*i.e.*, biodiesel and glycerol) as well as high tolerance to feedstock moisture and FFAs contents. These advantages reduce saponification and contribute to the production of up to 24% more pure biodiesel and glycerol, compared with that of homogeneous catalysts (75% purity). Nevertheless, heterogeneous catalysts also suffer from several disadvantages including more costly operating conditions (higher temperature and pressure), less contact with the reactants (lower conversion rate), and the possibility of leaching solid supports and consequent contamination of the produced biodiesel as well as loss of the catalyst [49].

Heterogeneous basic catalysts. Various types of heterogeneous basic catalysts including hydrotalcites, metal oxides, mixed metal oxides, supported hydroxides and oxides, and zeolites have been used in transesterification reaction. Among the alkaline metal oxides, calcium oxide (CaO) has been known as a non-corrosive and ecofriendly alkaline catalyst with a high catalytic activity. Mixed metal oxides have also been introduced as promising heterogeneous basic catalysts. These catalysts consist of two or more metals and the characteristics of the catalyst depend on the type and the amount of each of these metals. The efficacy of various unsupported mixed metal oxides including $CaMnO_x$, $BaMnO_x$, $CaFeO_x$, $BaFeO_x$, $CaZrO_x$, and $CaCeO_x$ in conversion of animal fats into biodiesel have been studied by Dias, Alvim Ferraz [59]. Although all the mixed metal oxides presented great basicity, the only unsupported mixed metal oxides that showed catalytic activity was $CaMnO_x$ with a biodiesel yield of 98% (4 wt.%, 60 °C, 9 h).

Taufiq et al. [60] synthesized $CaO–La_2O_3$ metal oxide as catalyst for transformation of jatropha oil into methyl ester. The catalyst was synthesized through co-precipitation procedure with various Ca:La atomic ratios. A yield corresponding to 87% was resulted when the reaction was carried out with 4% catalyst at 60 °C and methanol-to-oil molar ratio of 24:1. The catalyst was regenerated through washing with methanol and calcination at 900 °C, but it lost its activity after three cycles and the conversion of oil into biodiesel reduced to 18%. Sahani et al. [61] examined the strontium lanthanum mixed metal oxide as catalyst for converting *Schleichera Oleosa* oil into biodiesel. A FAME conversion of 76% was obtained in the presence of 1.5% of catalyst loading with methanol-to-oil molar ratio of 14:1 at 60 °C for 40 min.

Zeolites are another effective heterogeneous catalyst used in transesterification process. Zeolites are constructed by SiO_4 and AlO_4-tetrahedral structures, which constitute a crystalline aluminosilicate with high surface area. This microporous structure and high capability in adsorption mark zeolites as efficient catalysts in biodiesel production. These compounds are categorized in cation-exchange materials, which can generate various types of structures with different chemical and physical characteristics by substitution of cations during ion exchange process. Zeolites Beta, X, A, Mordenite, USY and ZSM-5 are the most common zeolites. Babajide et al. [62] investigated the catalyst activity of zeolite FA/NaX for conversion of sunflower oil into methyl ester. FA/NaX was synthesized from coal fly ash, a by-product of coal combustion, and ion exchanging with K^+. Conversion of oil was conducted in methanol-to-oil molar ratio 6:1 at 65 °C with 3 wt.% of catalyst concentration.

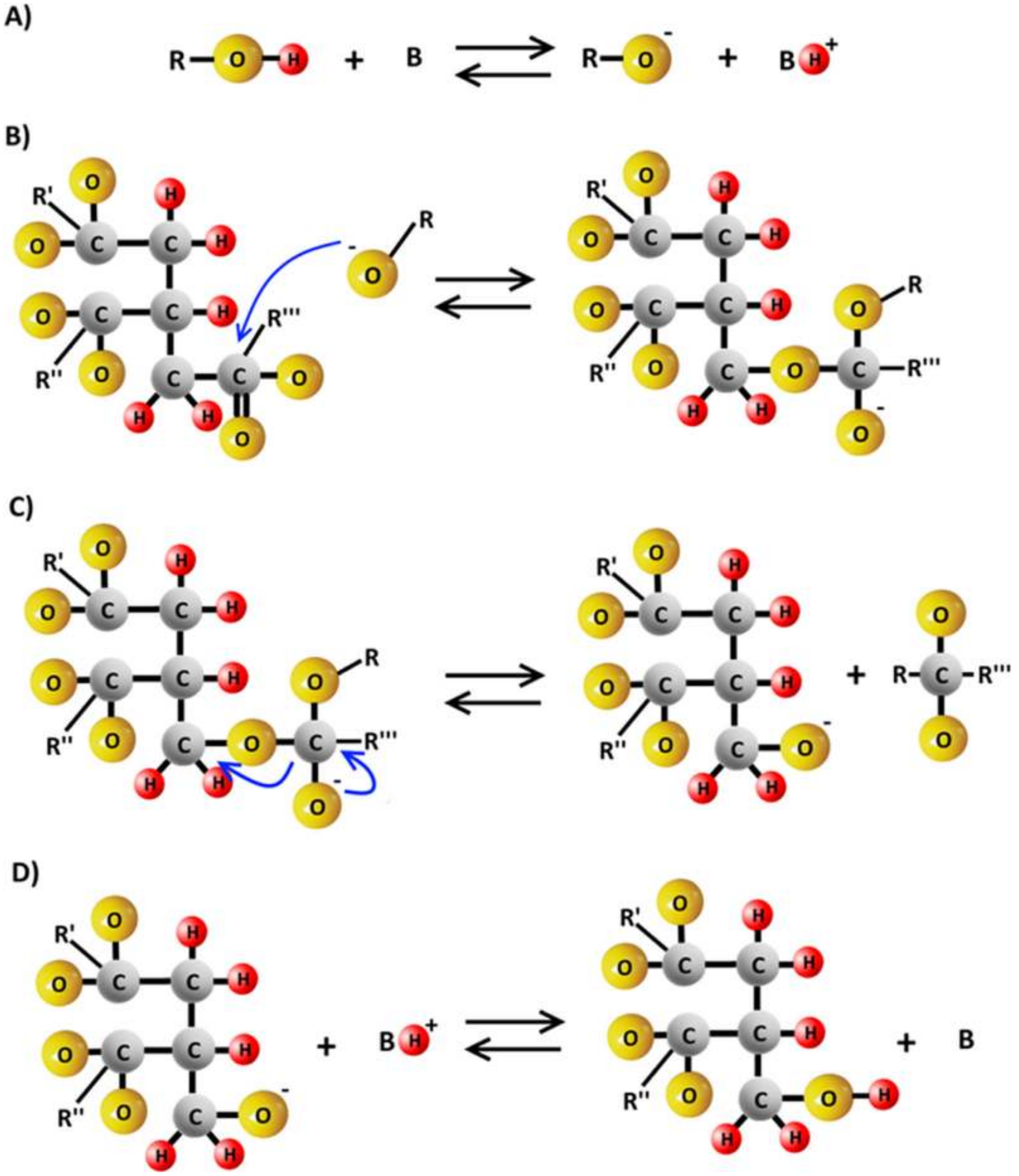

Fig. 1. Schematic steps of base-catalyzed transesterification.

The biodiesel production yield was reported as 56% after 8 h of reaction time. To achieve higher yields, they used ion exchange process with potassium acetate to synthesize the catalyst FA/KX. The substitution of catalysts increased the product yield to 83.5% with same reaction time. The catalyst was also reused for further reactions without activity loss after three cycles.

Hydrotalcites are anionic clays which are known as aluminum and magnesium hydroxycarbonates. Hydrotalcites can be thermally decomposed and mixed oxide elements including $MgAl_2O_4$ and MgO can be generated. These elements with high surface area provide suitable catalysts for biodiesel synthesis. In a study presented by Navajas et al. [63], magnesium-aluminium hydrotalcites (2 wt.%) was used for transformation of sunflower oil into methyl ester at methanol-to-oil molar ratio of 48:1 and reaction temperature of 60 °C. High yield (96%) was achieved after 8 h of reaction time and the catalyst was successfully recovered for reutilization. Another group of heterogeneous basic catalysts are alkaline hydroxides supported on inorganic oxides. Li et al. [64] explored the effect of various oxides as supporter of KOH on catalysts activity. Thirty percent (wt.) of KOH was loaded on different supporters including Al_2O_3, Nd_2O_3, TiO_2, and ZrO_2. The best results were obtained by using KOH/Nd_2O_3 with a yield of 90%, followed by KOH/Al_2O_3 with a biodiesel yield of 89%. Moreover, they found that KOH/Nd_2O_3 could be used five times without any loss in functionality.

Heterogeneous acidic catalysts. Heterogeneous acid catalysts must meet some criteria such as having hydrophobicity, high number of active sites, and mild acid strength to be appropriate catalysts for transesterification reaction [51]. Although acidic catalysts are less attractive than basic catalysts for biodiesel synthesis because of their low activity rate, recent investigations have led to new advancements in acidic catalysis minimizing their limitations. Development of solid acid catalysts which possess both characteristics of heterogeneous basic catalysts and mineral acids (such as cation exchange resin, hetero-polyacids, silica-alumina, sulfonated polystyrene, and zeolites) capable of performing simultaneous esterification and transesterification reactions while being resistant to water content and high FFA content is among such advancements [65].

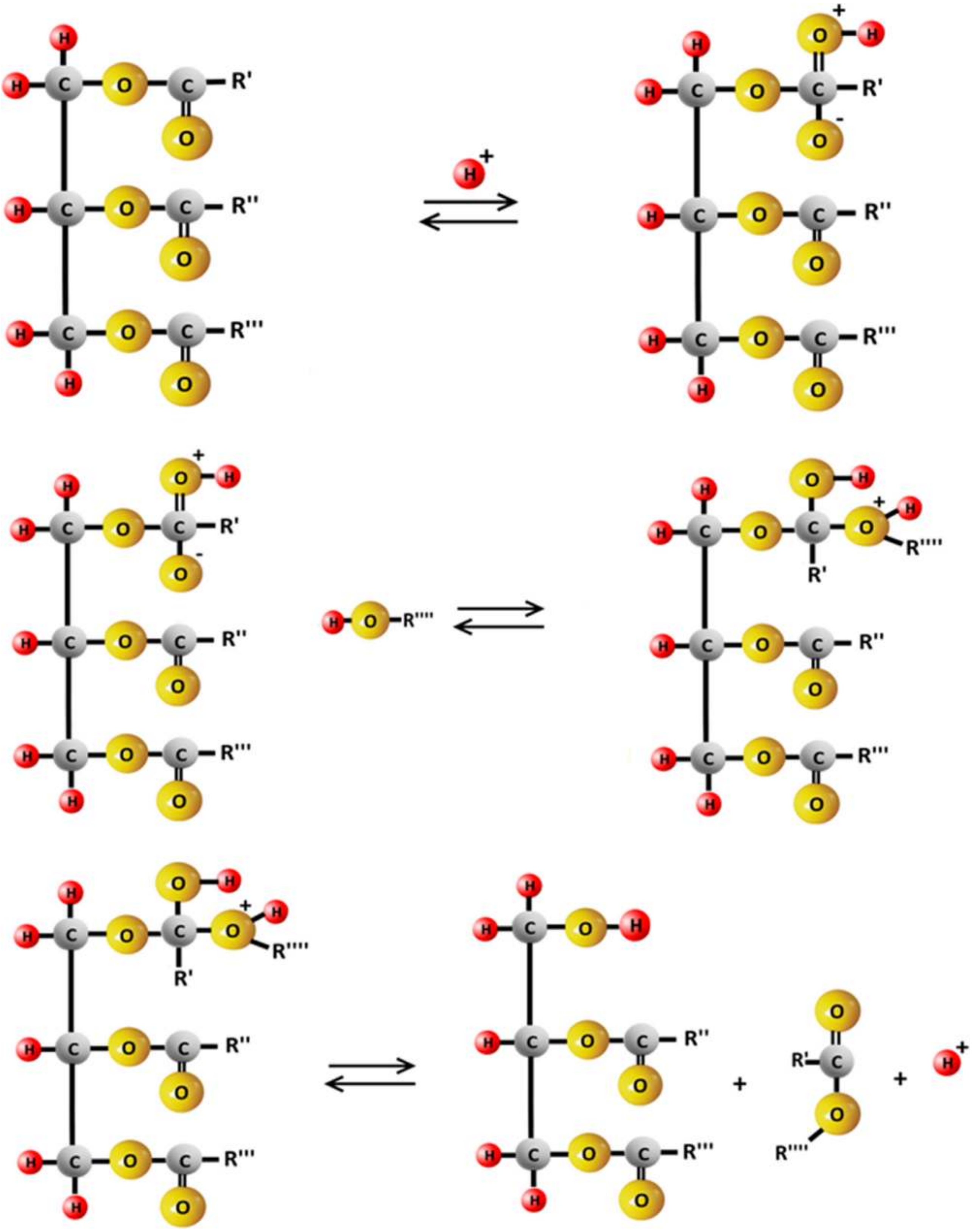

Fig. 2. Schematic steps of acid-catalyzed transesterification.

Table 2
Recent reports (2016 to 2018) on the application of different kinds of homogeneous and heterogeneous catalysts for converting natural oils and fats into biodiesel.

Feedstock	Alcohol	Catalyst	Conditions	Yield	Ref.
Soybean oil	Methanol (1:30)[1]	1 wt.% Cs-Na_2ZrO_3 Basic heterogeneous	65 °C, 15 min	98.8%	[71]
Waste cottonseed oil	Methanol (1:30)	5 wt.% Ti/SiO_2 nanoflowers	65 °C, 204 min	>98%	[72]
Macaw palm oil	Methanol (1:9)	2 wt.% Strontium and Nickel	65 °C, 300 min	97%	[73]
Canola oil	Methanol (1:24)	5 wt.% Li/TiO_2	65 °C, 180 min	98%	[74]
Sunflower oil	Methanol (1:9)	3 wt.% CaO-based/Au nanoparticles	65 °C, 180 min	94–97%	[75]
Soybean oil	Methanol (1:4.6)	15 wt.% CaO-K_2O	70 °C, 240 min	99%	[76]
Cooking oil	Methanol (1:12)	5 wt.% Zinc-doped calcium oxide	65 °C, 132 min	>98%	[77]
palm oil	Methanol (1:9)	5 wt.% Calcium oxide functionalized with strontium	65 °C, 30 min	98.31%	[78]
WCO	Methanol (1:10)	8 wt.% $FeCl_3$ -modified resin	90 °C, 120 min	92%	[69]
Castor oil	Methanol (1:12)	5 wt.% Si-MMT- pH-SO_3H	60 °C, 300 min	89.8%	[79]
Various oils	Methanol (1:12)	2.5 wt.% Sodium silicate	65 °C, 30 min	97%	[80]
Rubber seed oil	Methanol (1:9)	9 wt.% Sodium metasilicate	65 °C, 40 min	97%	[81]
Palm oil	Methanol (1:12)	9 wt.% CaO	60 °C, 120 min	90%	[82]
Scenedesmus obliquus lipid	Methanol (1:12)	15 wt.% Tungstated zirconia	100 °C, 180 min	94.58%	[69]
Canola oil	Methanol (1:7.6)	5.3 wt.% Calcined dolomite	60 °C, 150 min	96.6%	[83]
Castor oil	Methanol (8:1)	11 wt.% Ni doped ZnO nanocatalyst	55 °C, 60 min	95.20%	[84]
WCO	Methanol (1:10)	3 wt.% Magnetic SO_4/Fe-Al-TiO_2 solid acid	90 °C, 150 min	96%	[70]
Waste cotton seed oil	Methanol (1:40)	10 wt.% Mesoporous CeO_2/Li/SBA-15	65 °C, 240 min	>98%	[85]
Palm oil	Methanol (1:8)	5 wt.% 30Ca/APB-700	65 °C, 150 min	93.4%	[86]
WCO	Methanol (1:30)	5 wt.% Tungsten supported TiO_2/SiO_2	65 °C, 240 min	>98%	[72]
Soybean oil	Methanol (1:15)	1 wt.% Calcinated form of waste tucuma peels	80 °C, 240 min	97.3%	[87]
Soybean oil	Methanol (1:36)	8 wt.% Magnetic $LiFe_5O_8$-$LiFeO_2$	65 °C, 120 min	96.5%	[88]
Oleic acid	Methanol (1:9)	0.75 wt.% $SO_4{}^{2-}/La^{3+}/C$	62 °C, 300 min	98.3%	[89]
Soybean oil	Methanol (1:36)	6 wt.% Fe_3O_4@SiO_2@CPTMS@amine	160 °C, 180 min	96%	[90]
Soybean oil	Methanol (1:9)	6 wt.% Calcined marble slurry and hydroxyapatite	65 °C, 180 min	94%	[91]
Date seed oil	Methanol (1:12)	5 wt.% Egg shell derived catalyst	65 °C, 90 min	93.5%	[92]
Waste kernel oil	Methanol (1:15)	3 wt.% Mn@MgO-ZrO_2	90 °C, 240 min	96.4%	[93]

[1] Alcohol-to-oil molar ratio.

Non-edible oils or waste products of agriculture and food industry can be used for biodiesel production which in turn can solve, to some extents, the food *vs.* fuel debate [66–68]. If this is the case, the application of heterogeneous acid catalysts is critical for conversion of these low cost feedstocks. Guldhe et al. [69] tested tungstated zirconia (WO_3/ZrO_2) as a heterogeneous acid catalyst for biodiesel synthesis from microalgal lipids. They compared the tungstated zirconia activity with homogeneous acid catalyst and enzymatic catalysts. Their results demonstrated that 94.6% FAME conversion was achieved with WO_3/ZrO_2 at 100 °C which was comparable with that of the homogeneous catalyst but was superior *vs.* the enzyme catalyst. Recently, a magnetic solid acid nano-catalyst (SO_4/Fe-Al-TiO_2) was synthesized and used for conversion of WCO into biodiesel. The nano-catalyst showed high activities with 96% of FAME yield under experimental conditions with remarkable stability for reutilization over 10 cycles [70]. Table 2 tabulates a summary of the most recent research works conducted (2016–2018) on the application of different kinds of homogeneous and heterogeneous catalysts for converting natural oils and fats into biodiesel.

Table 3 tabulates some heterogeneous catalysts synthesized by different methods for biodiesel production. Moreover, this table summarizes available techniques for recovering and regenerating used catalysts.

2.1.1.3. Enzymatic catalysts. Application of enzymatic catalysts in transesterification reaction provides remarkable advantages over chemical catalysts. Enzymatic catalysts that are immobilized or soluble lipases are ecofriendly materials, which can be used as efficient catalysts to convert low cost feedstock such as non-edible oils into biodiesel in the presence of high amounts of FFA and water. In an enzymatic catalysis, feedstock treatment and catalyst removal are not needed. Moreover, the reaction occurs in mild conditions with low energy consumption, offering a sustainable way for biodiesel production. Lipases used as catalyst are mainly originated from biological sources such as microorganisms, plants, and animals [104,105]. Although the price of enzymatic catalysts are relatively high, their industrial applications have been adapted by some companies around the world such as Hainabaichuan Co. LTD and Lvming Co. LTD (China), Piedmont Biofuel (USA), and Sunho Biodiesel Corporation (Taiwan) [106]. Enzymatic mechanism (Fig. 3) is, however, slightly different as both positive and negative charges are available. Active sites containing acidic or basic characteristics initiate the reaction by donating or accepting protons in a mechanism known as Bi model. Accepting or donating behavior is in relation with the nature of the incorporated enzyme. Whilst enzymes like lipase act as a hydroxyl (OH^-) group acceptor, other enzymes like those bearing amine groups are expected to donate protons. Afterwards, the reaction is completed by the same steps previously discussed in the acidic or basic mechanisms (Fig. 3).

Table 4 tabulates a summary of the most recent research works conducted (2016–2018) on the application of enzymatic catalysts for converting natural oils and fats into biodiesel.

2.1.2. Effect of catalysts concentration on transesterification

Catalyst loading in transesterification reaction is recognized as one of the critical factors to achieve the maximum biodiesel yield. The lowest concentration of catalyst is normally decided in primary steps of process, and then it is gradually raised based on the reaction conditions and products content. Amani et al. [115] showed that FAME content increased to some point with increasing the catalyst loading. In their study, the optimum catalyst loading was characterized as 3 wt.% in which the FAME content stood at 90%. Higher concentrations of catalyst had negative influence on biodiesel production as the FAME content decreased to 83% in the presence of 4 wt.% of catalyst. According to Ezebor et al. [116], increasing catalyst loading leads to product adsorption and finally FAME yield reduction. Chuah et al. [117] examined the impact of basic catalyst loading on biodiesel production from WCO. They tested various NaOH concentrations ranging from 0.5 to 1.25 wt.% while keeping other reaction factors constant. Their results revealed that the conversion of triglyceride to methyl

Table 3
Heterogeneous catalysts synthesis and regeneration methods, and their reuse in conversion of various feedstocks into biodiesel.

Catalyst	Synthesis method	Regeneration	Deactivation and reusability (transesterification yield)	Oil feedstock	Ref.
Freshwater mussel shell	- Calcination-impregnation-at 900 °C for 4 h. - Activation at 600 °C for 3 h	Calcination in air at 600 °C.	90% in 7th cycle 80% in 12th cycle	Tallow	[94]
Ni doped ZnO nanocatalyst	- Co-precipitation method[1] - Calcinated at 800 °C	NA[2]	85% in 5th cycle	Castor	[95]
Layered Double Hydroxides and derived mixed oxide	- Co-precipitation method[3] - Calcinated at 450 °C	NA	NA	Sunflower	[96]
CaO-ZnO catalytic particles	- Catalyst base preparation[4]	Washed with ethyl alcohol and hexane, and calcinated at 300 °C for 3 h	64% in 2nd cycle	Soybean	[97]
$CeSO_4$+$MnSO_4$+K_2CO_3 catalyst	-Calcination method[5] - Co-precipitation[6] - Calcination at 600 °C for 5 h	NA	NA	Soybean	[98]
Eggshell waste-derived CaO catalysts	- Calcination of Dried and crushed eggshell at 800–1000 °C for 2 h	Simple calcination	97–99% in 13th cycle	Soybean	[99]
CaO-SiO_2 (3CaO.SiO_2)	- Mechanochemical method - Calcination at 700 °C for 2 h	NA	Sustained its activity up to 4th cycle	Sunflower	[100]
KOH supported on activated carbon	- Dried and activated carbon (at 110 °C) was added to KOH in water, mixed (30 °C, 160 rpm, 24 h), and dried at 60 °C	NA	80% in 3rd cycle	Corn	[101]
MoO_3	Catalyst synthesis[7] and calcination at 600 (10 °C/min, 4 h)	NA	≥90% in 8th cycle	Various oils	[102]
Acid-activated bentonite	- Acid activation[8]	NA	NA	Residual olive	[57]
SO_3H-functionlized multiwall carbon nanotubes	- Catalyst synthesis[9] - Sulfonation step (98% H_2SO_4, 110 °C, 3 h)	NA	NA	Residual olive	[57]
$LiFe_5O_8$-$LiFeO_2$ catalyst	- Solid state reaction[10] - Calcination at 600–900 °C	NA	>94% in 5th cycle	Soybean	[103]

[1] 1 M aqueous Zinc acetate stirred with 0.1 M Nickel acetate and 8% ammonia solution was added. After 2 h of continuous stirring, the nanocatalyst was precipitated from homogeneous solution by dropwise addition of 0.4 M NaOH, recovered by filtration, and dried (80 °C for 3 h).

[2] Not available.

[3] Two liters (L) of precursor solution containing 0.4 M $MgSO_4$ and 0.15 M $Al_2(SO_4)$ 0.59 Mg-to-Al ratio was added to 0.5 L of distilled water containing Na_2CO_3 as precipitating agent (60 °C, pH 8–10) under continuous stirring. After 20 min, the catalyst was recovered by filtration, repeatedly washed with distilled water (*i.e.*, filtrate pH of 5.5–6), and dried (*i.e.*, 12 h at room temperature, then 70 °C for 1 h).

[4] One gram (g) of ZnO stirred with 50 mL of 2 M $CaCO_3$ aqueous solution for 3 h and dried (120 °C, 24 h).

[5] Catalyst base was heated (4 °C/min) and kept at 100 °C for 75 min, followed by heating (3.5 °C/min) and keeping at 850 °C for 3 h, and cooling down to 20 °C (3 °C/min).

[6] $CeSO_4$,$MnSO_4$, and K_2CO_3 (1:1:1 ratio) dissolved into deionized water and precipitated by slow addition of aqueous solution of KOH into the solution while vigorously stirred at ambient temperature. After 2 h, the solid residue was washed, filtered, and dried at 50 °C.

[7] 10 mL hydrochloric acid (3.0 mol/L, aqueous solution) was dropwise added to 60 mL of aqueous solution of $(NH_4)6Mo_7O_{24}\bullet 4H_2O$ (166.7 g/L deionized water) in Teflon liner and stirred for 10 min. After autoclaving (150 °C, 12 h), yellow residue was repeatedly separated by centrifugation and washed with distilled water (10 mL) and finally dried in an oven (100 °C, 12 h).

[8] 250 mL 5 N H_2SO_4 was slowly added to 50 g bentonite (130 µm particle size) under continuous stirring (95–98 °C, 400 rpm, 2 h). The sample was neutralized by washing with deionized water and dried in an oven (130 °C, 2 h).

[9] Methane (carbon source, 50 mL/min) was decomposed over cobalt-molybdenum nanoparticles supported by nanoporous magnesium oxide (900 °C, 30 min) and the product swept by hydrogen gas (carrier gas, 250 mL/min) hydrogen. The product was purified with i) HCl (18% solution, 25 °C, 16 h), filtered and repeatedly washed with distilled water, then ii) dispersed in nitric acid (6 M solution, 70 °C, 6 h), filtered, dried, and heated (400 °C, 30 min).

[10] Fe_2O_3 and Li_2CO_3 (1:1 ratio) were mixed in water and grounded.

Table 4
Recent reports (2016 to 2018) on the application of enzymatic catalysts for converting natural oils and fats into biodiesel.

Feedstock	Alcohol	Enzyme	Conditions	Yield	Ref.
Castor oil	Methanol (1:6)[1]	5% Liquid lipase Eversa® Transform	35 °C, ≥8 h	94%	[107]
Microalgae oil	Ethanol (1:3)	10% Liquid Lipolase 100L	30 °C	97%	[108]
WCO	Methyl acetate (1:12)	6% Lipozyme TLIM	40 °C, 2 h	90.1%	[109]
Waste oil	Methanol (1:6)	40% Novozyme®435	50 °C, 14 h	72%	[110]
Soybean oil	Methanol (1:6)	ZIF-67	45 °C, 60 h	78%	[111]
Citrullus colocynthis oil	Methanol (1:5)	14% Novozym 435	43 °C, 3.7 h	97.8%	[112]
Rapeseed oil	Methanol (1:6)	20% Lipase immobilized on APTES-Fe_3O_4 magnetic nanoparticles	45 °C, 5 h	89.4%	[113]
Soybean oil	Methanol (1:4.5)	1.45% Callera™ Trans L lipase	35 °C, 24 h	96.9%	[114]

[1] Alcohol-to-oil molar ratio.

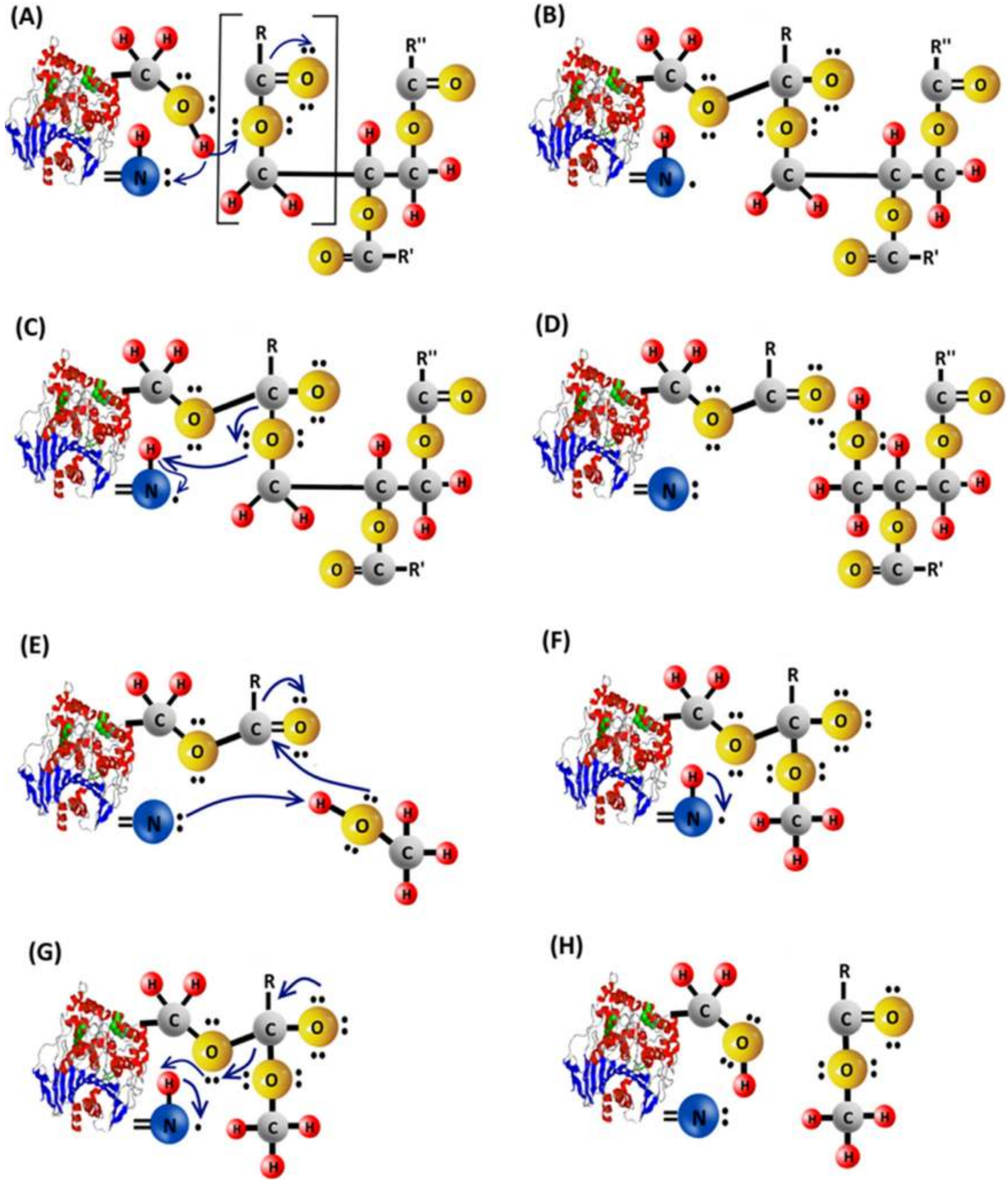

Fig. 3. Schematic steps of enzymatic transesterification.

ester occurred incompletely at catalyst concentrations of less than 1 wt.%, delivering just 63% yield at 0.5 wt.% NaOH. Increasing catalyst loading to 1 wt.% improved triglyceride conversion to 97%. In contrast, more catalyst concentration (1.25 wt.%) decreased the triglyceride conversion to 90%. The main issue about using high concentrations of basic catalysts is the reaction of FFA with catalyst leading to saponification and water generation, both of which finally contribute to reduction of biodiesel yield. It has been also reported that using 3 wt.% of H_2SO_4 resulted in 86.4% biodiesel yield whereas higher concentrations of the catalyst (5 and 7 wt.%) did not have significant effect on FAME yield [118].

2.1.3. *Effect of catalyst shape and size on transesterification*

Catalyst shape and size could influence reaction process as well as functionality of the system. Generally, catalysts with lower particle sizes have higher surface area; and therefore, could increase the transesterification reaction by reducing mass transfer limitations. Rahimzadeh et al. [57] synthesized and compared SO_3H-functionlized multiwall carbon nanotubes with acid activated bentonite and found that the latter had higher biodiesel production yield mainly due to its larger pore volume (0.76 *vs.* 0.25 cm^3/g) and surface area (230 *vs.* 92.37 m^2/g). However, separation of very fine catalysts from reaction medium could be problematic. Moreover, the application of these catalysts could plug packed bed reactors (PBRs) by occupying the spaces between pellets. Alternatively, some shape designs (*e.g.*, solid cylinders, hollow cylinders with axially extruded holes, *etc.*) allow synthesizing larger catalysts with high surface area while at the same time infers higher stability and rigidity. Therefore, it is obvious that the shape and size of catalysts are among the important criteria for determining the right packing particles for the reactor technologies consisting catalyst beds.

2.2. Methanol-to-oil molar ratio

The alcohol content determines biodiesel yield by preventing transesterification reaction from proceeding in reversible direction at the end of reaction. Various alcohols such as methanol, ethanol, tert-butanol, butanol, and isopropanol can be applied for transesterification of oils. Among them, lower alcohols, *i.e.*, methanol and ethanol, are the most common alcohol used in this process. Other alcohols are hardly applied because they are expensive and have no economic justification. Methanol is advantageous over other alcohols, mainly due to its specific chemical and physical characteristics. For instance, it has the capability to react quickly with triglyceride and dissolve very well in NaOH. The content of water in alcohol is also a significant factor in transesterification reaction as excessive water amount can react with triglyceride and causes saponification. Generally, it is supposed that high methanol-to-oil molar ratios facilitates the triglycerides conversion into monoglycerides and accelerates the transesterification process. Stoichiometrically, the alcohol-to-oil molar ratio must be 3:1, however, in a real reaction system a higher molar ratio is needed to raise the miscibility of methanol and triglyceride molecules as well as the possibility of their contact for improving the final product yield. Moreover, high amounts of methanol are required to dissociate the linkage between triglyceride and fatty acid to increase the productivity and complete the reaction in a shorter time. In this regard, the formation of alkyl esters is induced in commercial transesterification processes by surplus amount of dry alcohol, 6:1 $\leq$ alcohol-to-oil molar ratio [119].

Glycerol can be easily separated from reaction slurry by settling or centrifugation since it is essentially insoluble in biodiesel [120]. However, when using high alcohol-to-oil molar ratios, glycerol solubility in biodiesel increases and free glycerol may remain either as suspended droplets or as small dissolved amount in biodiesel [120]. This can be attributed to the fact that alcohols can function as co-solvents increasing the solubility of glycerol in biodiesel. In addition, separation and recycling of the remnant content of methanol at the end of reaction needs high amount of energy. Therefore, an appropriate amount of methanol must be determined to avoid yield loss and uneconomic methanol recycling process. In line with that, Wu et al. [121] probed the NaOH catalyzed-transesterification of soybean oil into biodiesel at methanol-to-oil molar ratios (4.5:1–9:1). The reaction was conducted in a 500 mL 3-neck mechanically-stirred flask reactor equipped with condenser and sampling port. Their findings indicated that a methanol-to-oil molar ratio of 7.5:1 resulted in FAME yield of 97.45% after 60 min residence time. The main reason for using the alcohol-to-oil molar ratio higher than 6:1 in this study was the employment of bentonite as moisture remover, which could adsorb small amounts of methanol as well. In another study, Sanli et al. [122] examined the effect of alcohol-to-oil molar ratio ranging from 3:1 to 20:1 on the transesterification process in the presence of potassium hydroxide, sodium methoxide, and potassium methoxide catalysts. They noted that the highest yield (99.08%) obtained at ethanol-to-oil molar ratio of 8:1 and 1.40 wt.% sodium methoxide after 2 h.

Behzadi and Farid [123] reported that the transesterification reaction is generally controlled by three important stages, *viz.* mass transfer, equilibrium and kinetic of the reaction. Notably, the mass transfer in reaction is the slowest stage among the others because of weak immiscibility of methanol and triglyceride. The kinetic of reaction is controlled through a second order mechanism with alcohol-to-oil molar ratio of 6:1 or follows a pseudo-first order mechanism for high ratios like 30:1.

2.3. Mass-transfer

The efficiency and the rate of the catalytic transesterification are considerably diffusion controlled. The slow reactions in initial and final stages are respectively due to reagents immiscibility and reactant unavailability, *i.e.*, catalyst extraction by glycerol. These phenomena slow down the reaction to the point that is not practical for an economic one-step process [124]. The miscibility can be improved by application of different types of mixers or agitators as well as optimization of mixing intensity, alcohol-to-oil molar ratio, pressure, temperature (heating system), and their combinations thereof.

2.3.1. Mixing system

Awareness about the effect of mixing intensity on the rate of transesterification reaction dates back to early 1980s [119]. In the biodiesel production process, agitation is a vital parameter due to its critical influence on mixing degree (*i.e.*, turbulence) between immiscible alcohol-oil phase, the mass transfer, and reaction rate of alcoholysis. Therefore, in-depth understanding of the impact of mixing on the transesterification process is a crucial parameter in the scaling-up and design of reactors.

Industrial agitators and mixers for biodiesel production process may include: anchor agitators, helix mixers, high-shear mixers, magnetic stirrers, mechanical stirrers, turbines agitator, micro-mixers, motionless or static mixers, two flat-blade paddle agitators, and ultrasonic mixers. Moreover, there are other novel mixing methods such as mixing with the help of the oscillatory frequency in baffled tubes in continuously oscillatory flow reactors. This novel mixing method provides a performance equivalence of 80 ideal continuously stirred tank reactors (CSTR) in series, which is enough to produce biodiesel commercially from rapeseed methyl esters in the presence of 50% excess methanol (0.3–0.5 wt.% NaOH, 60–70 °C, 15–30 min) [125]. Noureddini et al. [126] analyzed the influence of motionless and high shear mixers on continuous biodiesel production individually and in combination with each other. They recorded more than 97% conversion of soybean oil into FAME when at least one of the mixers was present in the process. However, it was emphasized that the motionless mixer was more effective than the high-shear mixer. Sánchez et al. [127] also applied high-shear mixer at 4000 rpm to vigorously increase mass transfer in transesterification reaction. In the presence of 1 wt.% catalyst and methanol-to-oil molar ratio of 6:1, nanodroplets of reagents were formed, and subsequently, converted into biodiesel within 60 s of dispersion at 22 °C. In another study, a mechanical stirrer was applied to synthesize biodiesel with American Society for Testing and Materials (ASTM) D 6751 properties through methanolysis of 50:50 wt.% blend of castor seed oil and waste fish oil (0.5 wt.% KOH, 8:1 methanol-to-oil molar ratio, 32 °C, 600 rpm, 30 min) with yield of 97.7% [128].

Sungwornpatassakul et al. [129] compared static mixer with mechanical stirrer with respect to reaction rate and droplet size. In addition to faster reaction rate, the former also formed droplets that 90% of them had diameter less than 5 µm. Ji et al. [130] developed alkaline-catalyzed transesterification method coupled with ultrasonic mixer (19.7 kHz). Similarly, soy-based biodiesel (94.71% yield) with ASTM D6751 and IS 15607:2005 standards was obtained using the same type of mixer adjusted at 35 kHz (6.15 wt.% KI-impregnated zinc oxide, 10.2:1 methanol-to-oil molar ratio, 62 °C) [131]. Ultrasound mixing system forms cavities in liquid-liquid interface, and subsequently creates micro fine bubbles. Then, micro jets are developed as a result of asymmetrical collision of the bubbles, causing an intensive blending of the liquids [132]. However, appropriate power of ultrasonic mixer must be optimized according to the size and volume of reactor; otherwise, excess mixing power generates heat. This heat introduces bubbles in the reaction system through vaporization of the solvent, which in turn, sequentially reduce solvent content, the interface area, and the yield of biodiesel. Compared with mechanical stirring, hydrodynamic and ultrasonic mixers have lower requirements for catalyst (up to three-time less) and shorter reaction times (10–60 min). Hydrodynamic mixer is even a better mixer than ultrasonic one, allowing better mixing for immiscible liquids as well as easier scale-up process regardless of geometric characteristics of reactor. This technology provides simultaneous injection of all reagent liquids in pre-defined proportions into a vessel through a mixing collector. Therefore, no mixing vessel is required for homogenization and both mixing time as well as energy consumption could be reduced while precision of portioning could be improved.

Joshi et al. [133] compared the contribution of hydrodynamic mixer (high-speed homogenizer, 12,000 rpm) to heterogeneous catalyzed-transesterification reaction of soybean and WCOs with that of the conventional stirring method with respect to reaction time. The former delivered microscale turbulence and fine emulsions, reducing the reaction time from 120–180 min to 30 min with same yields of biodiesels. Kolhe et al. [134] used cooking oil as feedstock and transformed it into biodiesel using hydrodynamic mixer (0.55 wt.% KOH, 4.5:1 methanol-to-oil molar ratio, 20 min). Compared with stirred tank reactor (STR; 88.5% yield, 60 min), over 5% more conversion of the same feedstock was obtained in three-time faster reaction rate. Yadav et al. [135] utilized hydrodynamic mixer for conversion of *Thevetica peruviana* (Yellow Oleander) oil into biodiesel (1 wt.% KOH, 6:1 methanol-in-oil molar ratio, 40–55 °C, 30–45 min) with 97.5% yield. The mixing system included a closed loop fluid circuit supported by a 10 L mixing collector, a 2.2 kW centrifugal pump, control valve, and 5 cm orifice plates containing up to seven holes ranging from 1–4 mm pore diameters.

Mixing performance has inevitable influence on designing reactors, which is crucial for the development of a homogeneous reaction environment. However, excess mixing reduces the economic feasibility of process by increasing equipment and operation complexities, interfering with the proper alcohol-to-oil molar ratio by making alcohol less available due to vaporization and/or bubble formation, and ultimately surging production costs because of higher capital and energy requirement and lower yield of conversion. As an example, power supply requirements for mild, moderate, and intense mixing in continuous reactors are 0.1–0.2 kW/m^3, 0.4–0.6 kW/m^3, and 0.8–2.0 kW/m^3, respectively [136]. The degree of mixing as a result of a moving part is mainly determined by frequency of mixer rotation, and to a lesser extent, by geometry of system, characteristics of mixer (*i.e.*, impeller, direction, *etc.*), and physical properties of fluid (*i.e.*, viscosity, volume, *etc.*). For a system with specific flow characteristics, geometric and power supply, the mixing rate can be determined by applying the interrelation of two dimensionless numbers as described in Eqs. (2) and (3) [136]:

$$N_p = \frac{pg_c}{\rho N^3 D_a^5} \tag{2}$$

$$N_{Re} = \frac{ND_a^2\rho}{\mu} \tag{3}$$

where N_p denotes the power number, N_{Re} the Reynolds number, P the mixer power consumption, g_c the Newton's gravity acceleration, ρ the fluid density, N the impeller speed, μ the fluid dynamic viscosity, and D_a the impeller diameter.

Stamenkovic et al. [137] measured size distribution of droplets during KOH catalyzed-methanolysis of sunflower oil in a stirred reactor (1000 mL, 10 cm diameter) with two-flat-blade paddle of 7.5 cm in diameter. Using microphotographic technique, it was observed that intensifying agitation forms smaller size drops with less size variations (*i.e.*, droplet size distribution). Similarly, Li et al. [138] reported a direct relation between increasing the rotation speed (200–800 rpm) and biodiesel production yield. The stirrer speed considerably controls the mass transfer kinetics with respect to economic transesterification of *J. Curcas* oil [139]. It has been revealed that the influence of stirring rate on the control of biodiesel production is highest during initial stages of reaction, and then its significance drops as the reaction proceeds. Different kinetics models have been presented for quantification of the impact of rotation frequency of mixer on transesterification process [42,46,140–143]. These models have the ability to predict the reaction evolution for only specified mixing scenarios, *i.e.*, single mixing model. This disadvantage was corrected in a methodology proposed by Brásio et al. [144] who further validated their model by applying it to independent sets of experimental data previously provided in some single mixing models.

2.3.2. Temperature (heating system)

Although there is a controversy regarding the role of temperature in transesterification reaction, operational temperature is considered by many as an important factor for proper production of biodiesel. Table 5 presents the contribution of temperature, in combination with alcohol-to-oil molar ratio, to the transesterification reaction rate of different feedstocks.

From Table 5, it can be postulated that at least no economically profitable reaction could be conducted at temperatures below 32 °C. Moreover, the application of temperatures lower than the melting point of oil, for example, 50 °C in the case of palm oil, would not be practical due to elevated viscosity. Generally, higher temperatures shorten the reaction time by facilitating mass transfer. However, beyond certain limits, the increase in temperature either has adverse effects on reactants/reagents (degradation, side-reactions, vaporization) or is not cost-efficient. Therefore, optimizing temperature is necessary for both designing reactors as well as commercial production of biodiesel. It is noteworthy that the temperature near to alcohol boiling point is the optimum temperature for non-enzymatic conventional processes. Beyond this temperature, both mass transfer and yield of transesterification reaction drop due to loss of one of the reagents, *i.e.*, alcohol through vaporization. To address this issue, novel processes have been introduced that use heat in combination with pressure (see Section 2.3.3).

Freedman et al. [119] reported temperature as a significant variable for speeding up the transesterification of various vegetable oils including cottonseed, peanut, soybean, and sunflower. According to their results, the reaction rate was four-time faster when conducted at ≥60 °C rather than 32 °C. Darnoko and Cheryan [44] assessed the influence of temperature (50–65 °C) on the methylation process of palm oil in a batch system (1 wt.% KOH, 6:1 methanol-to-oil molar ratio). They observed that relatively same yield of biodiesel was produced in higher temperatures within shorter time, compared with lower temperature. Thompson and He [153] produced canola-based biodiesel by several connected and continuously fed static mixers as the reactor. They emphasized that at a fixed reaction duration of 30 min, the catalyst concentration below 0.5 wt.% of oil and the temperature of 40 °C were the limiting factors for the progress of transesterification reaction. Aniya et al. [154] studied mass transfer during karanja FAME production. It was observed that both temperature and time govern the overall reaction kinetics in a batch reactor (1 wt.% KOH, 6:1 methanol-to-oil molar ratio, 600 rpm). A 20 °C increment in the reaction temperature from 35 °C to 55 °C improved the volumetric mass transfer coefficient by 6.5 times, reaching 20 L/h. Moreover, the methanolysis reaction was initially irreversible at high temperatures due to a more dominant equilibrium reaction rate.

Some examples of conventional heating systems in biodiesel production reactors are batch bath, heating coils, and jacketed reactors. More recently, infrared heater, microwave irradiations, and radio frequency heater have also been applied as new di-

Table 5
Contribution of temperature to the reaction rate and yield of transesterification of oil with various alcohol-to-oil molar ratios at atmospheric pressure.

Feedstock	Alcohol-to-oil molar ratio	Temperature (°C)	Reaction time	Yield	Ref.
Castor seed oil/waste fish oil	8:1	32 °C	30 min	97.6%	[145]
Jatropha oil	7.5:1	65 °C	60 min	99.8%.	[146]
Linseed oil	6–9:1	40–60 °C	40 min	88–96%	[147]
Linseed	10:1	40 °C	90 min	93.15%	[148]
Jatropha oil	30:1	65 °C	60 min	90.8%	[71]
Palm oil	6:1	55 °C	30 min	98.8%	[43]
Jatropha oil	12:1	90 °C	240 min	97.39%	[149]
WCO	12:1	40 °C	1440 min	90.1%	[109]
Canola oil	9:1	60 °C	90 min	97.4%	[150]
WCO	10:1	50 °C	30 min	88%	[133]
WCO	3.4:1	35 °C	2880 min	91.8%	[151]
WCO	8:1	60 °C	10 min	99%	[132]
Animal fat waste	4:1	50 °C	20 min	96.8%	[152]
Canola oil	7.5:1	60 °C	150 min	99.4%	[83]

electric heating technologies with improved economic feasibilities. Among these novel heating systems, microwave is the most extensively studied method for biodiesel production whereas radio frequency is most economic heating system. In a similar transesterification process, the outcome of microwave-assisted system is advantageous over its thermally heated counterparts in terms of reaction rate and energy consumption. Microwave irradiation improves reaction rate by affecting activation free energy and/or increasing the frequency of molecular vibrations. The latter factor leads to an induced molecular mobility. Commonly, microwave-heating is applied in conjunction with mixing to avoid formation of hot spots. Leadbeater and Stencel [155] applied a 600 W microwave heating system with a 5-L vessel for conversion of 3 kg of an unspecified vegetable oil into biodiesel in the presence of either ethanol or methanol (1 wt.% KOH, 6:1 alcohol-to-oil molar ratio, 50 °C, 1 min). The reaction mixture was continuously stirred with the help of an overhead paddle agitator with an unspecified rate. Azcan and Danisman [156] studied the possibility of applying 67% of exit power generated by a 1200 W microwave heating system for methanolysis of cottonseed oil (1% wt.% KOH/NaOH, 6:1 methanol-to-oil molar ratio, 50 °C, 3–5 min). Interestingly, they observed a positive correlation between biodiesel purity (96.1–99.4%) and reaction temperature (40–60 °C). Compared with conventional heating systems, the microwave-assisted process is up to six-time faster. Surprisingly, a much more reduction in reaction time (360 times) was claimed by Lin and Chen [157] during synthesis of biodiesel by microwave heating assisted methanolysis of pre-esterified jatropha seeds oil (1 wt.% KOH, 6:1 methanol-to-oil molar ratio, 65 °C, 200 rpm, 10 s). Milano et al. [158] stated that under optimize conditions (0.8 wt.% KOH, 59.6 vol.% of methanol:oil, 100 °C, 600 rpm, 7 min), a biodiesel yield of up to 98% could be obtained from alkaline-catalyzed methylation of a blend of *Calophyllum inophyllum* and WCOs (vol. ratio of 3:7) using a 850 W microwave-assisted process. During optimizing reaction time (2–10 min), they noticed that the reaction time was doubled by every 10 °C drops in the process temperature.

Compared with microwave-heating system, radio frequency heater is more efficient in conversion of electricity into electromagnetic power with more penetrative characteristics and more simple configuration. Heat is quickly generated as the result of direct collision of a radio frequency electromagnetic field with an object. Radio frequency heating was efficiently employed by Liu et al. [159] for the esterification of WCO with a high amount of FFA (3 wt.% H_2SO_4, 80 wt.% methanol, 8 min) as well as its subsequent methanolysis (0.9 wt.% NaOH, 14.2:1 methanol-to-oil molar ratio, 5 min), yielding 99% biodiesel. They emphasized that temperature influences the ionic conductivity of reagents, and subsequent radio frequency heating efficiency. Therefore, pre-heating by conventional heaters to increase the process temperature to 35 °C was suggested before application of radio frequency heater. In a separate study, Liu et al. [160] reported a conversion yield of 96.3% during transesterification of beef tallow using a radio frequency heater (0.6 wt.% NaOH, 9:1 methanol-to-beef tallow molar ratio, 5 min). Unfortunately, none of these two studies reported the reaction temperatures and had no control on it as well.

2.3.3. Mass transfer intensification systems

As elaborated earlier, to nullify mass-transfer limitation, either mixing or heating systems must provide significantly high amounts of energy, which is not economically favorable. Moreover, temperatures higher than boiling point of solvents, for example, 65 °C in the case of methanol is not practical at atmospheric pressure. Therefore, these systems (*i.e.*, mixing or heating) are applied together and are supported by a number of other intensification systems, including addition of co-solvents and/or alternative solvent, or phase-transfer catalysts (PTCs) to simultaneously cope with mass transfer limitation in the biodiesel synthesis process as well as to simplify the isolation of catalysts, products, and reagents. For instance, in alkaline-catalyzed methanolysis, mass transfer limitation occurs due to immiscible alcohol and oil phases. This barrier can be overcome through converting the system into single-phase by application of co-solvents, for examples, biodiesel, supercritical carbon dioxide (SCCD), hexane, methyl tert-butyl ether, propane, or tetrahydrofuran. However, the rate of co-solvent-added (single-phase) methanolysis reaction drastically falls due to drop of system polarity caused by catalyst precipitation [124]. To compensate this shift in polarity, alcohol-to-oil molar ratio must be considerably elevated, which makes the process complicated by raising the size of manufacturing plants.

Moreover, it was observed that in an enzyme-catalyzed methanolysis reaction of canola oil, the yield of biodiesel increases with co-solvent concentration to some point due to miscibility improvement, after which they show an inverse relation because of lipase inactivation [161]. Alternatively, phase separation during methanolysis can be prevented through application of supercritical methanol (SCM; 9–43 MPa, 200–350 °C), a popular alternative solvent method. Solvents at their supercritical states have gas-like diffusivity and liquid-like density. Regardless of catalyst application, these properties provide an ideal system for convenient, efficient, and quick production of FAMEs *via* transesterification of oils even in presence of water and FFAs [49]. The energy consumption of the supercritical technique can be reduced through introduction of co-solvents as well. Maçaira et al. [162] combined alternative solvent method with addition of co-solvent technique through application of SCM and SCCD as solvent and co-solvent, respectively. This catalytic process was used on a fixed-bed reactor for continuous production of biodiesel (yield of 88%) at 200 °C with 2 min reaction time. In a similar approach, propane was combined as a co-solvent with SCM to make soy-based biodiesel production process less energy intensive (24:0.01:1 molar ratio of methanol:propane:oil, 12.8 MPa, 280 °C, 10 min) [163].

SCM cannot be applied in enzymatic transesterification process since its high temperature (up to 350 °C) inactivates enzymes. On the contrary, enzymatic transesterification (20-30 wt.% Novozyme 435) could commonly be carried out using normal methanol and SCCD (6:1 methanol-to-oil molar ratio, 20 MPa, 45–50 °C) as acyl acceptor (solvent) and co-solvent, respectively [164]. Compared with catalyzed-SCM transesterification process, catalyst-free SCM transesterification involves a more simple, trouble-free, and ecofriendly purification step. For instance, tobacco-based biodiesel with yields more than 91%, meeting EN14214 standards, was reportedly produced *via* catalyst-free SCM methylation of *Nicotiana tabacum* seed oil (43:1 methanol-to-oil molar ratio, 27 MPa, 303 °C, 90 min) [165]. Aboelazayem et al. [166] converted 91% of WCO into FAME with EN14214 properties by adapting a non-catalytic SCM process (37:1 methanol-to-oil molar ratio, 19.8 MPa, 253.5 °C, 14.8 min). Similarly, a catalyst-free SCM system (5:1 molar ratio, 9 MPa, 270 °C, 20 min) was applied for *in-situ* methylation of wet spent coffee grounds, containing 86.33 wt.% esterifiable lipids [167].

Sakdasri et al. [168] analyzed the commercial feasibility of 40,000 t/year FAMEs production from palm oil in two different SCM systems; *viz.* advanced SCM with low alcohol-to-oil molar ratio of 12:1, and conventional homogeneous alkaline-catalyzed SCM with high alcohol-to-oil molar ratio of 42:1 using Aspen plus® software. Although the advanced SCM required about 1.5-time higher capital investment than the conventional method (4.91 million USD), it was commercially profitable by providing close to 22% greater net present value than manufacturing cost. In contrast, the conventional SCM was found uneconomic due to the requirement for recycling large amounts of methanol.

Alternative solvent technique can also be performed using ionic liquids, *i.e.,* organic salts that melt at or below ambient temperature. These non-volatile, easy-to-produce green solvents could provide flexible hydrophilicity/hydrophobicity through appropriate modifications in their anion or cation moieties. Therefore, these designer solvents are highly appreciated for their contribution in two-phase catalysis *via* simplifying the catalyst/biocatalyst dispersion (mass transfer improvement), recovery, and recycling. Wu et al. [169] applied 1-(4-sulfonic acid) butylpyridinium hydrogen sulfate as ionic liquid for methanolysis of cottonseed oil and achieved 92% yield of conversion. Isahak et al. [170] also used ionic liquid for the synthesis of choline chloride.$ZnCl_5^-$ catalyst for transesterification of palm oil. Yanfei et al. [171] generated soy-based biodiesel with a yield close to 95% in the presence of 4 wt.% $[(CH_3CH_2)_3N(CH_2)_3SO_3H]HSO_4$ ionic liquid of oil (14:1 methanol-to-oil molar ratio, 120 °C, 8.7 h). Additionally, 1-ethyl-3-methylimmidazolium methyl sulfate ionic liquid was coupled with microwave irradiation for *in-situ* methanolysis of wet alga *Nannochloropsis* sp. biomass (4:2:1 v/v/w ratio of methanol:ionic liquid:wet biomass, 25 min), leading to more than 42% yield of biodiesel per dry weight of alga [172]. Recently, Ding et al. [173] intensified the transesterification of palm oil by combining an ionic liquid 4-(3-methyl-1-imidazolio)-1-butanesulfonic acid hydrogen sulfate with microwave-heating system. A yield up to 99% was achieved in the presence of 9.2 wt.% ionic liquid and 11:1 methanol-to-oil molar ratio with 168 W microwave power (equal to 108 °C) for 6.43 h.

During transesterification process, further to the above-stated advantages, ionic liquids can also increase the stability and performance of enzymes against adverse effects of short-chain alcohols and accumulated glycerol, respectively. Many studies have applied different combinations of enzymes and ionic liquids for the production of biodiesel. Among many ionic liquids, 1,3-dialkylimidazolium salts in water soluble form, *i.e.,* 1-butyl-3-methylimidazolium tetrafluoroborate, $[BMIm][BF_4]$; and water insoluble form, *i.e.,* 1-butyl-3-methylimidazolium hexafluorophosphate, $[BMIm][PF_6]$ have been commonly utilized in various studies. $[BMIm][PF_6]$-containing 40% enzyme was used to catalyze methanolysis of waste oil into biodiesel with 72% yield (6:1 methanol-to-oil molar ratio, 50 °C, 14 h) [110]. Up to 99% biodiesel yield was achieved during Novozyme 435 catalyzed-methylation of sunflower oil using $[BMIm][PF_6]$ (2 wt.% lipase, 8:1 methanol-to-oil molar ratio, 1:1 wt. ratio of ionic liquid:oil, 58–60 °C, 10 h). While in both studies, the efforts to obtain high biodiesel yields using another ionic liquid, *i.e.,* $[BMIm][BF_4]$ ended unsatisfactory [110,174].

As mentioned earlier, addition of co-solvents and alternative solvents methods positively influence the mass transfer of transesterification reaction by integrating the phases system into single-phase system. A different principle is also applied in PTCs approach, in which, an appropriate compound speeds up the reaction between two immiscible liquid reagents through promoting the interphase transfer of species [175,176]. The superiority of this technique over conventional methods is aprotic-solvent-free and shorter reaction with easier scale-up process. In alkaline-transesterification of oils, the anion transfer between polar methanol/glycerol and non-polar oil phases, and subsequently mass transfer limitation as well as side reactions can be reduced *via* dissolving organic PTCs in the organic phase, *i.e.,* liquid-liquid PTC (LLPTC) mode [176]. Crown ethers, cryptates, and quaternary ammonium are commonly applied PTCs in chemistry. Despite the great adaptability of LLPTC, its application remained undervalued in biodiesel industry. PTC potential in transesterification process was first noticed during facilitated migration of reactants in the presence of a small amount of soap produced due to saponification phenomenon [177]. Then, Zhang et al. [176] investigated several PTCs containing different anions and cations in methylation of soybean oil. A biodiesel yield of 96.5 wt.% was achieved in the presence of tetrabutylammonium hydroxide or tetrabutylammonium acetate (1:1 KOH-to-PTC molar ratio, 6:0.2:1 methanol:total hydroxide:oil molar ratio, 60 °C, 15 min). The most recent study in this field was conducted by Hailegiorgis et al. [178], in which the reaction rate of *in-situ* transesterification of *J. curcas* L. was improved by the application of cetyltrimethylammonium bromide (CTMAB). They reported CTMAB-to-NaOH molar ratio of 1.5:1, methanol:biomass of 6.8 vol./wt., NaOH:biomass of 1.3 wt.%, 43 °C, and 1.8 h as optimum conditions.

2.4. Residence time

Another parameter that must be optimized for improving biodiesel yield is residence/reaction time, which can be defined as the time that chemical species expend in the reactor till the reaction is completed or stopped. The required residence time is directly dependent on other parameters that enhance the rate of transesterification reaction, such as mixing intensity, residence time distribution (RTD), and temperature. Unlike batch reactors, in which all chemical species have an identical residence time, the continuous (flow) reactors lead to a phenomenon referred to as RTD. RTD is generated due to continuous introduction of feedstock and removal of the products from these reactors. The RTD of the flow within a given geometry can be considered as a probability distribution for the time an element of fluid takes to travel within that geometry [179]. In another word, some chemical species stays less time than other chemicals, and consequently, leave the reactors upon their introduction into reactor through product outlet.

In two main continuous flow reactors, *i.e.,* CSTRs and plug flow reactors (PFRs), the major reasons of RTD are bypassing stream, dead zones, longitudinal mixing induced by vortices and turbulence, and even the failure of mixing system [180]. It is frequently favorable to establish plug flow operation rather than continuous stirred process since it provides very accurate control of the processing history, each element of fluid spends exactly the same time in each condition in the reactor [179]. This reduces by-products as compounds of fluid are not, for instance, subjected to higher temperatures for any longer than required for the conversion. It also greatly decreases the size of reactor. Both undertime and overtime processes lead to uneconomic production of biodiesel due to uncompleted conversion of oil (lower yield) and higher operating costs with lower productivity rate, respectively. Moreover, biodiesel may be evaporated or even degraded during an unacceptable lengthy process under harsh conditions.

In a batch reaction, the reaction time is the time after which the reaction is stopped and mixture is subjected to downstream processing, *i.e.,* separation, feed recycling, neutralization, and washing. In contrast, residence time for a continuous reaction is defined as reactor volume divided by flow rate. Darnoko and Cheryan [44] attained that variations of the plot of residence time in comparison with produced methyl ester from palm oil in a CSTR was so that with increasing the residence time, the methyl ester yield increased logarithmically. In their study, the optimal residence time was 60 min. Other researchers claimed that higher residence time could shift the reaction in the reverse side or biodiesel evaporation, reducing the overall conversion yields [181,182]. Alamu et al. [183] studied 30–120 min reaction time (with 15 min intervals) for alkaline-catalyzed ethanolysis of palm oil while other parameters were kept constant (1 wt.% KOH, 20 wt.% ethanol, 60 °C) and a plateau of yield (96%) was observed after 90 min. Falahati and Tremblay [184] studied the influence of flux and reaction time in the biodiesel synthesis from various feedstocks by means of a membrane reactor. They reported the reaction time as a main influential factor affecting the operating pressure in the reactor. The quantity of unconverted oil in the reactor increased at very low residence time, enhancing the pressure inside the reactor. In another study, Azam et al. [185] investigated the influences of catalyst loading and reaction time on biodiesel synthesis from palm oil *via* micro-tube reactors. The results showed that oil transformation and FAME yield were proportional to the catalyst loading and reaction time. This finding could be explained by the complete methylation process of oil in response to longer reaction times and efficient mixing in micro-tube reactor. Similar results have been previously observed by Ab Rashid et al. [186] and Rahimi et al. [187] who studied FAME synthesis from palm oil and soybean oil in a milli- and micro-channel reactors, respectively.

2.5. Composition of oil

The FFA content of feedstock, its composition, and water concentration are critical factors markedly affecting biodiesel yield and quality. These compounds have detrimental effects on yield during biodiesel production process, but the extent of their effects depends on production techniques. Generally, higher concentrations of alkaline catalyst would be required in the reaction in order to neutralize high FFA contents (>1%) or decreased yield should be expected. Increasing the FFA content from 0% to 4% resulted in 2.2% drops in biodiesel yield obtained from WCO [188]. The concentration of each fatty acid in oil feedstock determines the properties and quality of the triglyceride and the resultant biodiesel. The physical properties of triglycerides and fatty acids are determined by length of chain and quantity of double bonds [189,190]. It should be pointed out that the fatty acid compositions of oils are immune against transesterification reaction, and hence, their unchanged natures influence some fuel characteristics of biodiesel. As an example, high amount of saturated fatty esters in beef tallow oil resulted in a biodiesel with higher cloud point than that of soy-based biodiesel [191]. The effect of fatty acid composition on cloud point, cold flow, density, oxidation stability, pour point, and cetane number of produced biodiesel has also been highlighted in other studies [190,192–194]. Generally, cetane number, cold filter plugging point, iodine index, oxidation stability index, and cold flow characteristics improve as the degree of saturation of fatty acid in oil increases. The FFA content can be decreased to the appropriate amount for transesterification reaction through acid esterification process. Pinzi et al. [195] optimized the transesterification of several vegetable oils with different fatty-acids compositions (iodine values) and FFA contents. They analyzed the influence of fatty acid composition on the production of methyl ester through comparison of the obtained optima. Accordingly, it was concluded that the chain length of fatty acids influences biodiesel yield by controlling reaction time, with longer chains slowing the process by two times than shorter chains.

Similarly, higher iodine index of vegetable oils requires higher concentration of catalyst whereas lower amount of catalyst would be required for optimum biodiesel yield from vegetable oils with lower iodine index. Moreover, higher amounts of saturated fatty acids were prone to soap generation in the presence of excess catalyst. During conventional transesterification of oil, this negative side-product (soap) appears in larger quantities in presence of water. The other negative effect of presence of water is its contribution to the introduction of a mass of small bubbles in alcohol-oil mixture in combination with agitation, decreasing the mass transfer. In addition to lower yield, the operating cost would also be increased due to problematic separation of glycerol from biodiesel in the presence of soap. In contrast to conventional transesterification reaction, water content would have no significant effect on conversion yield during biodiesel production by SCM technique and even the yield was reportedly improved with the existence of water at certain concentrations [196,197].

Kwiecien et al. [198] examined the effect of acidity on the alkaline-catalyzed methylation process by adding various amounts of oleic acid, one of the most abundant fatty acid in vegetable oils (up to 80 wt.%), to artificially increase the acid number from about 0.9 to 12.3 mg KOH/g of oil. In each experiment, they calculated the necessary dose of KOH with respect to acid numbers to keep the concentration of catalyst constant. Under similar reaction conditions, the higher acid number of oil deteriorated biodiesel production due to both saponification as well as dissolution of biodiesel into glycerol phase. It also required higher alkaline catalyst and longer separation time, both of which are directly correlated with economic aspects of biodiesel synthesis [198].

3. Reactor technologies

3.1. Biodiesel production process modes

There are four main steps in a typical biodiesel production plant *via* oil alcoholysis with an additional step for treatment of glycerol. In the first step, reagents and reactants are added depending on the process mode into the reactor where the transesterification of oil takes place under controlled reaction conditions. Upon completion of the process, the resultant slurry is allowed to stand in a settling vessel (decanter) or subjected to centrifugation for inducing phase separation in the second step. In addition, other methods of separation such as filtration and sedimentation can be used [199,200]. In the third step, biodiesel and unreacted alcohol are sent to an evaporator or a flash unit to separate alcohol from

Table 6
Comparison of batch, semi-batch, and continuous process modes.

Parameter	Batch	Semi-batch	Continuous
Space requirement	High	Medium	Low
Capital requirement	High	Medium	Low
Operating cost	High	Medium	Low
Product quality	Batch-to-batch variation	Uniform	Uniform
Running time	Until chemical equilibrium	Until chemical equilibrium	Until catalyst inactivation or process maintenance
Production rate	Low	High	Highest
Reactor application	Low selectivity Higher versatility Good flexibility Simple scale-up Inferior heat transfer Suitable for slow reaction	High selectivity Lower versatility Good flexibility Complex scale-up Superior heat transfer Suitable for faster reaction	High selectivity Lower versatility Good flexibility Complex scale-up Superior heat transfer Suitable for quick reaction

biodiesel. Fourth step involves neutralization and purification of biodiesel from other undesired compounds such as catalyst, soap, and unreacted triglyceride by using wet or dry washing methods. In wet washing which is both water- (2–120 L of wastewater/100 L of biodiesel) and energy-intensive, the product is neutralized by acids followed by treatment with water. Treatment of generated wastewater and drying the final product are also costly processes. Dry washing is considered as a more environmental compatible approach compared with wet washing but because of using absorbents and additional equipment, it may not be economical under certain industrial circumstances [201]. Alternatively, the crude biodiesel may be purified using membrane filtration which has been discussed in detail in Section 4.3.1. In a subsidiary step, the generated glycerol is neutralized, washed using soft water, and directed towards the glycerol refining section. For feedstocks with high amounts of FFA, the system should be slightly modified with the incorporation of an acid esterification unit and storage tank for the acid catalyst [202]. Batch, semi-batch/semi-continuous, or continuous process modes are available depending on how these steps are conducted, each of them having specific cons and pros (Table 6).

The most commonly used method for commercial production of biodiesel is batch-mode process [136]. In a typical batch process, there are no streams flowing into and out of the reactor during the process, and therefore, a finite amount of product is synthesized in a specific period of time. At the end of batch-mode reactor, the entire slurry is sent to separation and purification sections. Semi-batch process mode is a variation of batch-mode process with a higher selectivity and better control on reaction temperature, in which as the reaction proceeds, one reagent or product may be intermittently or continuously added to or removed from the reactor, respectively. Moreover, large methanol-to-oil ratios can be maintained by gradual or intermittent introduction of one reagent, *i.e.*, oil to improve the reaction rate and process yield. The reaction equilibrium can be broken in favor of biodiesel production through removal of product as well. Similar to the batch-mode process, the production rate in semi-batch process is limited while operating cost is relatively high. However, like continuous process, the scale-up and design is more complex than the batch mode.

In contrast to the batch-mode process, feeds are continuously introduced into the flow/continuous-mode reactor while product stream leaving the system. In should be noted that biodiesel industry is shifting toward continuous process mode in order to address disadvantages of batch process operation [203–205]. Despite of this tendency, batch processes still contribute to major portion of the biodiesel production plants worldwide as it is the process of choice in small and medium scale biodiesel synthesis plants. It is worthy of mention that continuous processes offer lower operating costs whereas delivering higher quality and uniform products [128].

3.2. Types of chemical reactors for biodiesel production

Several types of reactors are available for biodiesel production through transesterification of oils, each of which allows different operating conditions with respect to chemical nature of reactants, reagents, and products as well as physical parameters of operation. These factors, together with the optimum pressure and temperature of reaction and production size (reaction mode), define the choice of reactor. In general, any reactor types should provide appropriate residence time, heat exchange, and mass transfer for efficient product formation. Reactors are classified based on phase numbers, existence of mixing systems, and process modes. Flow chart of various chemical reactors for biodiesel production is shown in Fig. 4.

Table 7 summarizes the operating conditions under which several types of reactors have been proven to perform desirably. The feasibility of these reactors for application in biodiesel industry is also highlighted. Although batch STR and CSTR have been reported to be of low efficiency and difficult to control, they are extensively applied at industrial scale due to their simplicity and low cost nature.

3.2.1. Tubular/plug-flow reactors

The simplest chemical reactor is tubular, also known as pipe or PFR, in which reactants and reagents are entered in one end, spent specific time for passing through pipes at a constant velocity, and mixed while flowing towards the outlet. This mixing can be performed successfully by passing highly turbulent flow through empty pipes and piping fittings (such as elbows). The length of mixing device as well as its time is significantly reduced by adjusting pressure. However, more laminar flow operating conditions are resulted in tubular reactors when fluid viscosity increases. To avoid this, and also to further improve the reaction time and size of reactor, side stream additive injection devices (impinging jet mixer, spray nozzle, Tee mixer), in-line mechanical mixer, or static mixer can be applied. Static/motionless mixers take advantage of stream energy to impose efficient radial mixing of two or more immiscible liquids when these fluids pass through it (Fig. 5) [216,217].

In the simplest configuration (Fig. 5A), static mixing can be obtained through tubular reactor with horizontal back-and-forth and vertical upflow-and-downflow configurations. Other configurations (Fig. 5B–F) includes installation of static mixing element inside a tubular channel or a pipe, whose suitability depends on Bodenstein number, type of reaction, diameter of reactor, reaction tem-

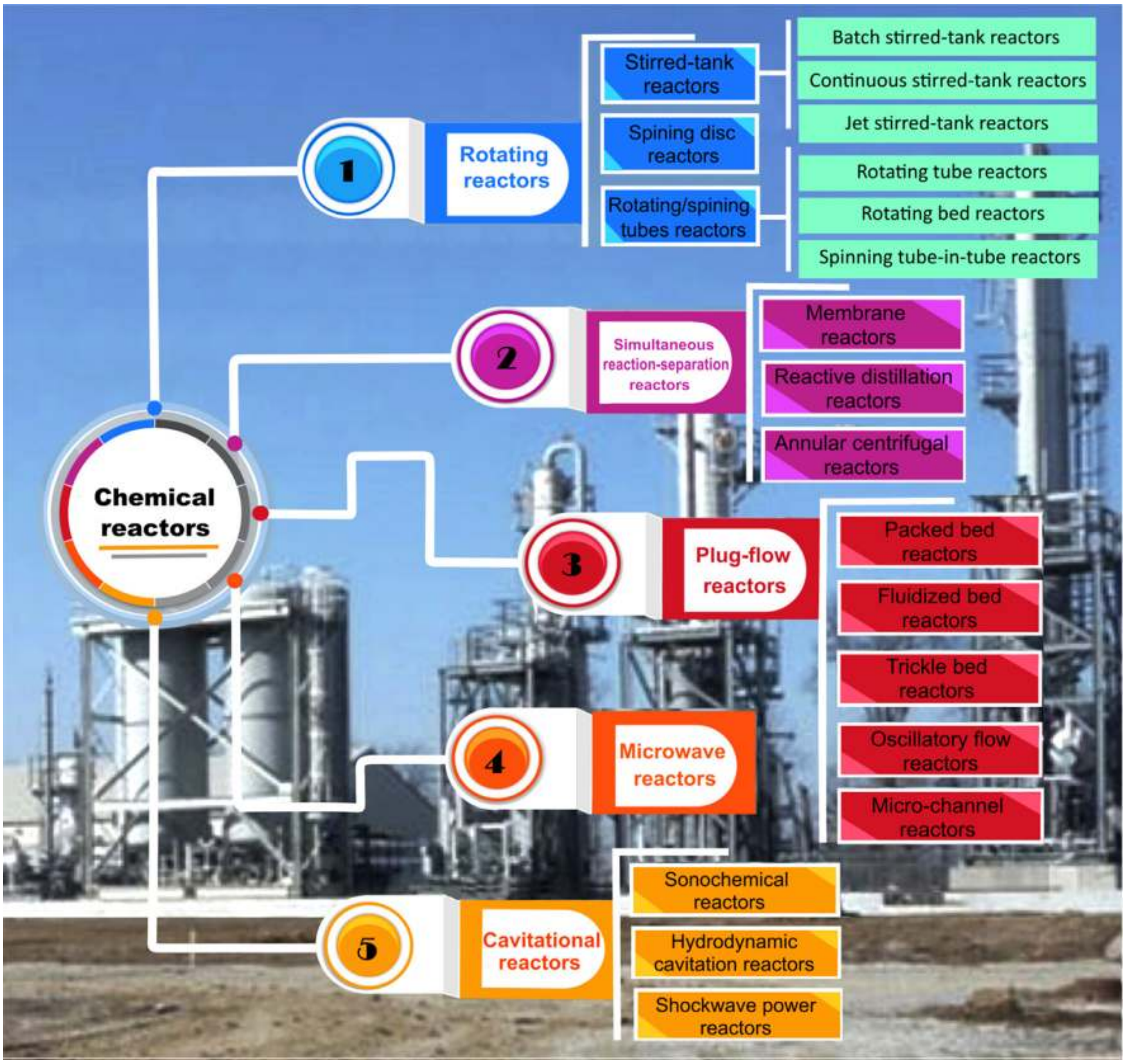

Fig. 4. Diagram of various chemical reactors for biodiesel production. Background image: courtesy of Bright Path Group, Inc. and Tribologiks, LLC.

Table 7
Characteristics of different types of reactors for the production of biodiesel.

Type of reactor	Residence time	Mass transfer	Temperature control	Current status	Ref.
Batch stirred tank reactor (BSTR)	1–2 h	Medium	Difficult	Industrial scale	[126]
CSTR	≥60 min	Good	Easy	Industrial scale	[204,206]
Jet-stirred reactor (JSR)	~38 min	Good	Difficult	Pilot scale	[207]
PFR	19 min	Good	Difficult	Pilot scale	[208]
Oscillatory baffled reactor (OBR)	30 min	Excellent	Easy	Pilot scale	[209]
Spinning tube-in-tube (STT)	<1 min	Excellent	Easy	Industrial scale	[209]
Membrane reactor	1–3 h	Low	Easy	Pilot scale	[209]
Reactive distillation reactor	Several minutes	Excellent	Easy	Pilot scale	[209]
Annular centrifugal contactor (ACC)	~1 min	Excellent	Easy	Industrial scale	[209]
PBR	2.8 h	Low-Good	Difficult	Pilot scale	[208,210,211]
Fluidized bed reactor (FBR)	–	Good	Easy	Pilot scale	[212]
Ultrasonic reactor	10–40 min	Good	Easy	Industrial scale	[19,177,213]
Hydrodynamic cavitation reactor	~30 min	Good	Easy	Industrial scale	[130]
Shockwave power reactor	–	Excellent	Easy	Industrial scale	–
Static mixer	30 min	Good	Easy	Lab scale	[153]
Micro-channel reactor	28 s–several minutes	Excellent	Easy	Lab scale	[209]
Microwave reactor	<10 min	Good	Easy	Lab scale	[156,214,215]

perature, Reynolds number, and viscosity of fluids. These configurations are suitable for both low and high viscosity fluids and the subsequent increase in polar-apolar interfacial area, particularly through local micromixing, significantly facilitates the transesterification of oils. Compared with a tank or vessel reactors, pipe reactors with/without static mixing internals provide more efficient and economic place for blending when quick mixing, short hold-ups, and low maintenance are desirable.

Tubular reactors require lower capital as well as space for construction. However, these reactors have a limitation for Reynolds

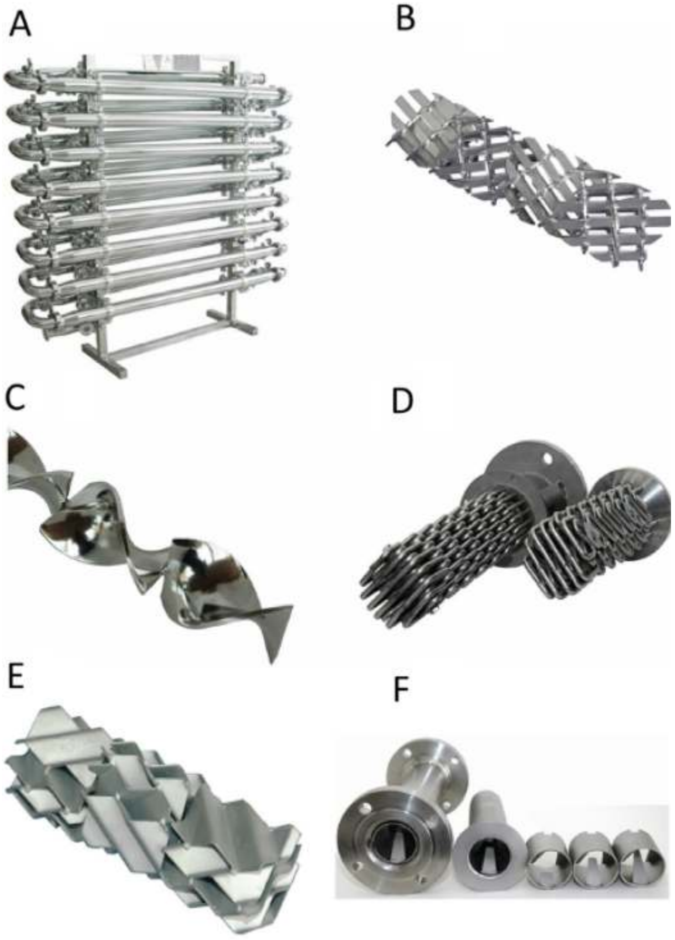

Fig. 5. Different configurations of static mixing elements which could be used in tubular reactors, A) Skit-mounted configuration, B) Grid static mixer, C) Helical static mixer, D) Cross tube type static mixer, E) Corrugated plate static mixer, and F) Lift tab static mixer. Courtesy of StaMixCo-USA/Switzerland http://www.stamixco-usa.com/.

numbers, which is necessary for appropriate generation of high velocity and suitable turbulence. Therefore, the ratio of length to diameter (L/D) should be greater than 20 and 200 for turbulent and laminar flows, respectively [218]. It should be noted that the RTD narrows as the ratio of L/D grows [218]. Narrow RTDs as well as large ratios of pipe wall to pipe volume lead to efficient heat transfer. Moreover, these reactors experience significant temperature changes at different points between inlet and outlet. To address this phenomenon, appropriate heating systems such as heating jacket or radiation heating exchange must be used during their application in the transesterification process. Similar to temperature, pressure drop is also observed at different points inside tubular reactors, which is correlated with viscosity of fluid, length of pipe, and the presence of internals. The drop in pressure reduces both mass and heat transfers.

Overall, tubular reactors can best be exploited under high pressures and continuous mode with steady-state condition of reagents injection rates and concentration of small size solid particles (catalysts, immobilized enzymes, *etc.*). The products are separated from discharged feed, and then methanol and untreated oils are recycled to the feedstock storage. The advantages and disadvantages of various types of PFRs are presented in Table 8 whereas Table 9 provides some examples of these reactors for biodiesel production *via* transesterification of oil.

3.2.1.1. Packed bed reactors. PBRs are popular reactors for the production of biodiesel by heterogonous catalysts (including basic, acidic, ion exchange resins, and superacids active catalysts) with the ability to switch into supercritical mode. Packed bed can provide a great substrate for enzyme immobilization in the transesterification process as well. Some support particles such as magnetic magnetite nanoparticle, poly(stearyl methacrylate-*co*-ethylene dimethacrylate) monolith grafted with vinylazlactone, or polyurethane foam have been successfully utilized in lipase-catalyzed PBRs [234–236]. PBR is in fact a PFR filled by roughly equal size of solid packing materials (such as catalysts, activated carbon, *etc.*). The catalyst size distribution and bed structure determine the accessible surface area, void spaces, and therefore, transport and performance of the system. As PBRs consist of fixed or immobilized bed of catalyst, they are also called fixed bed reactors.

The packing process in these reactors is controlled by (i) physical characteristics of container (pipe) and particle (catalyst), such as shape, size, and surface properties; (ii) the intensity, method, and speed of deposition; and (iii) treatment approach [237]. Undesirable flow distribution and pressure variations must be minimized by avoiding particles charging, segregation, and their irregular distribution during bed generation. Moreover, bed shrinkage phenomenon as well as packing reproducibility must be improved by applying appropriate procedures such as snow storm filling method. During loading, the free fall distance should be <50 cm to avoid significant damage to catalysts. Compared with PFRs, PBRs allow higher conversions of oils per unit mass of solid catalysts in shorter reaction time because the liquid flow is close to ideal plug flow [238]. A very high operation pressure can be applied in PBRs with high ratios of L/D because of absence of mixing system. Another advantage of PBRs is that the catalysts are fixed in the pipes (reactors), and hence, no downstream process would be required for their separation.

In spite of the advantages mentioned, PBRs are suffering from several pressure drops during operation attributed to a number of factors namely, friction of fluid around as well as its expansion and contraction through spaces among packing particles, length of reactor, and fluid viscosity. These pressure drops would increase the operation cost as higher energy in form of pressure would be required. On the other hand, increasing pressure could break the catalysts into small fragments. These minute particles could plug the spaces between pellets, and in turn, lead to pressure drop again. Therefore, based on intended process, catalysts with resistant shape configuration and higher surface area must be applied in PBRs. For instance, solid cylinders are pressure-resistant while providing 14.5% $<$ higher surface area as well as 25% less voidage values than spheres of same volume [237]. Raschig rings (hollow cylinders) are even better than solid cylinder owing to their positive influence on system pressure and providing extra surface area (20–30%) [237,239,240]. Nevertheless, the number and size of axially extruded holes must be optimized for better performance of hollow cylinders.

The RTD in PBRs narrows with increasing the ratio of bed depth to the diameter of particle (L/d_p), and is almost negligible at the ratio greater than 40 [238]. The application of larger catalyst size as well as lower liquid-solid mass transfer coefficients reduces the efficiency of PBRs [238]. In PBRs, a feed pipe and a distribution hood are applied prior to the flow of feedstock into the tube bundle or fixed bed in order to prevent flow bypasses. In better words, when there is no formation of flow bypasses, there is a significantly greater pressure loss in the entrance hood than in the tube bundle or fixed bed leading to uniform traverse of liquid with equal residence time in each tube [239]. Although PBRs are considered as continuous operation, however, since recycling of the ingredients might be necessary in most cases, therefore, by nature they

Table 8
Advantages and disadvantages of various types of PFRs.

Type of reactor	Advantages	Disadvantages
Oscillatory Flow Reactors	- Very low methanol-to-oil ratio, even lower than the stoichiometric ratio of 3:1 - Low capital and operating costs - High biodiesel yield - Long reactions in a significantly low length-to-diameter ratio - Continuous or batch mode - High mixing intensity - High heat and mass transfers	- Complicated design and operation in continuous mode - Still immature for industrial application
Fluidized Bed Reactors	- Uniform temperature distribution - High mixing intensity - Continuous or batch process mode - High heat and mass transfer - Convenient replacement or regeneration of catalyst - Lower possibility for membrane plugging	- High capital and operating costs - Requirement for expensive regeneration equipment - High catalyst attrition and reactor wall erosion - Only freely flow catalysts can be applied - Large pressure drop
Fixed Bed Reactors	- Compatible with very high pressure and temperature conditions - Higher conversion of oils per unit mass of solid catalysts - Simple and cost-efficient process - High yield - Semi-continuous or batch mode	- Difficult replacement of catalyst - Error-prone bed generation process (channeling, uneven flow distribution, pressure variation) - Lower heat transfer and more difficult control of temperature - Higher potential of side reactions
Plug-Flow/Tubular Reactors	- The simplest chemical reactor - Compatible with side-stream additive injection devices and other mixers to improve mixing - More efficient and economic than tank-reactors - Low maintenance - Low capital and construction space - Uniform product quality - Easy to clean - Efficient use of reactor volume	- Requirement for a large length-to-diameter ratio - Operative at stationary conditions - Inappropriate for slow reaction, *i.e.,* requiring slow mixing and/or large hold-ups
Trickle Bed Reactors	- Continuous separation of products - No need for separation of heterogeneous catalyst - Simple operation under high pressures and temperatures - Lower catalyst attrition	- Lower control on reactor parameters - Prone to channeling and flooding - Difficult to scale-up

have to be performed under batch mode [241]. For isothermal process (such as transesterification of oils), PBRs are commonly used in multi-tubular arrangements, in which heat carrier, *i.e.,* liquid (water, molten salt) or gas externally circulates around the tubes containing the catalyst and through an external heat exchanger [234–236,239].

3.2.1.2. Fluidized bed reactors. Liquid-solid FBRs, also known as expanded bed reactors, are used for transesterification reaction. These reactors consist of a reservoir for preparing the liquid feedstock, prior to being pumped into the FBR column. The column consists of a calming section for equalizing liquid flow, followed by a distributor, a fluidized bed (*i.e.,* catalyst bed), and freeboard. The length of calming section is up to several times of fluidized column, filled with immobilized packings (rings, saddles, spheres) or even fluidized bed packing (catalyst, immobilized enzyme), and has a wire screen at the bottom [242]. Distributor must generate a sufficiently large frictional pressure drop across itself, compared with the one occurring across the fluidized bed. Above the distributor, a laterally-directed uniform distribution of longitudinal liquid velocity must be formed. Multi-layer metal gauze or sintered metal glass plate are two examples of good liquid distributors [242]. Calming section and distributor reduce or eliminate channeling or bulk circulation in catalyst bed.

FBRs are similar to PBRs in many ways; however, their main difference is that solid particles in the reaction vessel of FBR are suspended by the upward-flowing drag of incoming gas or liquid [242]. In this case, solid particles inside the bed show a liquid-like behavior, allowing even fluid distribution, uniform temperature, and vigorous mixing with higher heat and mass transfers than in PBRs. Moreover, plugging is less likely to happen because foreign objects can be separated based on their density differences from packing particles, *i.e.,* heavier objects sink whereas lighter ones float [241]. For selection of proper packing particles, in addition to intrinsic static characteristics (density, shape, size), dynamic behavior of particles with respect to flow of fluid (buoyancy factor, drag coefficient, terminal velocity) must also be considered [242]. At low fluid velocities, the particles in the vessel remain still as the fluid passes within the voids in the material, similar to the PBRs. As the fluid velocity increases and at a specific velocity, drag forces will dominate the weight force so that the particles are capable of initial upward movement. This stage can be considered as incipient fluidization and takes places at this minimum fluidization velocity [243]. Once this minimum velocity is surpassed, particles begin to expand and swirl around in fluidized bed [244]. Next to fluidized bed is a freeboard that prevents the flowing of catalysts out of the column. Based on the operating conditions and characteristics of solid phase, different flow regimes such as inverse fluidization, upward fluidization, or vertical moving fluidized systems (continuous fluidization) can be used. Internal or external liquid-fluidized bed heat exchangers arranged either vertically or horizontally may be used to control reaction temperature. Alternatively, a pre-heating line can be used for this purpose. Compared with PBRs, intense mixing in FBRs could cause high attrition of catalysts due to particle-fluid, particle-particle, and particle-wall contacts forming solid fines. The elutriation and entrainment of these solid fines could lead to significant operational challenges [242].

3.2.1.3. Trickle bed reactor. TBRs provide a structure for contact of solid, liquid, and gas based on gravity or pressure forces. Liquid feed is supplied at the top of the column which flows downward over a solid catalyst bed forming droplets or fine films. The process may be in either continuous or semi-continuous modes with

Table 9

Examples of biodiesel production processes *via* transesterification of oil using different variations of PFR.

Type of reactor	Feedstock	Alcohol	Packing particle	Conditions	Yield	Highlights	Ref.
Oscillatory flow reactors (OFR), Continuous/ batch	Rapeseed oil	Methanol (1:12)[1]	1.5 wt.% KOH	60 °C, 2 min	>95%	Significantly enhanced the reaction rate and improved the water tolerance (1 wt.% water). Continuous mode produced higher yield of FAME.	[219]
OFR, Batch	Neem oil	Methanol (1:9)	1% H_2SO_4	25–30 °C, 10–15 min	NP	–	[220]
OFR, Batch	WCO	Methanol (1:6)	1 wt.% KOH	60 °C, 5 min, 4.1 Hz oscillatory frequency	82%	Yield was only dependent on temperature, oscillatory Reynolds number, and Strouhal number.	[221]
OFR, Batch	WCO	Methanol (1:6)	1 wt.% NaOH	60 °C, 30 min, 0.67 Hz oscillation frequency	72%	A 14% higher biodiesel yield in two-time faster reaction process in OFR was attained compared with STR under similar process condition.	[222]
Capillary FBR	Canola oil	Methanol (1:6)	0.5 g hydrotalcite	300 °C, >0.3 s, 0.15 mL/min oil feed rate	63%	Cold methanol and oil were atomized through a sparger.	[223]
						Argon was used as supplementary fluidizing gas.	
Magnetically FBR, Batch	WCO	Methanol (1:3.7)	10.2% Magnetic microspheres cells of *Pseudomonas mendocina*,	35 °C, 48 h, 136.6 Oe magnetic field intensity, 17 mL/min reactant flow rate	87%	Periodic injections of oxygen gas (after up to 20 min) were done for regeneration of catalyst. The biocatalyst was recyclable (10 times).	[151]
FBR, Continuous	Babassu oil	Ethanol (1:12)	12% Novozym® 435	50 °C, 8 h space-time	98%	Simultaneous glycerol removal *via* Lewatit® GF202 column was conducted.	[224]
Two-stage PBR, Continuous	Coconut/macaw oils	Ethanol (1:12)	Immobilized *Burkholderia cepacia* lipase on SiO2–PVA	50 °C, 14 h space-time	96–97%	Resin was regenerated by methanol. A simultaneous glycerol-removing column, Lewatit® GF 202 was annexed to the reactor.	[225, 226]
PBR, Continuous	Linseed oil	Diethyl ether and methanol (1:9.5:11.3)	160 g CaO	30 °C, 1.37 mL/min flow rate	98%	The half-life time of the immobilized lipase was 1512–1540 h due to removing glycerol. PBR was combined with co-solvent technique (Diethyl ether).	[227]
PBR, Continuous	Soybean oil	Methanol (1:42)	Dixon rings	22 MPa, 350 °C, 0.12 and 0.067 mL/min oil and methanol flow rates	91%	PBR was combined with alternative solvent additive technique, *i.e.*, supercritical methanol. A 27% higher biodiesel yield was obtained contain with basic PFR, *i.e.*, no packing material.	[228]
PFR, Continuous	Soybean oil	Ethanol (1:40)	No catalyst	20 MPa, 350 °C, 15 min	80%	–	[229]

(*continued on next page*)

Table 9 (*continued*)

Type of reactor	Feedstock	Alcohol	Packing particle	Conditions	Yield	Highlights	Ref.
PFR, Batch	Canola oil	Ethanol (1:40)	No catalyst	20 MPa, 350 °C, 30 min	98%	Biodiesel production under supercritical condition was carried out.	[230]
PFR, Continuous	Palm oil	Methanol (1:5 v/v)	4–12 g/L KOH	60 °C, 20 L/h oil flow rate, ultrasound clamps (16 × 400 W, 20 kHz frequency)	ND	Thermal energy was efficiently recovered because of spiral configuration of reactor. Integration of ultrasound clamp as a mixing device improved the process efficiency of short length PFR.	[231]
PFR, Continuous	Canola oil	Methanol (<1:5 v/v)	1.5 wt.% CH_3NaO	60 °C, 30 min, 1.1 L/min flow rate	ND	Integration of 34 fixed left- and right-hand helical static mixers to the reactor was performed.	[153]
PFR, Batch	Corn oil	Methanol (1:4.3)	1.8 wt.% KOH	26–30 °C, 30 min, 7.2 L/min flow rate	98%	The reactor dimensions were $L = 300$ mm and ID=4.9 mm. Integration of 20 helical static mixers ($L = 12$ mm and $D_{in} = 8$ mm) to the reactor was done.	[129]
PFR, Continuous	Soybean oil	Methanol (1:6)	1–2 wt.% KOH	60 °C, <1 min, 1.4–8.3 mL/min flow rate	75–98%	The reactor dimensions were $L = 260$ mm and ID=8 mm. Various static mixer elements were attached to the reactor.	[217]
Trickle bed reactor (TBR), Continuous	Sunflower oil	Methanol	CaO packed bed (1–2 diameter and 125 mm thickness)	100 °C, 3.8 and 4.1 mL/h methanol and oil flow rates	98%	The reactor dimensions were $L = 200$ mm and ID=10 mm. Easy and continuous separation of products was achieved.	[232]
TBR, Continuous	Rapeseed oil	Methanol	Ca/Al composite oxide-based catalyst (Bed volume of 91 mL)	65 °C, 0.3 and 0.6 mL/min methanol and oil flow rates	94%	Easy and continuous separation of products was obtained.	[233]

[1] Alcohol-to-oil molar ratio, unless specified otherwise.

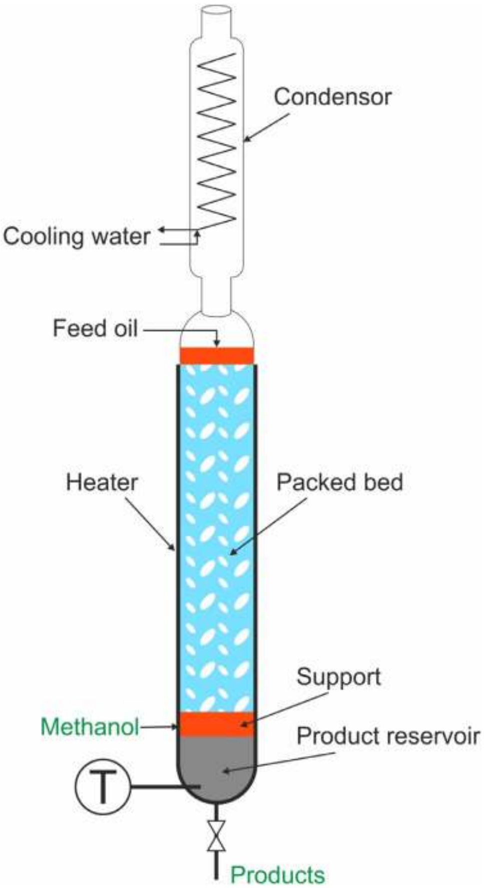

Fig. 6. Lab-scale configuration of TBR for biodiesel production [233]. With permission from Elsevier. Copyright© 2018.

concurrent or countercurrent flow of gas and liquid flows. Various equipment designs are possible for TBRs; however, the examined design for biodiesel production consists of a tubular tank with a support structure (wire mesh, sieve plate) for packed bed heterogeneous catalyst close to the bottom of the reactor (Fig. 6). The hold-up of the liquid, and hence, biodiesel yield can be improved by increasing the height of packed bed as well as by decreasing feed flow rate. The oil is fed from top of the column whereas the methanol can be fed from either top or bottom points. The desired temperature, *i.e.,* higher than boiling point of methanol is maintained by heating jackets (exterior heaters) on the reactor wall or heating coil in the packed bed (interior heaters). Moreover, the unreacted methanol is separated from products by a separate heating system placed at the bottom of TBRs. As the result of this heating system, methanol is completely vaporized at this point and starts rising in the column. A gas distributor breaks the methanol vapor into bubbles prior to its direct introduction into the packed bed catalyst, which causes intense mixing and dispersion of oil droplets within the bed before they are collected and refluxed by an upstream condenser. Similarly, an even distribution of liquid throughout the bed is maintained by using a bubble cap, fine layer of inert particles, or sieve plate distributor prior to packed bed.

There are two outlets in TBRs; one on top of the reactor for methanol gas recycling while the other one is located at the bottom of the reactor for liquids (products and unreacted oil). The application of TBR configuration for transesterification of oils into biodiesel has been reported in a few studies only. For instance, Son and Kusakabe [232] continuously produced sunflower-based biodiesel with 98% yield using a TBR with a calcium oxide packed bed (1–2 mm in diameter and 125 mm in thickness) at 100 °C, methanol flow rate of 3.8 mL/h, and oil flow rate of 4.1 mL/h. In a different study, Meng et al. [233] carried out the methanolysis of rapeseed oil in a TBR consisting of a packed bed of alkaline heterogeneous Ca/Al composite oxide-based catalyst with a 91 mL catalyst bed volume. A biodiesel yield of 94.5% was achieved using respective methanol and oil flow rates of 0.3 mL/min and 0.6 mL/min at 65 °C. The advantages and disadvantages of TBRs are previously presented in Table 8.

3.2.1.4. Oscillatory flow reactors. OFR are another type of vertical or horizontal continuous tubular reactors consisting of one or several tubes (continuous OFR; Fig. 7) each with equally distanced baffles. Bellows, diaphragms, or pistons at one or both of tube/s ends are used to generate oscillatory flow with periodic changes in flow direction (Fig. 7). A vortex mixing is produced and fills almost the whole cross section of baffles' downstream cavity because of directing or obstructing fluids by the baffles. This phenomenon also occurs in the opposite side of the baffles after reversing the bulk flow. The flow reversal cycle is repeated causing an efficient mixing due to interaction with the opposite vortices formed in the previous oscillation cycle [245]. Technically, in OFRs, each zone located between two baffles acts as a stirred tank. Therefore, a relatively ideal PFR can be obtained by implementing a sufficient number of baffles in series [125]. The interaction of bulk and imposed oscillatory velocities controls the RTD through intensifying radial mixing, which in turn improves heat and mass transfer under low shear and convenient global mixing conditions [125,209,246,247]. In general, OFR configuration allows vigorous mixing control using baffle geometry and feeding pulsation.

Standard meso-OFRs contain tubes of less than 15 mm in diameter and commonly orifice baffles, requiring low bulk flow rates of several millimeters per hour to maintain plug flow. Moreover, various baffle geometries such as central axial, helical, integral, and wire wool configurations are available for meso-OBRs to maximize mixing characteristics or to minimize frictional loss (Fig. 8) [245,248]. Integral baffle configuration provides very smooth constriction and is generally used for shear-labile reactions while the central axial baffle has found applications for single phase reactions and provides higher shears than the integral one. In contrast, wire wool configuration and helical baffles with a central insert design are advantageous for facilitating inter-phase dispersion of two-phase liquid-liquid systems (such as methanol and oil in the transesterification reaction). Other helical baffles can also be applied in various oscillation conditions for the production of an efficient plug flow.

Unlike conventional PFRs, mixing in OFRs is directly dependent on oscillatory conditions rather than Reynolds number of the bulk flow through the reactor. This would make possible successful completion of time-consuming reactions, such as transesterification of oil, in continuous compact tubular type reactor with significantly short *L/D* ratios. Consequently, these advantages lead to lower capital cost, lower operation cost (control, pumping, maintenance), improved yield of biodiesel, and lower reaction time. In OBRs, ratio of baffle spacing, open area of baffle flow, oscillatory and bulk flows, Reynolds numbers, Strouhal number, and velocities ratio of oscillatory to bulk flows determine the oscillatory conditions and the fluid mechanics. The first two parameters control eddy expansion and width, respectively, with optimum length of baffles to reactor inner diameter of 1–2 (l_b/D; commonly 1.5) and square ratio of baffle constriction diameter to reactor inner diameter of 0.2–0.4 [245,249]. An efficient mixing can be obtained by thinner baffles (1–3 mm), since thicker ones lead to vortex distortion from lengthy surface adhesion [250]. Moreover, it has been stated by Ni and Stevenson [251] that smaller gap sizes between the tube and baffles increases the axial dispersion coefficient, perhaps by preventing the generation of a second vortex ring. Compared with PFRs which require Reynolds number of 2100 for gen-

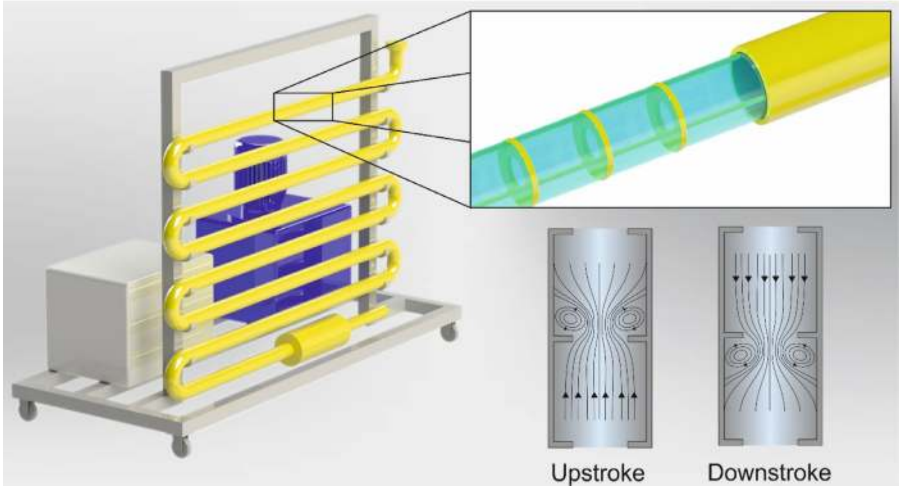

Fig. 7. Continuous oscillatory baffled reactor and different flow patterns in an oscillatory flow baffled reactor.

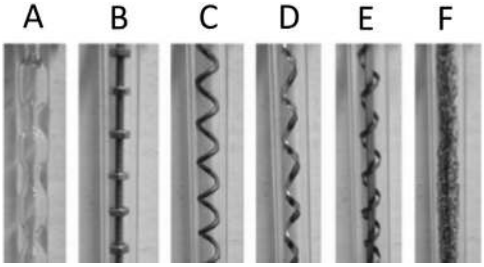

Fig. 8. Different geometries of meso-oscillatory reactor: A) Internal baffles, B) Central axial baffles, C) Round-edged helical baffles, D) Sharp-edged baffles, E) Sharp-edged helical baffles with a central insert, F) Wire wool baffles [200]. With permission from Elsevier. Copyright© 2018.

eration of flow separation, *i.e.,* transition to turbulent flow, meso-OBRs produce similar conditions with oscillatory Reynolds number of just 50 [245,246,252]. For biodiesel reaction screening purpose (such as selection/comparison of solid catalysts), novel meso-OBRs with lower diameters (4.4-5 mm) than the above-mentioned standard ones could be applied to save construction as well as feedstock costs. In these OBRs, oscillatory Reynolds number of 10 is sufficient to generate turbulent flow [245].

It should be mentioned that axi-symmetrical vortex rings are formed in each baffle cavity during each fluid oscillation with oscillatory Reynolds numbers of 100 and 250 in novel- or standard meso-OBRs, respectively [245,252,253]. These chaotic, non-axisymmetric, and intensely mixed flows generated within cavities could enhance axial mixing in a way similar to STRs. Velocity ratio of oscillatory to bulk flows must be more than one for efficient full flow reversal [246]. The Strouhal number is in inverse relationship with eddy formation; hence, a Strouhal number lower than 0.13 would be required for an intense eddy formation and the subsequent appropriate vortex generation in the adjacent baffle cavities [245,254].

3.2.1.5. Micro-channel reactors. Mirco-channel reactors (also known as micro-reactors or micro-structured reactors) use numerous narrow channels of millimeter range diameter allowing high surface-to-volume ratios and short diffusion distances for effective heat and mass transfer. According to Table 10, such configuration results in rapid reaction rates with high yields of up to 99.5–100%. Accurate temperature control, continuous mode, energy efficiency, and quick phase separation are among its other advantages [255]. All of these features are ascribed to the occurrence of a laminar flow, mainly diffusion, rather than a turbulence flow, making the movement of chemical species predictable and the reaction calculable [256]. However, for an efficient molecular diffusion, a lengthy path is required. To address this challenge and to facilitate molecular diffusion while the diffusion path is shortened, passive micromixers could be employed to improve contact surface between two or more liquids [257]. This type of micromixers can be applied as microfluidic working with no need for external force. They are categorized with respect to the arrangement of mixed phases into Dean vortices, droplet, injection, and lamination (parallel and serial) [257,258]. Moreover, some passive mixing channels with special geometries, called chaotic advection, can also induce advection through breaking, folding, splitting, and stretching (Fig. 9).

In parallel lamination, the inlet streams are split into several narrow sub-streams, which are subsequently merged into one stream as laminae. Under this concept, the basic configurations are T-shaped or Y-shaped micro-channels (Fig. 9) [257].

Serial lamination micromixers use the same concept as parallel lamination micromixers, *i.e.,* splitting the inlet streams and joining them later. However, in serial lamination micromixers, the merging occurs horizontally first, followed by vertically [257].

In injection micromixers, the oil stream is split into sub-streams. Then, alcohol is injected through an array of nozzles that are present on the top of one stream [257]. Droplet micromixers use an internal flow field for the production and transportation of the mixed liquids droplets by capillary effects, pressure, and flow instability between two immiscible liquids [257,259,260].

Although clogging and corrosion impose considerable challenges in the application of micro-channel reactors, the main disadvantage of using these reactors for biodiesel production is their very small liquid capacity [255]. A process known as numbering-up is used to address this issue by increasing the number of channels, and hence, volumetric capacity [255]. However, the shortcomings associated with this solution are channels arrangement in the reactor as well as uniform distribution of fluids through them. Kobe Steel Company designed a large-capacity micro-channel reactor, called stacked multichannel reactors (SMCR®), to solve these problems with the help of plates consisting of parallel multi-channels on either side. The channels on both sides are then connected to each other through a through-hole. Either T-shaped or Y-shaped mixing can be applied by combining channel configurations in the mixing part. A characteristic flow pattern in micro-channel reactor is slug flow, *i.e.,* the alternate arrangement of immiscible fluids (methanol and oil) in channels and large specific interfacial area. Other flow conditions including two-layer flow and annular flow

Table 10
Micro-channel assisted biodiesel production *via* transesterification of oil.

Feedstock	Alcohol	Catalyst	Reactor configuration	Conditions	Yield	Ref.
Cotton seed oil	Methanol (1:8)[1]	1 wt.% KOH	SIMM-V2 micro-mixer, ID: 0.6 mm, L: 14 m, 2.5 mL/min flow rate	70 °C, 44 s	94.7%	[263]
Cotton seed oil	Methanol (1:20)	3 wt.% H_2SO_4	SIMM-V2 micro-mixer, ID: 0.6 mm, L: 14 m	100 °C, 7 min (first step) and 120 °C, 5 min (second step)	99.5%	[264]
Soybean oil	CO_2 (as supercritical fluid) and ethanol (1:0.2:20)	–	ID: 0.571 mm, L: 97 m	20 MPa, 325 °C	84%	[265]
Soybean oil	Methanol (1:9)	0.2 g/mL NaOH in methanol	Slit channel micro-reactor with channel dimensions of 1, 1.5, and 2 mm.	55–65 °C, 3 min	100%	[266]
Soybean oil	Methanol (1:9)	1.2 wt.% KOH	T-shaped plexiglass micro-mixer, ID: 0.8 mm	60 °C, 3 s	98%	[187]
Pork lard	Methanol (1:6)	1.3 wt.% KOH	T-mixer micro-reactor, ID: 0.5 mm, L: 1.2 m	65 °C, 5 s	95.4%	[267]
Sunflower oil	Ethanol (1:9)	1 wt.% NaOH	Two micro-mixer designs (L: 35 mm; W: 1500 lm, H: 200 lm): T-micromixer (micromixer without static elements) and MSE (micromixer with static elements).	75 °C	91.5%	[268]
Sunflower oil	Methanol (1:6)	NaOH	Tubular micro-reactor carried out using stainless steel tubing with an ID: 710 μm and L: 5 m	60 °C, 4 min	~99%	[269]
Soybean oil	Methanol/hexane vol. ratio of 0.55 (1:6)	KOH	Micromixers designed with confluence angel of 45	57.2 °C, 9 s	98.8%	[270]
Palm oil	Methanol (1:24)	NA	Packed-microchannel reactor; Dimension of microchannel reactor section was $60 \times 1 \times 0.5$ mm	65 °C, 8.9 min	99%	[271]
Soybean oil	Methanol (1:9)	2 wt.% KOH	ID: 0.9 mm, wire coil inserted (L: 30 cm, average pitch 0.5 mm)	60 °C, 3 min	99%	[272]

[1] Alcohol-to-oil molar ratio.

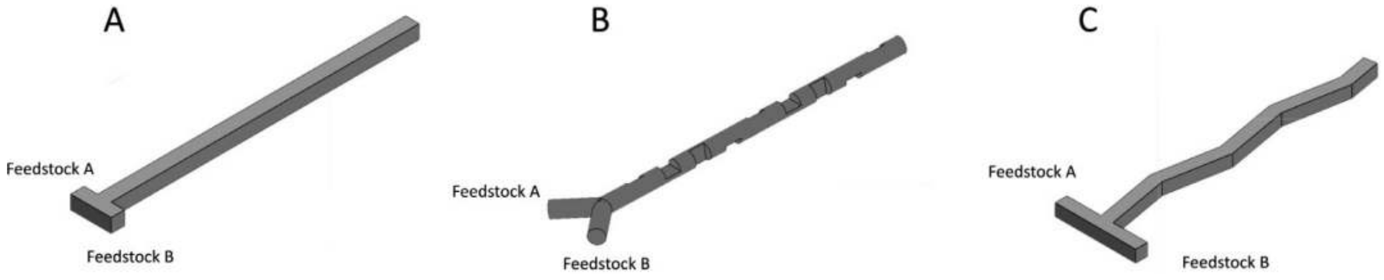

Fig. 9. A) T-shape mixer in parallel lamination, B) Y-shape mixer with obstacles on wall, and C) a zig-zag-shaped channel in chaotic advection micromixer.

are also possible (Fig. 10). The main factors affecting the final result of the reaction in the aforesaid systems were reported to be micro-channel size, mixing mechanism, residence time, and reaction temperature [255].

Martinez et al. [261] compared the impact of different internal geometries (omega, T-shaped, Tesla) on the performance of micro-channel reactors for ethanolysis of castor oil. Among them, the Tesla-shaped micro-channel reactor showed the most favorable performance by reaching 96.7% biodiesel yield. In another study on the mass transfer simulation of biodiesel production in micro-channel reactors, higher residence time and lower micro-channel reactor height (higher ratio of surface area to volume) were found as significant factors [262]. Table 10 summarizes recent experimental research works conducted on biodiesel production using micro-channel reactors.

3.2.2. *Rotating reactors*

Mechanical agitation facilitates the mass and heat transfer, decreases the hold-up of reactants and reagents, and allows the utilization of more efficient (usually costlier) materials in the fabrication of resulting smaller-sized reactors. Rotating reactors have single or multiple rotating elements with various configurations (discs, impellers, tubes, *etc.*) and rotational characteristics (power, speed). Various types of rotating reactors suitable for transesterification of oil have been discussed in this section.

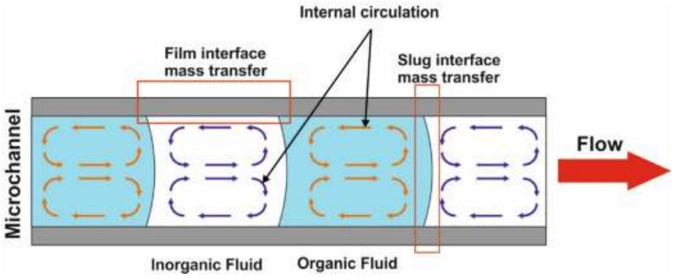

Fig. 10. Different flow patterns in a micro-channel reactor.

3.2.2.1. *Stirred tank reactors.* In general, a STR is a cylindrical vessel equipped with a central shaft which harbors one or more stirrers. Lack of mixing is usually observed in tanks of large sizes especially when multiphase reactions occur. This poor mixing can affect the rates of mass transfer and reaction [273]. Two forms of catalyst dispersion in a stirred tank are considered, including heterogeneous and homogeneous forms. Heat transfer in stirred tanks is managed through external jackets or by applying coils inside the tank. Although the application of internal coils provide higher rates of heat transfer in system, it can cause some issues such as increasing the possibility of fouling, disturbance of mixing, and difficulties in reactor cleaning.

Various methods have been developed to enhance mixing in STRs. For example, bottom to top movement of mixture is hindered by using vertical wall baffles fasten on the inner wall of the tank. The four most common stirrer types used in reactors are turbine, impeller, monolithic, and foam stirrers [274]. Additionally, more complicated stirrers such as Rushton stirrer can also be used to improve the mixing intensity. Rushton stirrer is a kind of turbine mixers that has been in use since 1940s [274]. This stirrer consists of six vertical blades placed on a disc, generating a radial flow in mixture. Physical characteristics of mixture and geometry of vessel mainly determine the power properties of this stirrer [275].

Gas-distributing inlets can also be used for improving the mixing rate in stirred tanks [274]. For instance, gas-inducing impellers could introduce an unreactive gas phase to the liquid phase in a reactor in order to enhance mixing and productivity [276]. In a CSTR with a gas-inducing impeller, electrical capacitance tomography (ECT) could also be used for monitoring the gas flow in the liquid phase and consequently to increase the efficiency of the gas distribution in the system, further improving mixing times and reaction parameters [277]. Another type of mixing system used in CSTRs is the monolithic stirrer suitable for reactions with dispersed catalysts. This type of stirrer consists of a ceramic part with many channels placed in parallel. The first idea for developing monolithic stirrers was presented by Albers et al. [278] for low viscose mixtures. Immobilization of enzymatic catalyst or other types of catalysts inside the channels may be an advantage of monolithic stirrers. In addition, there is no need for catalyst separation step while immobilizing the catalysts inside the channels [279,280].

Solid foam stirrer is a more recent stirrer, which consists of two foam blocks with a reticulated structure. The blocks possess high surface area providing an ideal situation for catalyst immobilization. It has been demonstrated that tanks equipped with foam stirrer present higher yields of liquid-solid and gas-liquid mass transfer [281,282]. Some examples of STRs are presented in Table 11.

Batch stirred tank reactor. As mentioned earlier, BSTR was the premier biodiesel production technology and is still very popular for industrial-scale production processes. For a batch process in a ideally stirred tank, the reaction rate is the same as the changes in reactants or product/s concentrations [238]. Fig. 11 represents a schematic illustration of a typical batch stirred reactor.

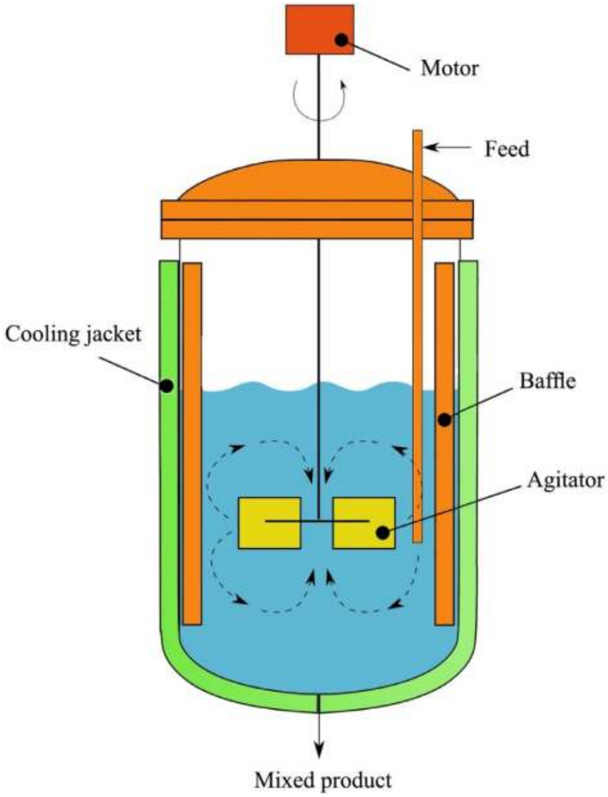

Fig. 11. A schematic illustration of a typical batch stirred reactor.

Batch reactors are classically composed of a mixed tank in which a reaction is initiated by adding the reactants and catalysts and proceeds during a determined time. Batch reactors were extensively used at the initiation of chemical industry era dating back to the seventeenth and the eighteenth centuries. Along with the development of the chemical industry in the twentieth century, continuous reactors were introduced and employed in various industries. In spite of that, batch reactors still possess some significant kinetic features as well as advantages making them as an important system for various reactions (Table 6).

Batch reaction systems are frequently developed by direct scale up from laboratory trials. If the feed concentration and reaction temperature are kept identical to the lab operational condition, similar residence time is often needed for the same reaction since the reaction rate (kmol/hr/m^3 or lb mol/hr/ft^3) does not vary with the reactor volume. The minimum required reactor volume could be determined on the basis of the yearly desired production rate and the time for a complete batch cycle, including times for charging the reactants, heating, reaction, product discharge, and cleaning. A slightly larger reactor than standard size might be chosen for a different run schedule or increases in production rate [238].

A critical factor to reach high productivities in batch systems is the precise calculation of the time required for complete conversion of reagents into products. In a batch system, optimum temperature profiles are determined through the chemistry of reaction. For instance, in exothermic reversible reactions, temperature is adjusted to increase with initiation of reaction so that the process proceeds in the desired pathway. Thereafter, the temperature decreases with certain time to inhibit the reduction in chemical equilibrium constant. The temperature profile is different for endothermic reversible reactions. Under this condition, temperature increases quickly as much as possible to the highest amount because raise of chemical equilibrium constant depends on temperature elevation.

Table 11
Application of STRs for biodiesel production *via* transesterification of oil.

Reactor	Feedstock	Alcohol	Catalyst	Conditions	Yield	Ref.
BSTR	Triolein oil	Ethanol (1:6)[1]	1% KOH	25 °C, 1800 rpm, 5 min	70%	[283]
BSTR	Castor oil	Ethanol (1:16)	1% $NaOCH_2CH_3$	30 °C, 400 rpm, 30 min	99%	[284]
BSTR	Jatropha oil	Ethanol (1:6)	2% NaOH	25 °C, 300 rpm, 2 h	~100%	[285]
CSTR	Palm oil	Methanol (1:6)	1% KOH	60 °C, 60 min	97.3%	[204]
CSTR	Rapeseed oil	Methanol (1:6–7.8)	KOH	60 °C, 3–8 mL/min flow rate	98.6%	[286]
JSR	Soybean and sunflower oils (85:15 wt.%)	Methanol (1:6)	1% NaOH	~35 °C, 5 min, two impinging injectors, 5 mm nozzle diameters, 15 cm internozzle space	>90%	[207]
JSR	WCO	Methanol (1:15)	4% KOH/γ-Al_2O_3 millimetric particle	65 °C, 3 h, two impinging injectors, 2 mm nozzles diameter, 0.5 or 1 cm internozzle space, 4 L/min volumetric flow rate	76%	[287]

[1] Alcohol-to-oil molar ratio.

In a batch operation, the concentration of reagents is in their maximum amounts at the beginning of the reaction which causes a high reaction rate that needs high heat transfer load. The process must be checked frequently because the batch system is a time-varying process in which main parameters can change with time. Thus, applying control planning such as “gain scheduling” is needed during the process. A non-linear model is used for analyzing batch reactors while in a condition close to steady-state level which occurs in continuous systems, a linear model is usually used [288]. The non-linear behavior of batch process contributes to complexity in reaction kinetics that leads to inaccurate measurements. Consequently, this would prevent complete optimization of conditions to obtain maximum productivity and economic benefits. Overall, a batch system can be operated optimally through two approaches. The first is to specify optimal set points of significant process parameters such as temperature of reaction and the second step is to monitor the system through a controlling approach to obtain the optimal profile [289,290]. Modeling errors are usually unavoidable due to external disturbances and complex conditions of batch systems affecting the final products yield. To solve these problems in control process, often on-line optimization has been used to efficiently estimate the desired profile [291]. Examples of BSTR for biodiesel synthesis using transesterification of oil are provided in Table 11.

CSTR. A CSTR is simply a vessel equipped with feed input (inlet), product outlet (output), an agitator, as well as cooling and heating jacket. It is more suitable for the industrial scale biodiesel production [206] due to several benefits over batch operation as elaborated in Table 6. This reaction system can make products continuously every time it is run, whereas a typical BSTR is operational for only about half the time of CSTR. CSTR can be integrated with other reactor types to improve effectiveness. For example, PBR in the forms of columns have been integrated with mixing/rotating nature of CSTR reactors to develop a simple rotating PBR (RPBR) (Fig. 12). The enhancement achieved in mass transfer in RPBRs is due to the decline in boundary layer of reactants over the heterogeneous catalysts, and the subsequent reduction in mass transfer resistance [292]. More complex RPBRs are discussed in detail in Section “3.2.2.2”.

In the CSTR configuration, controlling temperature is straightforward than in the BSTR configuration due to the fact that the reaction rate is fixed and the heat release rate does not vary with time [238]. Finally, conversion and selectivity may show batch-to-batch variations in a batch reaction system, whereas they are more likely to be fixed in a CSTR system with appropriate controlling means [238]. A CSTR system is generally modeled with respect to conditions in which there are no variations in temperature, concentration, or reaction rate throughout the vessel. Composition and temperature of output stream are exactly the same as the mixture in the tank throughout the reaction. This feature is also true for concentration of reactants/reagents in both vessel contents and stream of products. The rate of conversion and quantity of reactants are in a reverse relation, in better words, a high rate of conversion needs a low amount of reactants. Apparently, the reaction rate is highly dependent on primary throughput of reagents. This issue can be solved thorough increasing the volume of reactor vessel [288].

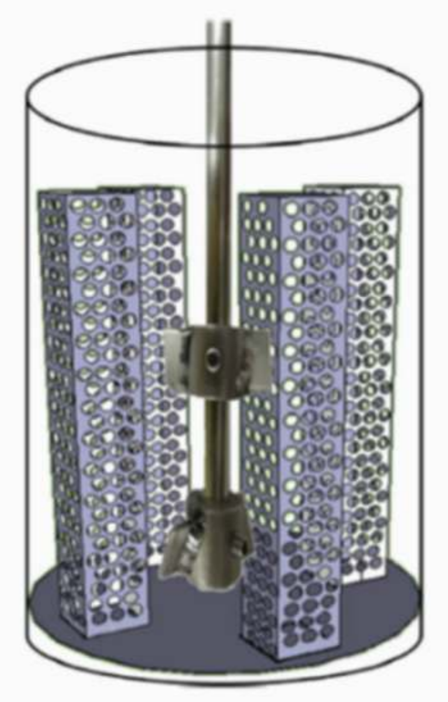

Fig. 12. Stirring packed bed reactor [138]. With permission from Elsevier. Copyright© 2018.

The design of appropriate controlling strategy, which is important for achieving maximum conversion possible with minimum cost, is very challenging in CSTRs due to highly second order complex non-linear dynamics [242]. Accordingly, external disturbance attenuation, one relative degree, state estimation, and zero dynamics are four difficult issues in controlling CSTR. Feedback linearization, general predictive control, multi-model control, proportional-integral-derivative controller, Taylor-linearization, and terminal sliding mode control model have all been used for controlling different parameters of CSTRs applied for biodiesel production [293–297]. Zhao et al. [297] have designed two new output integral terminal sliding mode strategies, namely sign integral terminal sliding mode control and fraction integral terminal sliding

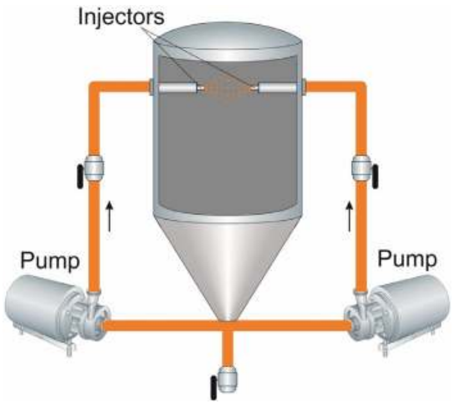

Fig. 13. Simplified diagram of jet flow stirred reactor. Redrawn from [207]. With permission from Elsevier. Copyright© 2018.

mode control, with powerful robustness to system disturbances. In a different study, an event triggered sliding mode control was designed by Sinha and Mishra [298] for maintaining the temperature and concentration states of an CSTR at equilibrium points. This controller was in a relaxed status when the predefined conditions were not violated and could provide stability in the system with lower computational load and cost within a short period of time.

Jet-stirred reactors. The main advantage of JSRs over PFRs and shock tubes is that both time and space are zero-dimensional whereas in the latter two reactors, only one parameter can be zero-dimensional. Potentially, the mixing time is shorter than residence time and both can be dissociated from each other in a JSR. In contrast, mixing and residence times can never be separated in PFRs [299,300]. However, JSRs have been rarely employed for biodiesel production from natural oils and fats.

As an example, Reyes et al. [207] developed a self-heating batch transesterification reaction system using two-impinging-jet-flow as hydrodynamic agitation driving force and converted soybean and sunflower oils (85:15 wt.% blend) into biodiesel in the presence of 1 wt.% of NaOH at methanol to-oil molar ratio of 6:1 (Fig. 13). They obtained more than 90% relative biodiesel yield in the first 5 min of the process while this value was increased to 98% after 60 min of residence time. The reactor consisted of a 9-L tank connected to two centrifugal pumps at the conical bottom. These pumps forced the mixture to pass through two injectors located in the top part of the reactor wall. This configuration generated dual opposite radial jet flows in internozzle distance of 15 cm to produce a local zone of high mass transfer with small size droplets of oil due to the collision of oil jets at that space. They also examined four nozzle diameters ranging from 5 to 13 mm and argued that nozzles size had an inverse relationship with Reynolds number and reaction temperature. More specifically, the highest initial Reynolds number of 6470 was delivered by nozzle diameter of 5 mm. This could be ascribed to the high temperature of the mixture in response to high friction created which in turn lowered density and viscosity of the mixture, and consequently led to flow increments [207].

In a more recent study using JSR configuration, Ghasemi and Molaei Dehkordi [287] used KOH/γ-Al$_2$O$_3$ millimetric particles for accelerating the transesterification process of WCO. The millimetric size catalyst eliminated some drawbacks associated with their conventional smaller size counterpart, *viz.*, leaching of potassium moiety into the solution, dropping of activity in recycled catalyst, and separation difficulty. However, intense mixing was required to overcome the external mass transfer resistance all over the solid catalyst particles [287,301]. Therefore, they applied two-impinging-jet technique in the JSR to deliver vigorous micromixing of reaction mixture. The catalyst was located in the reaction chamber and a wire screen was used to prevent their washing from this chamber. The volumetric flow rate of 4 L/min was found as the optimum value for suspending the catalyst within the chamber and eliminating external mass transfer resistance [287]. It was found that jet velocity and Reynolds number were appropriately raised at this flow rate. Similar to the previously explained study [207], the lowest diameter of examined nozzle (2 mm) also provided better yield of biodiesel by providing a higher Reynolds number. The internozzle distance influenced the collision of the jets; and therefore, suspension of the solid catalyst within the chamber. The distances of 0.5 and 1 cm were reportedly appropriate for the complete suspension of catalyst, and hence for the maximum reaction rate [287]. A biodiesel yield about 76% was obtained under optimum transesterification conditions (4 wt.% KOH/γ-Al$_2$O$_3$, 15:1 methanol-to-oil ratio, 65 °C, 3 h) [287].

Overall, JSRs are more suitable for heterogeneous catalyzed-transesterification reactions, compared with mechanical stirrers due to protecting structures of solid catalysts.

3.2.2.2. Rotating/spinning tubes reactors. Rotating tube reactors. Rotating tube reactors (RTRs) use tubular geometry with low shear stress. To fulfill that, they rotate a moveable hollow cylinder with a typical rotational speed of less than 1000 rpm. In these reactors, a sheared thin liquid film (0.7–1.4 mm in thickness) is formed, which improves mass and heat transfers by significantly elevating the ratio of surface area to volume (about 1000:1) as well as generating a small conduction path length [48,302]. Therefore, together with low pressure drop over the cylinder as well as simple design, RTRs are capable of providing a suitable basis for bulk transesterification processes. This technology has been successfully examined by Lodha et al. [302] for continuous production and separation of canola-based biodiesel in the presence of NaOH. They injected a mixture of methanol and oil into an RTR and controlled the temperature by means of cooling/heating jacket. Under optimized conditions (1.5 wt.% NaOH, 1:6 methanol-to-oil molar ratio, 900 mL/min flow rate, 40–65 °C, 670 rpm, 45 s), a high oil to biodiesel conversion rate of 97.6% was obtained. The result was very promising compared with membrane reactors (480-time longer residence time, 147.5-times lower flow rate) as well as CSTRs (eight-time longer residence time, 2.4-times lower flow rate) [302–304].

Rotating bed reactors. RPBR (Fig. 14) are the most common type of rotating bed device in HiGee technology that has been mentioned in the literature. Other rotating devices are also possible which include blade packing rotating packed bed, counter-flow concentric-ring rotating bed, crossflow concentric-baffle rotating bed, rotating fluidized bed, rotating zigzag bed, rotating bed with blade packing and baffles, single-block rotating packed bed, split-packing rotating bed, two-stage counter-current rotating packed bed [305]. RPBR is an intensified variation of PBR in which a centrifugal force is applied to facilitate alcohol-oil interface, micromixing (molecular scale mixing of two liquids), and mass transfer while reducing both height and volume of the conventional PBR up to 10.5–11.1 times [306]. It has been reported that mass transfer coefficients have inverse relations with average lifetime of liquid film [306]. In fact, a resistance is observed when surfaces of two immiscible fluids (such as alcohol and oil) are approaching each other, forming a liquid film [307]. In the case of pure miscible liquids, zero lifetime of liquid film, *i.e.,* no resistance is encountered and the surfaces immediately mix and vanish. In RPBRs, the most important part of the reactor for mass transfer is the end-effect zone of packing. More specifically, RPBR produces a high energy dissipation region and passes the liquid stream through it [308,309]. This part extend from the inner edge of the packing to the capture site of liquid, by the rotary packing [306]. Maximum relative velocity, between liquid and rotat-

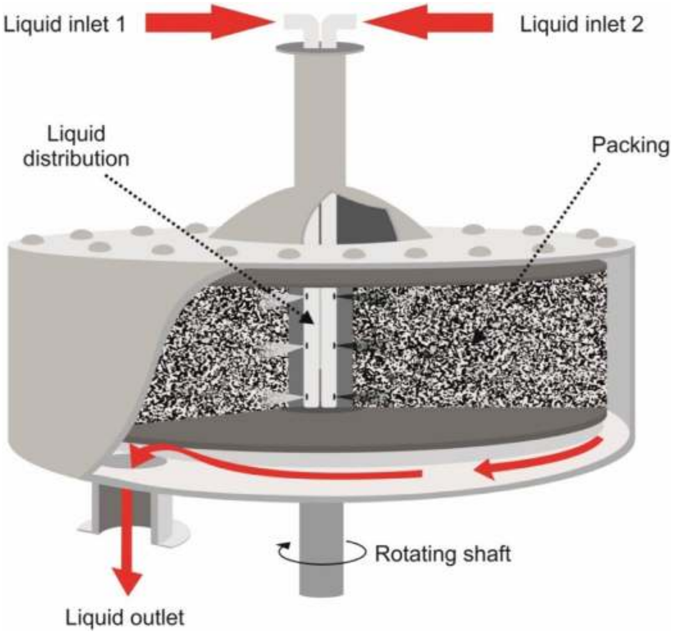

Fig. 14. A schematic drawing of a rotating packed bed reactor. Redrawn from [309]. With permission from Elsevier. Copyright© 2018.

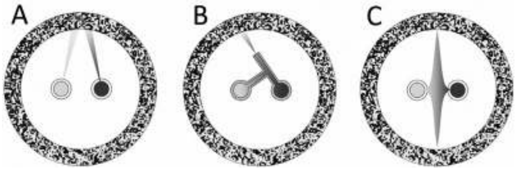

Fig. 15. Three most common patterns of liquid distribution in a rotating pack bed reactor; A) Distribution pipes, B) Premixed distributor, and C) Impinging stream distribution [309]. With permission from Elsevier. Copyright© 2018.

ing packing, tears and shears the liquid in this section. Consequently, smaller droplets and thinner liquid films are formed enhancing surface area, and hence, volumetric mass-transfer coefficients are surged 10–100 times [306]. The high gravitational force (500–2500 rpm) improves the speed of reaction, which is already speeded up because of packed bed process.

RPBRs' lower capital and space requirements as well as its process intensification power justify its higher energy consumption for rotation. RPBR consists of a motor mounted either on the side or underneath the reactor according to the rotation axis. It spins a ring-shaped cylindrical packed bed rotor (moving part) with or without a series of concentric perforated baffles placed in a cylindrical casing, *i.e.*, housing (static part) (Fig. 14). The center of rotor is a hollow structure called as eye that distributes liquid. The packing bed is composed of three sections, *viz.*, inner rim (impingement zone), bulk zone, and outer rim. Both rims have a high liquid hold-up whereas the bulk zone has a high liquid distribution and lower hold-up. The introduction of alcohol and oil into the rotating packed bed can be performed by three approaches (Fig. 15), *viz.*, distribution pipes spraying droplets of alcohol and oil separately, premixed distributor spraying droplets of previously mixed alcohol and oil feed, or impinging stream distribution jet-spraying alcohol against oil in the eye of the rotor [309]. The liquid streams then sharply collide, *i.e.*, impinge with the rotating packed bed in its first 7–10 mm in length (also called the impingement zone). Subsequently, the liquid is fed in the same direction as of centrifugation rotation towards the outer rim. The rate of passing the alcohol-oil mixture through the bulk zone is dependent on the rotational speed which can in droplet, film, or pore flow forms at low, medium, or high centrifugal forces, respectively [310]. The process is completed by flowing the stream of liquid into the housing and leaving the reactor through outlets [309].

RPBR efficiency depends on operational parameters, including flow rate of liquid, speed of rotation, volumetric ratio of two liquid streams, and fluid viscosity; as well as design parameters, including packing (length, inner and outer radii, type, porosity), liquid distributor (pipe, premixed, impinge), and liquid velocity characteristics [308,309]. Rotational speed has a linear relationship with segregation index, to some point, after which its influence is nonlinear [309]. Micromixing is facilitated at higher rotational speeds by providing higher energy dissipation [309]. Similarly, the flow rate of liquid and the volumetric ratio of two supplied liquid streams have more or less inverse relationship with segregation index. In contrast, viscosity has a proportional relationship with segregation index and at higher viscosities, the average size of liquid fragments increases whereas the deformation and shrinkage of liquid elements are reduced at a given energy dissipation rate [309,311].

The application of RPBRs for the transesterification of oils is still immature. It has been expressed that RPBRs can enhance the transesterification reaction by intensive mixing of reactants and reagents within a short time [292,301]. More specifically, the micromixing time and RTD of liquid are about 10^{-4} s and within several seconds [308, 312]. The subsequent centrifugation results in glycerol phase separation and heterogeneous catalyst recovery (in the case of its application). This strategy has been successfully performed for continuous production of biodiesel from homogeneous or heterogeneous-catalyzed methanolysis of soybean oil [292,301]. KOH catalyzed-methylation of soybean oil (3 wt.% KOH, 6:1 methanol-to-oil molar ratio, 60 °C) was conducted under continuous flow rates of methanol (69 mL/h) and oil (271 mL/h) at 900 rpm centrifugation. Yield and productivity of 97.3% and 0.83 mol/min were achieved with 43.2 s residence time, respectively [292].

Spinning tube-in-tube reactors. STT reactor or inline high shear mixer is another reactor with tubular geometry which was patented by Richard Holl in 2010 [313]. It works by quickly rotating one tube inside another concentric fixed tube to generate high shear micro-mixing. Major components of the system are rotor (rotating cylinder), stator (stationary cylinder), two inlets, and one outlet. Stator encompasses rotor with a narrow annual gap of 0.25–0.44 mm between them. Once reactants and reagents are entered into this small annual space, the Couette flow and high rate of shear induces instant mixing of the two liquids and their subsequent movement as a coherent thin film through the gap. This leads to a very large interfacial contact area which in turn increases the reaction rate [314]. The enhanced rate of reaction reduces reaction time and energy consumption in the form of mixing. The reactor volume and centrifugal force are typically 10–1000 mL and 3000–12,000 rpm, respectively.

In the biodiesel production processes using STT reactors, two separate streams of oil and methanol/catalyst are fed into the reactors from their individual inlets. STT fluid flow is depicted in Fig. 16. Fluids flow through the slots or holes around the rotor and stator and pass through a gap between rotating and stationary parts of the reactor. High shear interaction of the two reactants leads to elimination of mass transfer resistance and improves heat transfer as well. It may be assumed that STT reactors may not be an appropriate option for large-scale production of biodiesel due to their low reaction volume. However, these reactors have been already utilized by COSTELLO Company for industrial scale biodiesel production (Fig. 17) [209]. The commercial version of STT system, *i.e.*, Cryon^{TM} Reactor allows rapid scale-up as well as instant mixing of alcohol and oil for trans/esterification reactions (Fig. 18). This

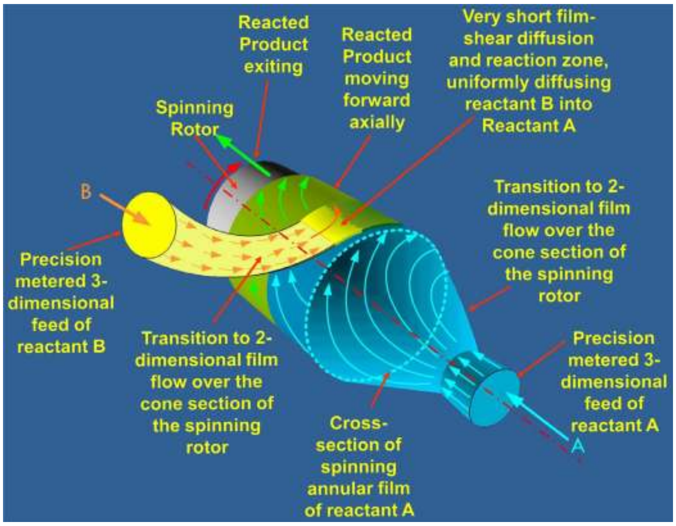

Fig. 16. Depiction of spinning tube in tube fluid flow. Courtesy of Bright Path Group, Inc. and Tribologiks, LLC.

process can support rapid (<1 s) continuous process in a single reactor with single pass delivering minimal soap formation and high conversion yield.

According to COSTELLO Company, the application of STT reactor can increase the process yield up to 3% while providing higher feedstock flexibility. The process requires about 33% lower capital cost, no requirement for water wash step and hence save water recovery costs, and occupy low space.

3.2.2.3. Spinning disc reactors. Spinning disc reactors (SDRs) take advantage of thin liquid flow (≤100 µm) for perfect heat and mass transfer (Fig. 19). The thickness and radius of liquid film that flows across the surface of spinning disc are directly controlled by rotational speed, which forms characteristic finite-amplitude waves (concentric, spiral) and sophisticated interfacial dynamics [274,315] (Fig. 20). An increase in the liquid flow rate and/or rotational speed triggers radial velocity growth [316]. This excellent fluid dynamics allows a continuous and efficient production of chemicals using a compact SDR operating under appropriately high rotational speeds. Moreover, SDR provides a great degree of control on side-reactions, and hence, increases the process yield while reduces the cost of downstream purification. Both homogeneous reactions and heterogeneous catalysis (*i.e.*, disc as the catalysis support) can be conveniently performed by SDRs [315].

Wave formation in SDRs can be further intensified through the application of a temporally and spatially varying electric field with specific intensity and electrode geometry [318]. Further improvement was done in a SDR variation known as rotor-stator spinning disc reactor (RSSDR), consisting of three discs, *i.e.*, one rotating disc (rotor) and two stationary discs (stators) [319]. The rotor is placed between the stators with an axial distance of 1 mm with a speed of up to 4500 rpm. Later, another variation of SDR was also patented [320], consisting of two rotatable discs each with an input and an output. The first rotatable disc was larger and contained a hollow disc-shaped cavity where the second smaller rotatable disc with channeled cavity was located. Both discs had an input and an output and were concentric about an axis at a distance of 0.05 mm. The discs were counter-rotating or co-rotating with a rotational speed of up to 5000 rpm to provide efficient multi-phase contacting.

Studying disc radius and rotational speed of disc and volumetric flow rate of liquid is important for scale-up process of SDRs because they determine liquid film thickness as well as residence time. In the case of scaling-up of the RSSDR, it is important to increase the number of rotors-in-series rather than the diameter of rotor. This is because increases in the latter would result in a significant surge in energy consumption [274,321,322]. Dur-

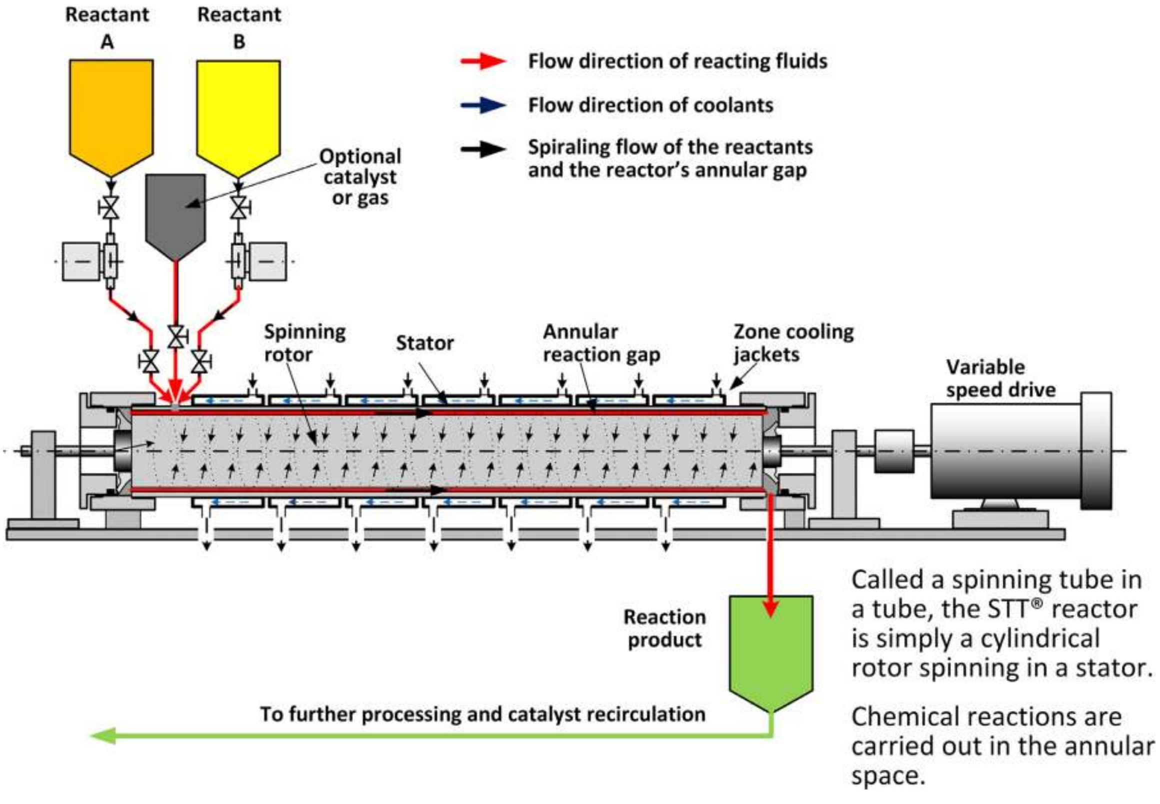

Fig. 17. Spinning tube in tube schematic view. Courtesy of Bright Path Group, Inc. and Tribologiks, LLC.

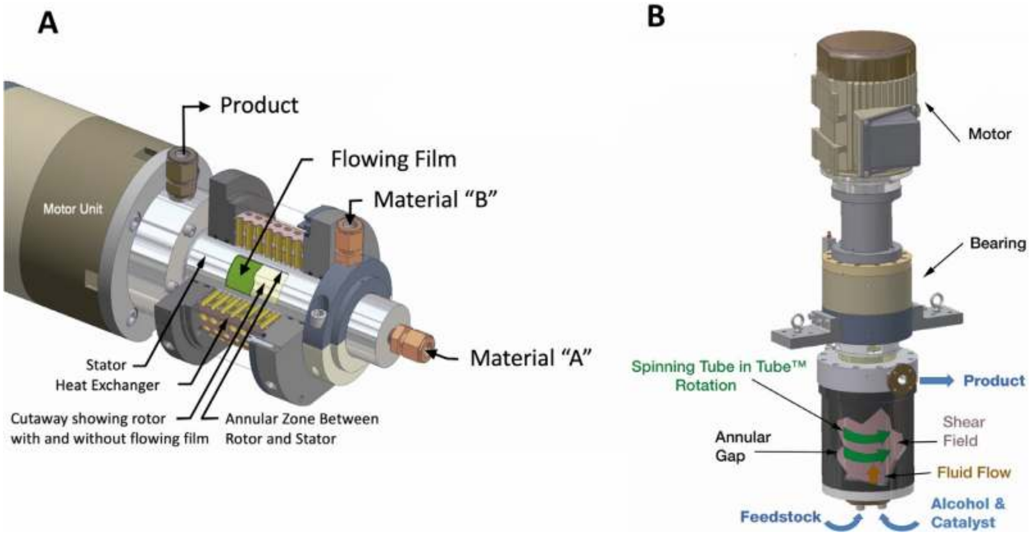

Fig. 18. Spinning tube in tube for biodiesel production; A) The system, and B) Cryon^{TM} Reactor. Courtesy of Bright Path Group, Inc. and Tribologiks, LLC.

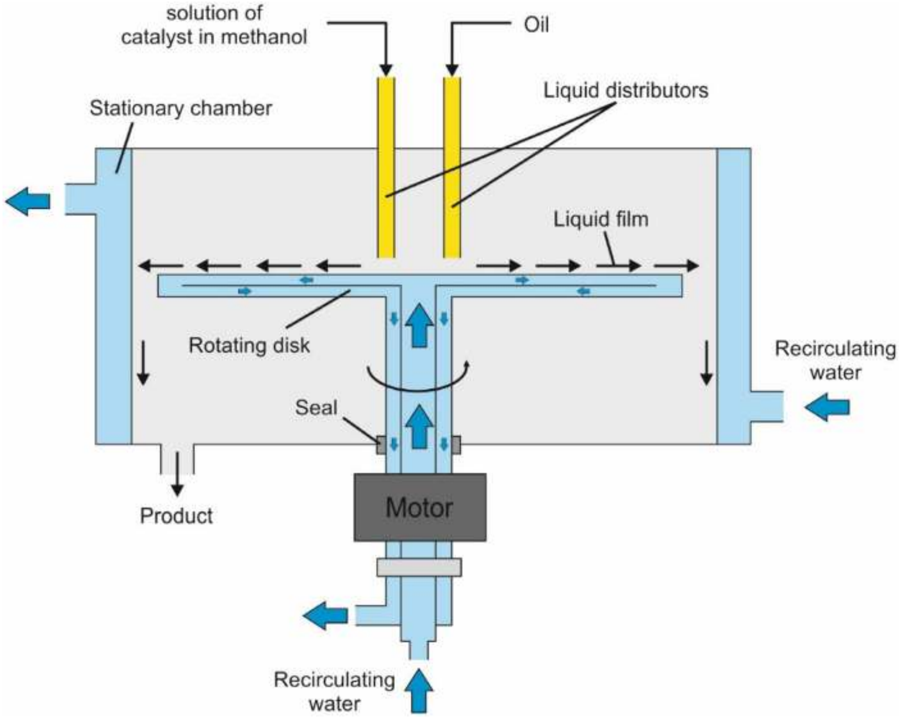

Fig. 19. A sample of spinning disk reactor for biodiesel production. Redrawn from [317]. With permission from Elsevier. Copyright© 2018.

ing transesterification of oil using SDRs, the liquid feedstock is introduced into the center of reactor chamber containing rotatable disc. Consequently, a liquid film with thin, unstable, and wavy characteristics is distributed across the disc. The movements of liquid within this film is plug flow and from center to the periphery [318,323]. A two-disk spinning reactor (one rotating and one stationary) was studied by Qiu et al. [324] for continuous NaOH-catalyzed transesterification of canola oil (1 wt.% catalyst, 6:1 methanol-to-oil molar ratio, 1000 rpm, 30–50 °C, few seconds). They observed a 20–40 folds shorter reaction time than BSTR under similar conditions. They also argued that conversion was most importantly influenced by sick surface morphology, rotation speed, feed rate, and the intra-disk gap. Among them, the most influential parameter was found to be the intra-disk gap (optimum distance of 0.1 mm), which was inversely correlated with local shear stresses, mixing intensity, and hence, the conversion. The optimum gap distance led to 55% conversion at room temperature. Similarly, Wen and Petera [325] investigated the potential of a two-disc SDR for intensifying the biodiesel production process. The two flat discs were concentric with a gap of 0.2 mm between upper rotating disc and lower stationary disc. Methanol and triglycerides was coaxially fed along the center line of stationary and rotating discs. They noticed that despite the lower residence time, increasing the rotational speed improved the conversion process. More recently, Chen and Chen [317] applied a SDR for continuous soy-based biodiesel synthesis (1.5 wt.% NaOH, 6:1 methanol-to-oil molar ratio, 773 mL/min flow rate, 60 °C, 2400 rpm, 2–3 s). Under such optimum conditions, a yield of up to 97% was achieved with a production rate of 1.86 mol/min. The findings of these studies highlighted the suitability of SDR and its intensification capability for

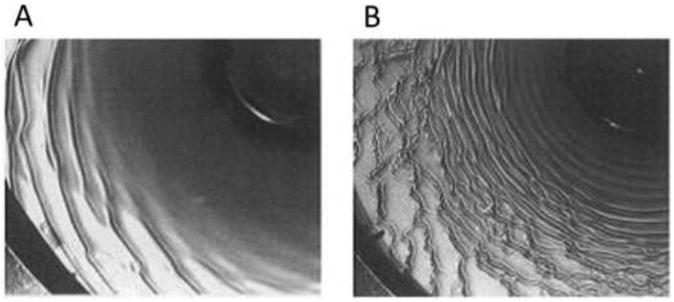

Fig. 20. Wave formation in SDR with respect to rotor speed; a) 200 rpm, and b) 600 rpm [315]. With permission from John Wiley & Sons, Inc. Copyright© 2018.

simple and efficient synthesis of biodiesel in a small production space.

3.2.3. Simultaneous reaction-separation reactors

This group of reactors combines chemical reactions with simultaneous extraction of products from reactants and unreacted reagents in a single unit operation, an intensification method also known as reactive separation process. This intensification process is generally used for equilibrium reactions, for example, transesterification. The separation of product changes the equilibrium of the reaction in favor of products formation. Moreover, these reactors provide excellent mixing, and hence, better quality and higher yield of conversion are achieved. Two classes of reactors, *viz.,* membrane reactors and annular centrifugal contactors (ACCs), and one technology, *i.e.,* reactive distillation using simultaneous reaction and separation principle for biodiesel production are discussed in this section. Other types of reactive separation technologies, including reactive absorption and distillation, reactive adsorption, reactive chromatography, and reactive extraction have not been covered in this review due to space limitations.

3.2.3.1. Membrane reactors. Membranes offer a selective way to transport the target substances through them, which could be used in separation of liquids, vapor, and gasses with different mass transfer rates [326]. The intensification of biofuel production processes with membranes is becoming increasingly attractive [327]. However, the application of membrane separation technology in biodiesel production process is relatively a new concept [328]. It can be applied as either complementary step (*i.e.,* separation and purification method) or integrated process (*i.e.,* simultaneous reaction-separation reactor) in the transesterification process of oil for biodiesel synthesis. In general, membranes are classified based on their geometry, separation basis, and nature and are used for enhancement of biodiesel quality to meet, for examples, DIN EN 14214 and/or ASTM D6761 standards for biodiesel with 100% purity. The selection of the right membrane type for a given process depends on various parameters such as reaction condition, productivity, separation method, lifetime, and the cost of membrane [326].

Separation and purification of biodiesel *via* membrane technology have significant advantages, compared with conventional methods. This ecofriendly technology produces low amounts of wastewater and utilizes low energy. Moreover, membrane can be used as a mean for the treatment of wastewater generated during separation and purification of biodiesel [329,330]. Membranes are resistant to organic solvents and occupy a small area for their operation. In addition, membrane reactors could provide higher quality biodiesel *vs.* conventional separators [331]. For the separation and purification step, three configurations (*i.e.,* hollow fiber, plate-and-frame, tubular), three membrane processes (*i.e.,* microfiltration, ultrafiltration, nanofiltration), and two structures (*i.e.,* asymmetric, composite) containing organic [*i.e.,* cellulose acetate, polyacrylonitrile, poly(dimethylsiloxane), polysulfone, poly(vinylidene difluoride)], inorganic materials (*i.e.,* carbon, ceramic, α-Al_2O_3/TiO_2, ZnO_2/C), or their hybrid (*i.e.,* organic-inorganic membranes) have been investigated [328,332–338]. The above-mentioned conventional configurations are the most common systems for membrane housing and for preventing the negative impact of operating pressure. Plate-and-frame membranes have a planar arrangement, which is mainly in rectangular form providing a moderate aspects ratio (surface-to-volume ratio). Some disadvantages of this configuration are possibility of plugging at flow stagnation points, difficult cleaning, and high cost [339]. While hollow fibers offer high membrane aspect ratios and low energy utilization; however, they are susceptible to plugging by particulates. In addition, the replacement of the whole module is inevitable due to possible fouling of fibers [340].

Asymmetric membranes differ from their composite counterparts in the number of building materials. In another word, asymmetric membranes are produced from a single material whereas composite membranes include at least two structural elements produced from two different materials.

Various membranes have successfully been applied for the retention of glycerol (0.261–10 wt.%) from crude biodiesel with or without the presence of alcohol and/or oil. After passing crude biodiesel through these membranes, glycerol content in permeates was reportedly dropped to about ~0.01–0.19 wt.%, corresponding to glycerol rejection percentages of more than 90–99.6 [328,341,342]. The mechanisms of glycerol retention could be reversed micelle formation by glycerol or glycerol and soap molecules in microfiltration, swelling of glycerol droplet by adsorption of added water in ultrafiltration, or simply by sieving effect in nanofiltration [328,334,341–343]. It should be noted that the amount of glycerol in crude biodiesel plays a significant role in biodiesel quality on the permeate side, possibly due to the action of trapped glycerol as filter aid.

Inorganic membranes are more frequently studied for the separation and purification of biodiesel, compared with their organic counterparts. This is because inorganic membranes are chemically inert and provide unique surface characteristics with good resistance against microbial contamination while also withstand harsh industrial operation conditions such as high temperature, mechanical stress, and organic solvent [340,343]. Despite many considerable advantages of inorganic membranes, some critical disadvantages of these membranes including brittleness, complicated sealing at high temperatures, difficult scale-up, low aspect ratio, low selectivity (with few exceptions), and high capital and maintenance costs hinder their industrial application [343,344]. Therefore, the application of organic membranes such as polymeric nanofiltration and reverse osmosis are recommended [343]. It should be noted that polymeric membrane materials are pH-labile; and therefore, the pH of biodiesel must be reduced from 12.4 to below 8.7 to avoid physical damage to membrane structure [338,343].

Saleh et al. [334] efficiently reduced the glycerol content of crude biodiesel from 0.04 wt.% to as low as 0.013 wt.% (59–71% glycerol rejection) using ultrafiltration membrane of polyacrylonitrile, supported on frame-and-plate configuration. The ultrafiltration was conducted with molecular cut-off of 100 kDa at pH 7, 25 °C, 0.55 MP with the cross flow velocity of 0.6 m/s. Under these optimum conditions, the membrane flux was 10 $L/m^2/h$. The permeate was taken whereas the retentate was recycled back to the feed tank. This biodiesel purification process required slight amounts of water for improvement of the two-phase system, and hence, very low amount of wastewater (1 kg water/500 L of the treated FAME) was generated [334]. It is worth mentioning that the efficiency of separation is generally decreased with increased concentrations of methanol in this step due to increasing glycerol solubility in FAME [334].

Torres et al. [338] prepared polymeric nanofiltration composite membranes, named PVDF-12SI, by covering the surface of asymmetric membrane of poly(vinylidene difluoride) with 12 wt.% poly(dimethylsiloxane) solutions in hexane. Interestingly, PVDF-12SI could tolerate harsh conditions (pH ~12, 60 °C, 1.5 MPa) of ethyl ester purification with high stability permitting flux recovery ratios of up to 0.95 after 20 cycles of use. Under these conditions, PVDF-12SI rejected 70% of the glycerol and 69% of the total glyceride with a membrane flux of 7.4 L/m^2/h.

The oily nature and viscosity of crude biodiesel mask the good selectivity and impurities rejection of solvent resistant nanofiltration membranes by minimizing biodiesel permeation and membrane performance efficiency [337]. Nevertheless, the flux permeation may be increased by application of organic-inorganic membranes [337,345]. Such type of void-free membrane is generated by dispersion of inorganic particles into polymeric matrix. Some examples of inorganic particles incorporated into polymeric membranes to form organic-inorganic membranes are hydrotalcite, multiwall carbon nanotubes, ZrO_2, and $Zr(SO_4)_2$ [337,346,347]. Inorganic phase can be used as carrier of catalytic sites (in the case of catalytic membrane in membrane reactors) and/or as support to improve membranes characteristics. Other advantages of organic-inorganic composite membranes are fouling resistance, and good hydrophilicity and selectivity [337]. Peyravi et al. [337] added different concentrations of functionalized multiwall carbon nanotubes in the polyimide casting solution for fabrication of nano-composite solvent resistant membranes. They used these membranes for purification of laboratory synthesized canola-based biodiesel and achieved up to 100% glycerol removal (pH 7, 25 °C, 0.5 MPa).

Transesterification membrane reactors are a type of simultaneous reaction-separation intensification process in which the reaction is integrated with *in situ* membrane separation. In the biodiesel production process, membrane system prevents passing glycerol molecules or rejects the unreacted triglyceride molecules from biodiesel stream [333]. Overall, compared with conventional methods of biodiesel production, the application of membrane reactors provides lower operating cost because there is no need for additional intermediate steps. Cao et al. [333] synthesized biodiesel from various substrates with different FFA contents *via* continuous membrane reactors. They obtained high yields of final product with lower amount of glycerol in comparison with the conventional batch techniques [348,349]. Some other examples of membrane reactors applied for transesterification of oils have been presented in Table 12.

Membrane reactors have two simultaneous functions, *viz.* proceeding transesterification reaction, and separation of undesired compounds such as alcohol, catalysts, and glycerol from biodiesel stream. These roles can be fulfilled through three most popular membrane reactor configurations (Fig. 21), namely, extractor membrane-reactor, distributor membrane-reactor, and flow-through membrane-reactor [354,355]. In the first configuration, the yield of equilibrium-limited reactions is improved by selective removal of the generated products by membrane so that the reaction is shifted towards the products formation (Fig. 21A). The second configuration selectively regulates the concentration of one reactant/reagent that is required in successive reactions with the help of membrane (Fig. 21B). Therefore, distributor membrane-reactor minimizes the side reactions or further conversion of the desired products. In the case of flow-through membrane-reactors, inert or catalytic membranes could be used. In the former, the inert membrane only acts as mixing system by forcing reactants and reagents to flow through the membrane (Fig. 21C) while in the latter, which is the most common configuration used for biodiesel synthesis by alcoholysis reaction in membrane reactor, the catalytic membrane participates in the reaction to generate biodiesel permeate [352,356] (Fig. 21D). Technically, this configuration involves the immobilization of desired catalyst on or into a suitable membrane (such as ceramic or polymeric membrane), which acts as microstructure catalyst carrier and may also perform separation task in the case of integration of pervaporation technique (see further information at the end of this section) or hydrophilic polymeric matrices (glycerol, methanol, and water separation) [351,356]. Mechanical and thermal stability of these membranes can be improved through cross-linking technique with appropriate amount of a suitable compound. Cross-linking is also applied for the generation of catalytic membrane by introducing catalytically active site(s) for performing reactions. For example, the application of cross-linking agents containing sulfonic groups, which also act as active sites, produces more stable catalytic membrane for biodiesel synthesis by alcoholysis of oil [356].

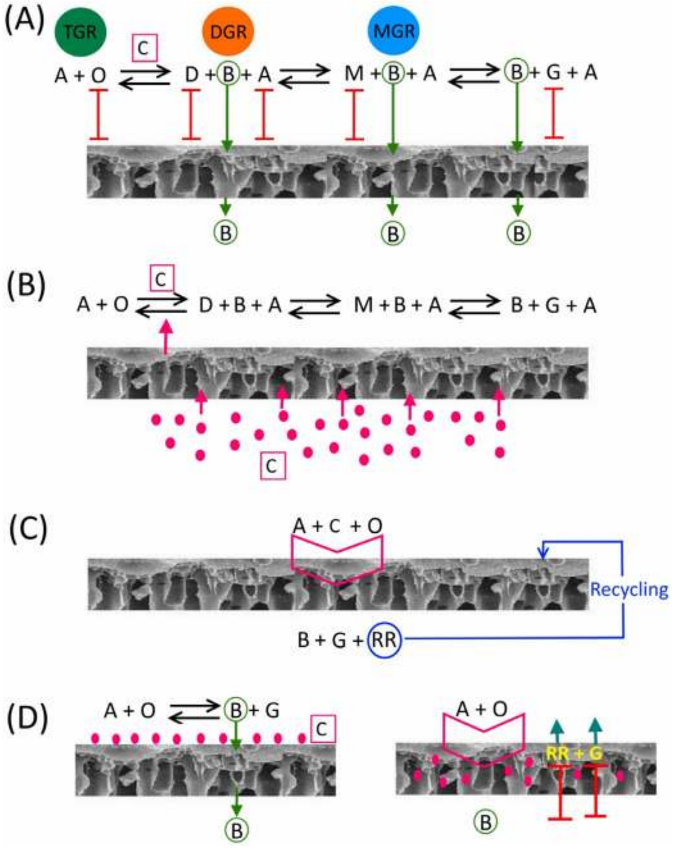

Fig. 21. Some possible roles of membranes in catalytic membrane-reactors for biodiesel synthesis through alcoholysis of oil; A) Improved yield by extractor membrane, B) Improved selectivity by distributor membrane, C) Flow-through inert membrane, and D) Flow-through catalytic membrane with immobilized catalysts on or within the membrane. Abbreviations: A: Alcohol; B: Biodiesel; C: Catalyst; D: Diglyceride; DGR: Diglyceride reaction step; G: Glycerol; M: Monoglyceride; MGR: Monoglyceride reaction step; O: Oil (triglyceride); RR: Remnant (unreacted) reagents/reactants; TGR: Triglyceride reaction step.

As mentioned earlier, membrane reactors can also be classified based on the position of catalyst and membrane into (i) inert membrane reactor and (ii) catalytic membrane reactors. The catalyst is physically separated from the membrane in the inert membrane reactors and the membrane (*e.g.*, ceramic membrane with a microporous structure, carbon membrane, *etc.*) does not directly participate in the reaction, but acts as a barrier to reactant, reagents, and some products. In contrast, in the latter membrane reactor type, either the catalyst is dispersed in the membrane or membrane itself acts as catalyst. Homogeneous catalysts, glycerol, and biodiesel are soluble in methanol whereas the lipid

Table 12
Application examples of membrane reactor for biodiesel production *via* transesterification of oil.

Feedstock	Operation mode	Alcohol	Catalyst	Membrane characteristics	Reaction conditions	Yield	Ref
Catalytic membrane reactors							
Soybean oil	Batch	Methanol (1:5 v/v)	Solid acid (sulfonic groups and acidic active sites)	Flat sheet poly(vinyl alcohol) membrane modified with sulfossucinic acid, 0.8 mmol/g Bronsted acid sites	60 °C, 0.1 MPa, 29 h	ND	[350]
Eruca sativa Gars	Batch	Methanol (1:95)[1]	$H_3PW_{12}O_{40}$	Agarose membrane with 38 wt.% embedded $H_3PW_{12}O_{40}$, SA: 16 cm^2	65 °C, 8 h, 33 mL/min feed flow rate	~90%	[351]
Soybean oil	Continuous	Methanol (1:9)	Na_2SiO_3 and N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride	Polypropylene nonwoven fabric membrane modified with Na_2SiO_3 and N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride, pore size:10–50 µm, SA: 7.95 m^2/g	60 °C, 65 min, 1 mL/min feed flow rate	>97%	[352]
Inert membrane reactors							
Canola oil	Semi-continuous	Methanol (1:11–46)	0.5 wt.% NaOH	Tubular carbon membrane, pore size: 0.05–1.4 µm, ID: 6 mm, L: 12 cm, SA: 0.022 m^2	55 °C, ~0.21 MPa, 2–3.1 h, 3.3 mL/min methanol flow rate	88.9–98.7%	[332]
Canola oil	Continuous	Methanol (1:23.9)	1 wt.% NaOH	Tubular composite ceramic (TiO_2 support), 300 kD molecular weight cut-off	65 °C, 0.276 MPa, 60 min, 50 mL/min methanol-catalyst feed rate, 50 mL/min oil feed rate	55–60%	[333]
Canola oil	Continuous	Methanol (1;24)	0.5 wt.% NaOH	Composite ceramic (TiO_2 support)	65 °C, 0.46 MPa, 5 min, 50 mL/min methanol feed flow rate, 50 mL/h oil feed flow rate	>98%	[335]
Palm oil	Continuous	Methanol (1:1 v/v)	157.04 g KOH supported on activated carbon per unit volume of the reactor	Tubular ceramic TiO_2/Al_2O_3 membrane, pore size:0.05 µm, D: 16 mm, L: 40 cm, SA: 0.0201 m^2	70 °C, 0.21 cm/s cross flow circulation velocity	94%	[336]
Soybean oil	Continuous	Methanol (1:24)	0.27 g/mL MCM-41 supported *p*-toluenesulfonic acid	Ceramic membrane, ID: 6 mm, L: 20 cm	80 °C, 0.08 MPa, 4.15 mL/min circulation velocity	84.1%	[353]
Canola oil	Semi-continuous	Methanol	1 wt.% NaOH	Tubular carbon membrane, pore size: 0.05 µm, ID: 6 mm; L: 12 cm, SA: 0.022 m^2	70 °C, ~0.14 MPa, 6 h, methanol feed flow rate 3.2 mL/min, circulate speed 15.2 mL/min	96%	[303]
Canola oil	Semi-continuous	Methanol	2 wt.% H_2SO_4	Tubular carbon membrane, pore size: 0.05 µm, ID: 6 mm; L: 12 cm, SA: 0.022 m^2	70 °C, ~0.14 MPa, 6 h, methanol feed flow rate 6.1 mL/min, circulate speed 15.2 mL/min	64%	[303]

[1] Alcohol-to-oil molar ratio, unless specified otherwise.

droplets are suspended in the mixture. Inert membrane reactor prevents unreacted lipid to pass through it because the molecular size of lipid molecules differs with soluble elements of the mixture [333,348].

From simultaneous reaction-separation process, catalytic membrane reactors are better choice than inert membrane reactors [354,357]. Catalytic membrane performs separation and conversion through interaction between functional groups of membrane and specific molecules in a mixture. Agarose, polypropylene, and poly(vinyl alcohol) are some examples of membrane that have been respectively applied as supports for catalytically active compounds including Tungstophosphoric acid ($H_3PW_{12}O_{40}$), Na_2SiO_3 and N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride, and acid sulfosuccinic for biodiesel production *via* transesterification of oil (Table 12). In the transesterification process by this type of membrane, methanol and glycerol generate bonds with OH groups of the membrane and are eliminated from the reaction slurry whereas biodiesel and unreacted lipids are rejected by the membrane due to their different chemical structures [334,350]. The suitability of poly(vinyl alcohol) for fabrication of catalytic membranes is due to its inherent ability to be functionalized by acidic functional groups [350]. Poly(vinyl alcohol) and Nafion membranes were experimentally compared with each other for transesterification of soybean oil. According to the results obtained, poly(vinyl alcohol) showed better characteristics as a basic substance for catalytic membrane fabrication [358].

Membrane reactors, particularly organic synthetic hallow fiber or plate-and-frame membranes, can act as good carriers of lipase used in enzymatic transesterification. More specifically, lipase can be immobilized on membrane to form catalytic membrane reactors through adsorption, covalent binding, entrapment, microencapsulation, or their combination thereof [359]. However, it should be noted that the activity of enzyme could be reduced due to loss of enzyme during immobilization process [360]. Moreover, reaction processes with immobilized enzymes have lower mass-transfer, compared with enzyme-free reactions. Despite these drawbacks, improved stability of immobilized enzyme leads to higher economic profitability of overall production process [360].

Among the different enzyme immobilization techniques introduced, adsorption is the most simple and cost-effective technique [360]. In this method, lipase is adsorbed on the surface of membrane through the weak linkages of hydrogen bonds, hydrophobic interaction, ionic binding, and van der Waals interaction. However, this method is also associated with some drawbacks including enzyme loading limitation and convenient desorption of enzyme by aqueous solvent or even due to ionic strength, pH, and temperature of the reaction [359,360]. Covalent binding of lipase to various organic and inorganic carriers is considered as the most advantageous immobilization technique in terms of improved stability of enzymes, high loading capacity, and minimized enzyme leaching issue. Nevertheless, this method is time-consuming and often requires harsh conditions such as toxic coupling reagents that may inactivate enzyme [360]. Overall, very little is available in the published literature on the use of enzymatic membrane reactors for transesterifying oils.

Another technique known as pervaporation may also be coupled with inert or catalytic membrane reactors to separate mixtures of liquid by partial vaporization. Separation based on this technique employs a non-porous dense membrane, composed from zeolite or polymer [361]. In this method, separation occurs based on relative rates of permeation mediated by specific membrane. Pervaporation separation is mostly used for removal of organic substances from an organic or aqueous mixture. The most distinguishable feature of pervaporation method is that both permeation and evaporation occur in one module. The main mechanism to pass the substances is solution-diffusion, which is observed in nonporous membranes [362].

The process flow diagram of a typical inert membrane reactor for biodiesel synthesis by transesterifying oils is depicted in Fig. 22. This configuration normally comprises a packed or fluidized bed of catalysts (in the case of heterogeneous catalyst) or a feedstock/catalyst mixing chamber (in the case of homogeneous catalyst).

The critical parameters which could impact membrane-based biodiesel production include temperature, alcohol-to-oil molar ratio, catalyst dosage, residence time, as well as membrane thickness and pore size. The optimum temperature for biodiesel synthesis *via* a membrane reactor is 50–70 °C depending on oil droplet size [336,363]. Higher temperatures decreases FAME yield by complicating the separation of alcohol and lipid phases due to increases in the homogeneity of the system. It has been demonstrated that elevation in methanol to-oil molar ratio enhance the process yield in membrane reactor and the common methanol to-oil molar ratio in a separation membrane reactor is 24:1 [333,336]. The separation quality in a membrane reactor also depends on catalyst dosage. Increasing the catalyst loading can enhance the reaction conversion through elimination of mass transfer limitation in a membrane reactor [336]. Otherwise, more residence time will be required to compensate for the low amount of catalyst. Another critical factor in membrane reactors is the membrane pore size, which is determined with respect to the molecular size of the compounds of the reaction mixture. In the transesterification reaction, oil droplets have an average size of 12–1400 µm [333]. Therefore, the pore size of membrane should be in the range of 0.05–1.4 µm to prevent passing of oil molecules to the permeate stream [333]. The stage of a reaction is a main factor to determine the membrane thickness. Accordingly, at the initiation of the process, the conversion rate increases with reducing the membrane thickness. However, the membrane thickness has no effect on the reaction rate and conversion at the end of process.

3.2.3.2. Reactive distillation reactors. Traditionally, in reversible liquid-phase reaction, the synthesis of products is induced according to Le Chatlier's principle through recovering of one or more products in a separate process with the help of distillation [364]. Thereafter, the unreacted reagents are recycled back into the reactor for further conversion into products. Alternatively, surplus amount of one reagent (such as alcohol) is added to the process to obtain higher desired product yields (such as biodiesel) by better conversion of other reagents (such as oil) at the expense of higher cost of distillation and recycling process. In contrast, this goal can be achieved *via* continuous removal of the products allowing neat operation of transesterification of oil, *i.e.,* at the stoichiometric molar methanol to-oil ratio of 3:1, pulling the equilibrium to efficient conversions. Although this conventional process is effective for overcoming equilibrium limitations, it significantly increases both capital and operating costs up to several times. Reactive distillation (Fig. 23) is a breakthrough process engineered by merging chemical reaction and product separation (*i.e.,* distillation) in a reactive distillation column and could address the abovementioned challenges.

Technically, in reactive distillation, as the separation is induced by thermal driving forces through distillation, the process is applicable when there is a difference in chemicals' boiling point or vapor pressure [366]. In an ideal scenario, one product is the heaviest and the other one is lightest with reactants as intermediate boiling components [364,366]. The size of the reactive distillation column can be greatly lowered by a deliberate addition of an appropriate entrainer, which selectively reacts with one compound for its simple removal from solution, or increasing the column pressure. The process integrates enthalpy exchange, mass flow, multiple cat-

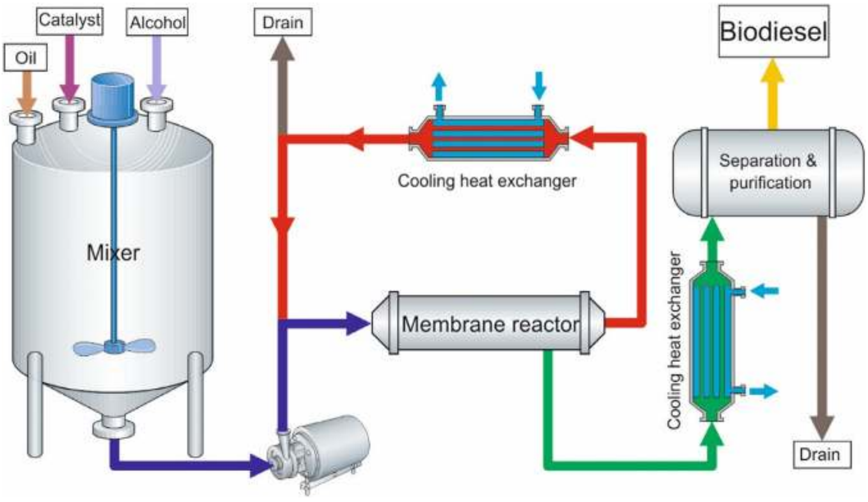

Fig. 22. Process flow diagram of a typical inert membrane reactor for biodiesel synthesis by transesterifying oils.

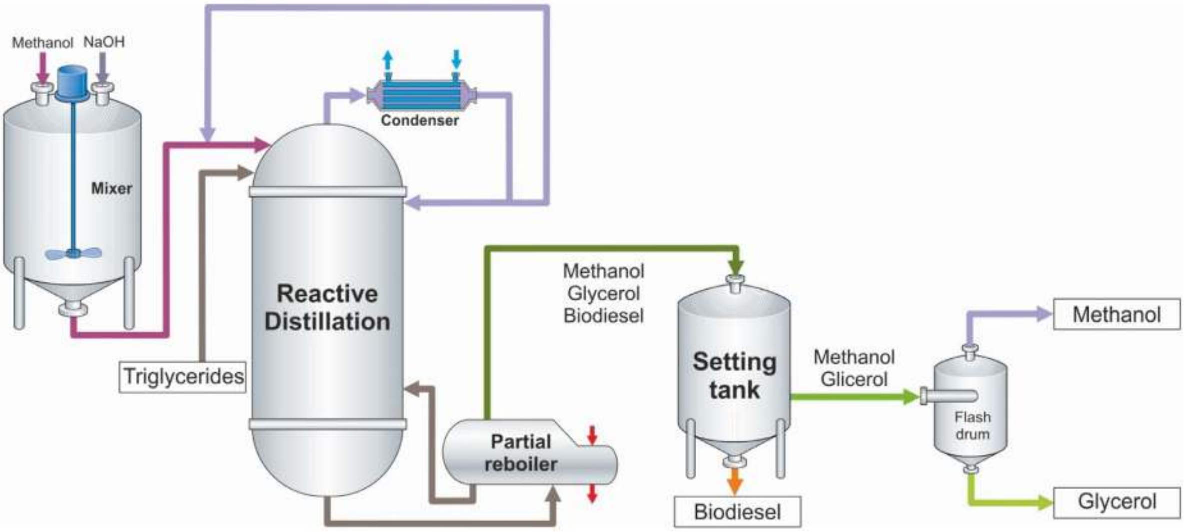

Fig. 23. Basic process flow diagram of a reactive distillation column-based biodiesel production plant. Adopted from [365].

alyst systems, liquid and vapor traffic over the catalyst, and separation into one unit [364]. Reactive distillation has many socio-economic and environmental advantages, including safer process, lower capital (small and simple plant size) and operating costs (20-time faster, maximum conversion, lower energy consumption, long uninterrupted process), and lower emission, over conventional sequential processes.

From the operation point of view, a reactive zone is placed between a rectifying zone and a stripping zone [238]. The distillation column may be packed or be built from a set of distinct stages (trays). Typically, heavier reagents should be supplied at the top of the reactive zone whereas the lighter reagents should be supplied at the bottom of the reactive zone. In the case of biodiesel production, the preheated alcohol and oil can be fed separately into the reactive zone at different stage points or they can be mixed in a pre-reactor to bring the system close to chemical equilibrium, and then, the mixture of products, reagents, and reactants is fed to the mentioned zone [238].

In the case of heterogeneous catalyzed-transesterification, baskets or screens are placed between trays of column to confine the catalyst particles. An alternative solution would be the application of a packed bed prepared with standard catalyst shapes such as rings and saddles. The countercurrent flow in small particles packed bed is intensified by integrating crimped wire meshes into the design with catalyst held between their layers [238]. The transesterification reaction proceeds in the container of agitated fluid on the distillation trays while aerating with alcohol (commonly methanol) vapors produced in a re-boiler. Finally, the products, reagents, and reactants, leave the reactive zone and enter one of the two distillation zones, either rectifying or stripping zones, based on their volatility differences leading to their purification. The rising methanol vapor, produced from unreacted methanol in the re-boiler, takes part in the reaction while also contributing to system agitation (through bubbling) and stripping water from the reaction. This causes increasing concentrations of water and products (glycerol, FAME) towards the top (rectifying zone) and bottom (stripping zone) of the distillation column, respectively (Fig. 24). In the rectifying zone, methanol and water are enriched, sent to condenser, and separated from each other with the help of decanter. Water is removed from the system as distillate whereas methanol is recycled back as a reflux and feeding stream. In the stripping zone, the products, *i.e.,* biodiesel and glycerol are enriched, followed by their heating in a re-boiler and pumping to decanter (settling tank). In the settling tank, biodiesel is separated from the mixture and then methanol is separated from glycerol and other impurities in a flash drum. Methanol is recycled back as vapor into

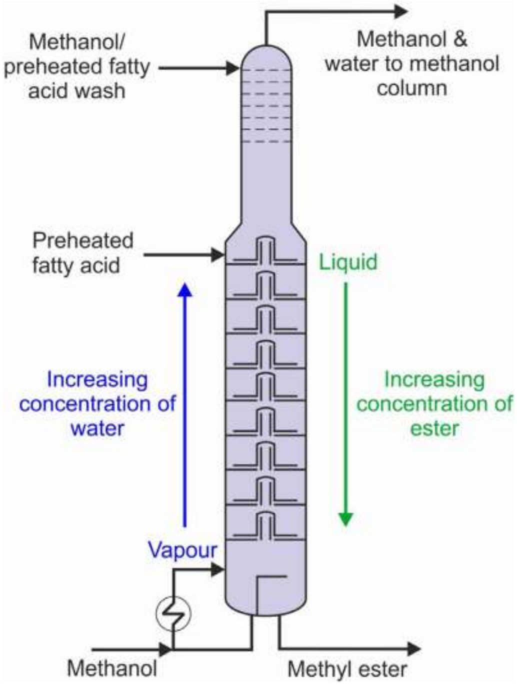

Fig. 24. Separation of water, biodiesel, and glycerol in reactive distillation column by rising methanol vapor within the column.

system. Glycerol can be deliberately purified in another distillation column. If homogeneous catalyst is used, it is introduced at top of column with water and methanol, which must be later decanted from water and recycled back to the column [364].

Reactive distillation is an active field of study for many scientists, concentrating on the process control as well as operation conditions, *i.e.*, agitation intensity, catalysts loading and concentration, condenser, re-boiler duties, feed inlets ratios, reflux ratios, and temperature profiles.

The economic profitability of reactive distillation can be significantly increased by improving heat exchange efficiency and the ability of the system to maintain, adsorb, and recycle back the energy in the form of heat, for example, using thermal coupling method. Such novel integrated process is suitable for a variety of feedstock (palm fatty acid distillate, WCO, and animal tallow) and is associated with reduced heating and cooling demands by 43% and 47%, respectively [367]. Petchsoongsakul et al. [368] designed a single reactive distillation column, packed with amberlyst-15 in top and CaO/Al_2O_3 in bottom as two heterogeneous catalysts, for combined esterification and transesterification processes to continuously produce biodiesel from WCO. The column required four esterification and 20 transesterification stages when operated at atmospheric pressure (0.1 MPa). They reduced the reactive stages from 24 to 8 stages (three esterification stages, five transesterification stages) by increasing the column pressure to 0.3 MPa. Moreover, the developed hybridization process required a net specific energy of 216 kWh/kmol biodiesel, which was 8 and 449 kWh/kmol biodiesel lower than that of two reactive distillation columns in series and conventional process, respectively.

Simasatitkul and Arpornwichanop [369] applied the reactive distillation to convert from palm fatty acid distillate into biodiesel and improved the performance of both reaction and separation phases. Their simulation outcomes showed that a reactive distillation system could discount not only production cost but also total investment cost in comparison with a conventional two–step catalyzed system. In addition, they also concluded that a reactive distillation without upstream recycling offered more benefits compared with a reactive distillation with upstream recycling because of the lower total investment cost and energy requirement [307]. However, a higher production cost was recorded in the absence of upstream recycle (*i.e.*, alcohol recovery). Overall and based on the data presented, it could be deduced that despite the higher total production cost of biodiesel production using reactive distillation without recycling upstream, this process would be the most economical one in terms of return on investment and net present value.

Noshadi et al. [370] continuously converted WCO into biodiesel in a reactive distillation column using methanol in the presence of catalyst 12-tungestophosphoric acid hexahydrate ($H_3PW_{12}O_{40}{\bullet}6H_2O$). Under optimum conditions (10 wt.% catalyst, 67.9:1 methanol to-oil molar ratio, 116.2 mol/h total feed flow, 1.3 kW re-boiler duty), a 94% biodiesel yield was achieved with recycling the catalyst and pure methanol from the product stream and condenser, respectively. This unacceptable large methanol to-oil ratio about 70 may be ascribed to the shortcoming of this research in considering the temperature of reactive distillation column. In better words, more favorable results could have been obtained if the authors had considered higher temperature values beyond the sub-optimal range considered, *i.e.*, 20–30 °C. Moreover, the total flow rate range considered in this study was 115–150 mol/h with the optimum value recorded at 116.2 mol/h. The proximity of the optimum point to the minimum limit of the range could be indicative of the weakness of the boiler duty in delivering high heat energy to quickly raise the temperature of the column. It is noteworthy that feed temperature as well as boiler duty must be carefully assessed as they determine the process yield by directly influencing methanol availability, reaction rate, or biodiesel degradation.

He et al. [205] designed a bench-scale reactive distillation system containing 20 sieve-trays for continuous production of up to 75 mL/min biodiesel (90.7% yield) by methanolysis of canola oil at 65 °C. The catalyst, *i.e.*, $KOCH_3$ was introduced into the system as a mixture (32 wt.%) in methanol feed stream of 11.64 mL/min. The methanol-oil ratio was 4:1 and oil flow rate was 70 mL/min. The hold-up of about 5 min makes this proposed reactive distillation reactor up to 12–36 times faster than the existing industrial batch reactor processes. In another study by Prasertsit et al. [371], a simple lab-scale reactive distillation packed column was applied for KOH catalyzed-methylation of palm oil (1 wt.% KOH, 4.5:1 methanol-to-oil molar ratio, re-boiler temperature of 90 °C, 5 min hold-up in column). Up to 93% biodiesel was produced under these conditions with a requirement for 25% less fresh feed methanol than the conventional process.

3.2.3.3. Annular centrifugal contactors. ACC, also known as centrifugal reactor/contactor, has been developed since more than four decades ago. Its prototype was designed at the Savannah River Laboratory, and Argonne National Laboratory modified it further to produce ACC. Monostage ACC uses single unit for mixing and separation of liquids by means of a vertical centrifuge. Multistage ACC has several mechanical stages and is simply formed by interconnecting several monostage ACCs. The separation is performed due to difference in the specific mass, *i.e.*, density between liquids. The process begins with feeding two immiscible liquids through two separate inlets located close to the top of ACC into narrow annular spaces between the stationary housing wall and spinning rotor. This gap defines the intensity of mixing, liquids volume hold-up, and residence time [372]. In this region, liquids are mixed and chemical reactions occur. Then, the fluid is directed through radial stationary vanes in the housing base toward the rotor bottom, *i.e.*, beginning of separation zone working by action of the spinning rotor. The fluid rotation in a vortex manner is prevented by these vanes. Subsequently, the mixed liquids are accelerated toward the wall as soon as they enter the separation zone with a speed corresponding to that of the rotor. The high-speed rotation facilitates the phases separation by about 300 times, compared with gravity conditions [372]. Moreover, it causes an upward movement of fluid in the separation zone which extends from diverter disk to the lighter phase weir [372–374]. This extended zone allows the required transition time for the formation of a sharp liquid-liquid interface, which in turn split off by flowing over their respective weirs and exit through their respective outlets by gravity. At this point, first mechanical stage is completed and each phase either enters into next mechanical stage and so on (in the case of multistage ACC) or collector (in the case of monostage ACC). A suitable heavy phase weir ring, together with proper rotational speed, is used for positioning the interface midway between the lighter fluid weir and the heavier fluid undercurrent at the uppermost point of the separation zone [374]. This separation strategy is robust in response to slight changes in liquid ratios or flow rate as the efficiency of separation is not reduced by considerable shift in distance of interface position. In contrast, bulk flow rate, density, and viscosity of two liquids with respect to reaction temperature and rotational speed must be considered for an optimized performance. Moreover, it should be mentioned that Taylor number which defines the significance of inertial forces (centrifugal forces) depends on rotation direction, radius ratio of the cylinders, and column height.

The main challenge in ACC is their uncontrollable and extremely low residence time (up to 10 s) that does not allow complete transesterification reaction. This drawback can be partially addressed by using additional delay loops and processing. Alternatively, Wardle [372] reported that an improvement in mixing zone residence time and generation of smaller droplet size could be obtained through operating ACCs at less than half of its maximum capacity with a four straight vane design. This approach lowers the flow rates, and hence, increases hold-up volume as well as overall performance in processes with kinetic limitation [310]. Nu-Energie, LLC with cooperation of Oak Ridge National Laboratory developed a novel ACC to increase the residence time to several minutes [375–377]. For this purpose, they decreased the pumping rate from the outer chamber to inner chamber by modifying the inlet between the mixing and separation zones. Additionally, this variation of ACC could provide convenient reagent addition (methoxide/methanol), online sampling, and monitoring of the transesterification reaction due to incorporation of recirculation and sampling zones into the design [375,376]. For batch production of biodiesel by this modified ACC, two liquid phases, *i.e.,* soybean oil and methanol including base catalyst were separately supplied to the reactor. They were mixed and reacted with each other in the mixing zone (0.6 wt.%, 5.1:1 methanol-to-oil molar ratio, 0.26 MPa, 80 °C, 3600 rpm, 2 min) and then, the immiscible products, *i.e.*, methyl esters and glycerol were recovered in the separation zone and collected by their respective weirs. It was reported that after a single-pass, ASTM specifications for bound acylglycerides were reached; higher quality biodiesel could be achieved through the second and third passes of the biodiesel obtained in the previous pass with minor addition of methanol [375]. Moreover, the yield could be increased to as high as 95% by a total of 10 min residence time, *i.e.*, five consecutive stages (5×2 min) with addition of methanol only in first stage [375,376]. It was also reported that at 60 °C and 4200 rpm and by increasing the pressure of system, a continuous production of ASTM-passed biodiesel in the ACC could be achieved with 1 min residence time [375].

CINC Industries also designed a series of liquid-liquid ACC with a capacity of 1.9–757 L/min (Fig. 25). This series provides a good environment for batch or continuous chemical processes and performs neutralization and separation in one-step with optimum mass transfer to reduce solvent usage. The device is equipped with an internal clean-in-place system, allowing easy and quick cleaning of the reactor with no need for disassembling.

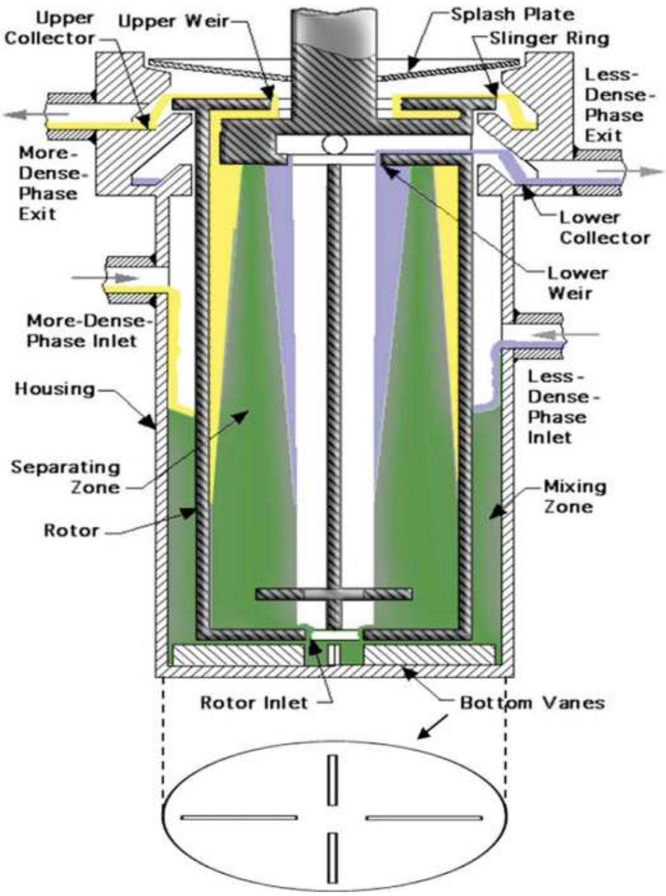

Fig. 25. Schematic cross section of the ACC designed and fabricated by CINC Industries [267].

The performance of the CINC ACC, particularly CINC V02, for continuous synthesis of biodiesel has been examined by some scientists. For instance, Kraaj et al. [378] fed a CINC V02 with two separate feed streams; a stream of sunflower oil and a solution of sodium methoxide in methanol, with flow rates of 12.6 mL/min and 3.1 mL/min, respectively. Under optimum conditions (1 wt.% CH_3NaO, 6:1 methanol-to-oil molar ratio, 60 °C, 2400 rpm), a continuous production of biodiesel with a yield of 96% was delivered. Similarly, Abduh et al. [379] achieved a biodiesel yield of 98 mol% with a volumetric production fatty acid ethyl ester (FAEE) of $112\ kg/m^3{}_{liquid}/min$ through sodium ethoxide catalyzed-ethylation of *J. curcas* L. oil at optimum conditions (1 wt.% C_2H_5ONa, 6:1 ethanol-to-oil molar ratio, 60 °C, 2100 rpm, 28 mL/min oil flow rate, 10.3 mL/min ethanol flow rate containing dissolved C_2H_5ONa) in a CINC V02. In this study, the ACC provided a similar conversion yield corresponding to about 57% less than standard yield that obtained with optimized batch reactor. However, the process was found suitable for small-scale mobilized biodiesel units with appreciable robustness, size, and flexibility in production.

3.2.4. Cavitational reactors

Two types of energy, acoustic or flow energy, are used in cavitational reactors to intensify chemical processes through the cavitation phenomenon [380]. The other two types of energy, *i.e.,* optic or particle energy are not appropriate for induction of good chemical and physical intensification of reactions [380]. The formation of cavities, their subsequent growth, and their collapse release huge energies over a very small area leading to large energy densities, which in turn efficiently improve the physical and chemical characteristics of reaction [380]. In better words, as a result of the simultaneous incidents of cavitation (at ambient conditions) within the reactor, local hot spots with over hundred mega Pascal pressure and thousands Celsius temperature are formed. The cavitation also facilitates the transport process (mixing intensity) through promotion of micro-turbulent eddies, shock waves, and acoustic streaming (liquid micro-circulation) [380–382]. Additionally, free radicals responsible for chemical transformation are probably formed under this condition. Maximum size and life of the cavity are the two important characteristics of any cavitational reaction which respectively determine the amount of pressure pulse upon collapse of the cavity and active volume of the reactor [380,383]. Therefore, various parameters must be optimized to increase these quantities for maximum intensification of the process [380]. During the transesterification of oils, very fine emulsions are generated due to disruption and mixing caused by cavitational collapse near or at the two liquids interface. Consequently, the surface area at which alcohol, catalyst, and oil interact with each other is increased, followed by an increase in the reaction rate. The advantages of cavitation as an emulsifying technique is the generation of smaller and more stable emulsions than conventional techniques in the presence of little to no surfactant, which is perfect for biphasic systems or PTC technique.

3.2.4.1. Sonochemical/ultrasonic reactors. These reactors are based on acoustic cavitation which involves sonochemistry, *i.e.,* enhancing chemical reaction due to modification in pressure through the passage of sound waves. The most common sound waves are ultrasound in the range of 16 kHz to 100 MHz [380]. Complete sinusoidal waves including both expansion (positive pressure) and constriction (negative pressure) generate sonoluminescence bubbles (vacuum micro regions filled with reagent vapors). In contrast to the number of cavitation bubbles, the size of cavitation bubble, and hence, energy released by bubble implosion has an inverse relationship with the ultrasonic frequency. Cavitation occurs as the formed bubbles expand and collapse [384]. With respect to biofuel production, ultrasound-assisted technologies have been proven to be beneficiary far beyond the scope of esterification/transesterification reactions [385]. It is crucial to appropriately select energy intensity in relation with average behavior of bubbles, control active cavitation population (cavitational efficiency), and provide uniform distribution of the ultrasonic activity for an efficient utilization of ultrasonic energy as well as cavitational effects [380,385]. Every ultrasound-assisted reaction consists of three main steps [386]. In the first step, electrical energy is converted into mechanical energy by means of piezoelectric or piezomagnetic transducers. Then, acoustic energy is transmitted from the emission tip to the medium in the second step, followed by energy conversion to the final form leading to the chemical transformation in the last step. Any energy loss during these three steps reduces the overall process efficiency [386].

Different aspects should be considered while designing ultrasound-assisted reactive systems including angle, depth and position of probe with respect to geometry, size and working capacity of reactor, quantity and output densities of transducers, as well as skin morphology and shape of probe [387–389]. For example, cavitational blocking phenomenon, which is observed when power densities near to the emission tip are very high, can be avoided by using several low-output transducers. Moreover, in multi-transducer systems, lower erosion and particle shedding is observed as the ultrasonic intensity is concentrated on the central axis and away from the vessel walls [380]. Manickam et al. [390] compared single, dual, and triple sonochemical frequencies and obtained the highest yield of palm oil conversion into biodiesel using triple frequency operation in the hexagonal reactor design (Fig. 26). They successfully decreased the reaction time to 15 min with a yield as high as 93%, compared with a 3 h conventional stirring process with a biodiesel yield of 75%. However, further improvements in yield were not economically feasible due to higher costs of downstream processes.

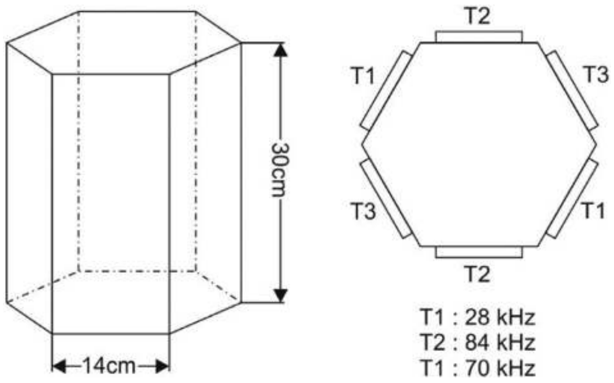

Fig. 26. Hexagonal configuration for ultrasound assisted biodiesel production reactor [390]. With permission from Elsevier. Copyright© 2018.

Ultrasonic horn reactors are the most common sonochemical reactor design [380], which typically utilize an immersion type of transducers to produce very high pressure intensities next to the horn. The intensity is lowered exponentially by increasing the distance from horn depending on the operating frequency and power input [391]. The efficiency of this sonochemical reactor design is enhanced either by constraint of liquid within longitudinal high-intensity region or vigorous mixing of liquid. Two variations of this design are sonochemical reactors with concentrator horn and those with telsonic horn (with radial vibrations) [392,393]. Complex scale up, erosion and particle shedding on the surface of emission tip, and cavitational blocking are among the main disadvantages of this design and its variations.

Bhangu et al. [394] speeded up *Candida rugosa*-derived lipase-catalyzed transesterification of canola oil from 22–24 h to 90 min by applying a 3.5 cm ultrasonic horn (40 W, 20 kHz frequency). The second common sonochemical design, *i.e.,* ultrasonic bath (cleaner) reactor consists of an ultrasonic bath encompassing the bottom of the reactor. The irradiation of the working liquid is conducted by single or multiple transducers. This configuration limits the active zone to a vertical plane on top of the transducers with the highest intensity at the center of transducer [380]. Therefore, increasing the bottom surface area of the reactor increases the irradiating surface, and hence, improves the emission of sonochemical energy in the reactor. Consequently, a higher pressure intensity is obtained with lower ultrasonic intensity at the end of the cavitation process [395]. Other configurations or sonochemical designs include (i) tubular reactors with one transducer and one reflector at opposite ends or one transducer at each end, (ii) transducers on each side of a hexagon, and (iii) parallel plate reactors each irradiating with different or same frequency [380].

Sonochemical reactors result in better transesterification operation parameters, including lower alcohol-to-oil molar ratios, lower catalyst concentrations, lower temperatures, shorter residence times, than conventional processes [382]. For homogeneous catalyzed-batch transesterification processes, the intensification is mainly achieved by replacing magnetic or mechanical stirring devices with ultrasonic probes. Feedstock streams of catalyst and raw substances are generally mixed in an individual pretreatment chamber. Ultrasonic irradiation step could be followed by different downstream separation/purification scenarios. The process flow diagram of a typical of homogeneous ultrasound-assisted biodiesel production system is represented in Fig. 27.

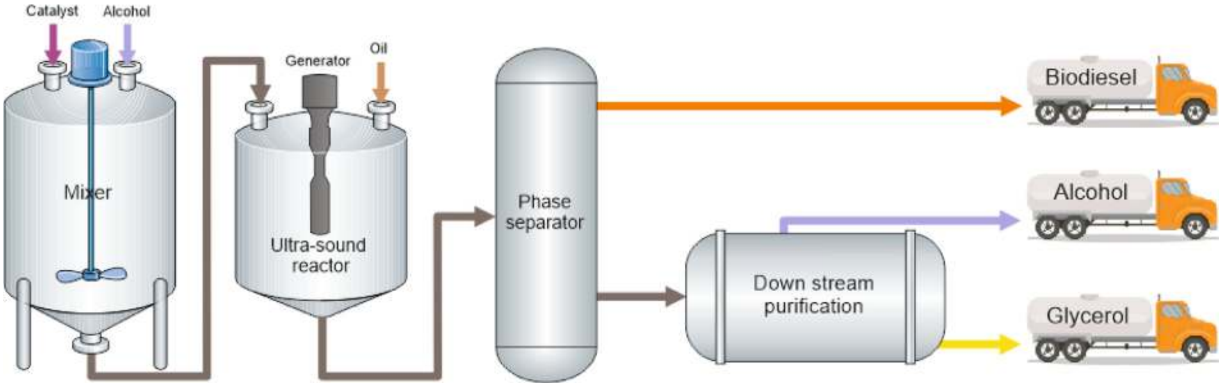

Fig. 27. A typical process flow diagram of homogeneous ultrasound-assisted biodiesel production system.

Georgogianni et al. [396] compared different homogeneous and heterogeneous catalysts during ultrasound-assisted synthesis of rapeseed biodiesel. Amongst Mg-MCM-41, Mg–Al hydrotalcite, K-impregnated zirconia, and NaOH, the last catalyst led to the lowest mass resistance and highest efficiency. Sequential ultrasound and microwave irradiation was studied by Hsiao et al. [397] for converting rapeseed oil into biodiesel in the presence of NaOH in a step-wise process of 1 min ultrasound and 2 min microwave irradiation. They reported that the method quite was successful for biodiesel production due to lower energy requirements, lower operation temperature, as well as elimination of mechanical stirring and cooling systems.

Sáez et al. [398] emphasized on the significance of appropriate fatty acid compositions of oil feedstocks for batch sonochemical biodiesel production (20 kHz frequency). Accordingly, shorter hydrocarbon chains and higher saturation resulted in higher production of FAME and lower glyceride concentrations *vs.* when longer hydrocarbon chains and unsaturated fatty acids were used. They also emphasized that the combination of three ultrasound amplitude cycles (generated by an ultrasonic probe at 20 kHz frequency, 50% amplitude, and 70% duty cycle) with two 5-min agitation intervals conducted at 900 rpm for 13 min and 48 s at 50 °C was an efficient method for transesterification of vegetable oils [352]. Recently, a high-frequency, energy-efficient piezoelectric ultrasonic reactor was introduced and analyzed from technical, energetic, exergetic, exergoeconomic, and exergoenvironmental viewpoints and optimized using advanced soft computing techniques [11,132,399,400].

Table 13 presents more examples of sonochemical production of biodiesel. Accordingly, it can be deduced that methanol, calcium oxide, and potassium hydroxide are the most frequently used alcohol, heterogeneous catalyst, and homogeneous catalyst, respectively. It is worth mentioning that alcohol molecular size and structure could have significant effect on the transesterification reaction [283]. More specifically, as the number of carbons in alcohol structure increases, transfer of ester molecules formed in the glyceride phase will be hindered more [283]. Additionally, primary straight chain alcohols are the most suitable structure of alcohols among primary, secondary, and tertiary alcohols [401,402].

Arisdyne System, Inc. has developed a commercial retrofit biodiesel reactor, called controlled flow cavitation (CFC^{TM}) process, based on sonochemical cavitation to form micro droplets and subsequent emulsion. The process provides a tight control with repeatable droplet size distribution, delivers lower amount of monoglycerides with no increase in catalyst concentration, and reduces residence time and catalyst consumption (up to 25%) [413]. The advantages of this add on the reactor are efficient and rapid process, simple installation, little pipefitting and small space requirements, and low maintenance. Similarly, Hielscher Company supplies continuous biodiesel processing equipment based on ultrasound technology. In their technology, the oil is heated (45–65 °C) and continuously mixed with catalyst by adjustable pumps and an inline static mixer. The mixture receives 5–30 s ultrasonic cavitation exposures (up to 16 kW power, 20 kHz) by passing through the flow cell. Then, it enters a reactor column for allowing the transesterification reaction to complete (60 min retention time). Finally, the mixture is subjected to centrifugation to separate the biodiesel and glycerol [413].

3.2.4.2. Hydrodynamic cavitation reactors. The second type of cavitational reactors is hydrodynamic cavitation reactors, mainly consisting of a pump and a constriction channel or interface, located at the downstream of the pump's discharge. Similar to sonochemical reactors, these reactors also enhance the reaction rate through cavity formations by pressure variations. These pressure variations, unlike acoustic cavitation, are generated by using specific geometry of the system that causes velocity variation when a high flow of fluid passes through the constriction channels/interface (orifice, throttling valve, venture, *etc.*) [414]. This passage elevates the velocity of stream at the expense of its pressure. A permanent loss in pressure is resulted because of the generation of eddies motion. Once pressure drops below the cavitation threshold pressure (vapor pressure in the liquid at reaction temperature) millions of cavities are produced [380]. As the stream proceeds, the pressure recovers partially and the cavities collapse leading to an intense local agitation [380,415]. The number of cavities can be modified by opening the valve fully or partially. Moreover, flow rate can be controlled with the help of a bypass [416]. Irreversible loss in pressure head and friction as well as turbulence loss are the principal factors affecting the cost of fluid pumping.

The advantages of hydrodynamic cavitation reactors are their simplicity with respect to design, structure, operation, maintenance, and immediate scale-up [416]. Moreover, this type of reactors provides a specific reaction or physical condition through modification of pressure and temperature pulses. These pulses can be adjusted by manipulation of bubble behavior through physical and geometrical parameters, for examples, discharge pressure, diameter ratio of constriction channel to pipe, and the dimensions of the pipe located downstream of the constriction channel [416]. In contrast to linear pressure change in the case of permanent orifice, a rotating valve can be applied to exert a sinusoidal varying pressure field on bubbles that are generated at the shear layer. Additionally, bubbles with more violent collapse (large pressure and temperature pulses) can be obtained through installation of two or three successive orifices to develop a fluctuating pressure field at the shear layer [416]. Compared with acoustic cavitation, hydrodynamic cavitation leads to lower erosion issues because the cavitation takes place at the shear layer in bulk [416]. An intense

Table 13
Examples of sonochemical reactors used for transesterification of different oils into biodiesel.

Feedstock	Alcohol	Catalyst	Conditions	Ultrasonic specifications	Yield	Highlights	Ref.
Homogeneous catalyzed transesterification of oil							
Jatropha oil	Methanol (1:5)[1]	0.5 wt.% KOH	Ambient temperature, 7 min	100 W (50% amplitude), 20 kHz, pulse 0.3 s cycle	97.6%	Higher yields and 10–20 times faster downstream separation was achieved in comparison with the conventional transesterification. The ultrasound radiator was compatible with CSTR and plug flow systems.	[403]
Silybum marianum oil	Methanol/ethanol (1:8)	1.5 wt.% KOH	60 °C, 20 min	250 W, 40 kHz	95.7%	The production of FAEE required 50% longer residence time and 20 °C higher reaction temperature while delivering 3.4% lower biodiesel yield than FAME production.	[404]
Palm oil	Ethanol (1:9–11)	1.5–1.7 wt.% KOH	35–40 °C	1.5 kW, 20 kHz	92%	The process was continuous mode. Higher temperatures led to reduction of viscosity and consequently reduction of cavitational activity. When the primary cause of the activation was cavitational collapse, a low operating temperature was advantageous. Higher values than the reported reagents molar ratios led to the lower accessibility of ethoxy groups to triglycerides.	[405]
Muskmelon oil	Methanol (1:6.6)	1.15 wt.% KOH	41.9 °C, 3.56 min	400 W, 20 kHz	97.9%	Artificial neural network approach provided superior simulating efficiency than response surface methodology.	[406]
Heterogeneous catalyzed transesterification of oil							
Sesame oil	Methanol (1:6.7)	1.8 wt.% $Ba(OH)_2$	31.9 °C, 40.3 min	1.2 kW, 20 kHz	98.6%	Higher temperatures than the optimum value retarded the extent of cavitational effect and reaction rate. Artificial neural network showed more accurate prediction over response surface methodology.	[407]
Palm oil	Methanol (1:9)	8 wt.% CaO	60 min	120 W, 20 kHz	92.7%	–	[408]
Jatropha oil	Methanol (1:11)	5.5 wt.% CaO	64 °C	35 W, 35 kHz	95%	Alcohol-to-oil molar ratio and catalyst concentration were reportedly influenced the efficiency due to the formation of methoxy ions. Ultrasound sonication had marked impact on the transesterification reaction but no effect on the esterification reaction. Four times higher activation energy was required for the heterogeneous-catalyzed reaction than its homogeneous counterpart.	[409]
Jatropha crude oil	Methanol (1:20)	20 wt.% activated carbon-supported heteropolyacid	60 °C, 40 min	300 W, 20 kHz (with 10 s on and 3 s off working pattern)	87.3%	High tolerance to FFA and water contents in the oil was observed.	[410]
Soybean oil	Methanol (1:7)	7 wt.% Magnetic $NaSiO_3@Fe_3O_4/C$	54 °C, 80 min	4.5 W/mL (27 W), 20–25 kHz	97.9%	Magnetic catalysts were reused for five reactive cycles with 94.9% recovery with biodiesel yield more than 80%. Replacement of soybean with Jatropha oil resulted in 94.7% yield under same conditions.	[411]

(*continued on next page*)

Table 13 (*continued*)

Feedstock	Alcohol	Catalyst	Conditions	Ultrasonic specifications	Yield	Highlights	Ref.
Soybean oil	Methanol (1:10)	6 wt.% CaO	62 °C, 60 min	35 W, 35 kHz	90%	Three-phase heterogeneity of the system increased the activation energy compared with the homogeneous-catalyzed system. At temperatures close to boiling point of alcohol, sonochemical system facilitated the reaction through ultrasonic micro-streaming rather than cavitation bubble.	[412]
Canola oil	Methanol (1:7.5)	5.3 wt.% CaO	60 °C, 2.5 h	40 W	99.4%	–	[83]

[1] Alcohol-to-oil molar ratio.

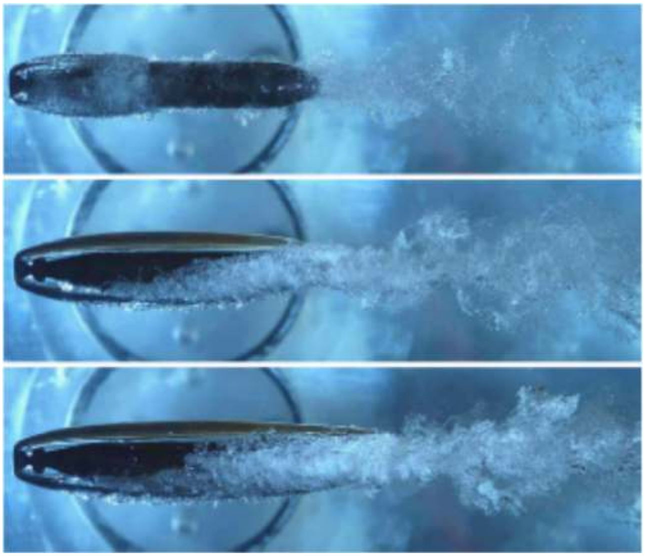

Fig. 28. Formation, growth and collapse of the cavity [209]. With permission from Elsevier. Copyright© 2018.

turbulence and the subsequent uniform cavitation throughout the reactor allow efficient conduction of reactions requiring milder conditions of pressure and temperature. Interestingly, hydrodynamic cavitation requires up to 10 times lower energy input per unit of reactant/reagent volume than ultrasound cavitation [380,416]. Compared with conventional mixing processes, hydrodynamic cavitation is a more cost-effective alternative as it reduces the energy consumption by more than half [417]. Formation, growth, and collapse of hydrodynamic cavities (Fig. 28) release an energy density equal to 1×10^{18} kW/m^3 [418].

Pal et al. [417] used a hydrodynamic cavitation system consisting of a feed tank, a pump, an orifice, and control valves to produce biodiesel with Thumba (*Citrullus colocyntis*) oil. The process achieved 80% yield within 30 min residence time. Same process approach was reported by Gole et al. [419] who esterified and transesterified non-edible *Nagchampa* oil. In the transesterification step, 20 min treatment of pre-esterified oil with 1 wt.% KOH and 6:1 alcohol-to-oil ratio yielded 92.1% biodiesel. Sunflower oil was successfully transesterified into biodiesel (1% w/w NaOH, 6:1 methanol-to-oil ratio, ~8450 rpm, 0.86 L/min inlet flow rate, 3.5 min) with a yield of 88% using hydrodynamic cavitation reactor [420]. Bokhari et al. [421] also used a hydrodynamic cavitation for cleaner synthesis of rubber seed (*Hevea brasiliensis*) oil methyl ester. They synthesized FAME with 96.5% yield in 50 L pilot hydrodynamic cavitation reactor consisting of orifice plate with 21 holes of 1 mm each and inlet pressure of 0.3 MPa (1 wt.% KOH, 6:1 alcohol-to-oil molar ratio, 55 °C, 18 min). Compared with mechanical stirring, hydrodynamic cavitation resulted in up to 4.9, 5, and 6.5 times higher rate constant, less reaction time, and higher energy efficiency, respectively [421]. It should be pointed out that pressures beyond the optimum condition could lead to the chocked cavitation phenomenon in which downstream is filled with a cavity cloud resulting in liquid scape without collapsing, and consequently reduced microturbulence and conversion [422].

3.2.4.3. Shockwave power reactors. SPRs (Fig. 29A) are in fact rotating hydrodynamic reactors that have a rotor with dead ended cavities (Fig. 29C). Low pressure zones are created at the bottom of the cavities due to rotor spinning [423]. Therefore, micro-cavities are formed as the mixture of methanol and catalyst is fed into the machine housing and passed through the specially designed rotor [209]. The collapse of these low pressure zones leads to collapse of micro-cavities and heat and/or mass transfer, a process known as shockwaves. The cavitation is controlled and is away from the metal surfaces to minimize the corrosion damage (Fig. 29B). Hydro Dynamics, Inc. supplies SPRs in various models for biodiesel production with annual input capacity ranging from 3–495 kton based on continuous flow and 95% uptime [423]. Various feedstocks such as beef tallow, poultry fat, and low-grade soybean oil can be utilized and the process can be handled either in batch or continuous mode. SPRs also have the advantages of the conventional hydrodynamic cavitation reactors mentioned in the previous section.

3.2.5. Microwave reactors

Microwave is an electromagnetic base irradiation with wavelengths ranging from 0.01 to 1 m and the corresponding frequencies of 0.03 to 300 GHz [424]. The advantages of microwave irradiation (*i.e.,* simple control, time and thermal efficiencies, clean products, and less downstream processing) as well as microwave-effect were partially explained under Section 2.3.1. In spite of its promising features, one of the main problems associated with microwave reactors is the difficulty of controlling power and temperature, and hence, low process reproducibility [425,426]. A microwave reactor consists of a microwave source equipped with a power supply and controls (the duty cycle) that transfer the electromagnetic energy through either coaxial cables (for lower power) or waveguide (for higher power) into the chemical reactor, enclosed within an applicator (a metallic cavity) [426,427]. The reactor vessel or tube can be constructed from various materials such as polytetrafluoroethylene, polyether ether ketone, quartz, or silicon carbide which are transparent or adsorptive of microwave energy, allowing heating of reactants/reagents directly or indirectly, respectively. In commercial microwave ovens, stirrers are used or the reactor vessel is rotated to homogenize the electric field profile [426,428]. These reactors are also equipped with online pressure and temperature control systems and have a specific geometry design with respect to the penetration depth. All commercial microwave reactors support pressures and temperatures up to 3–8 MPa and 250–300 °C, respectively [426]. Generally, the reaction is completed within several minutes, although microwave reactors have the ability to be operated for longer times (several hours).

Biodiesel production can be assisted with microwave energy through two main routes, including oil extraction from some feedstocks [429,430] and transesterification reaction of oil into biodiesel. The second route has been discussed hereafter in which microwave irradiation is mainly used as an alternative for heating system (see also Section 2.3.2). Conventional heating, *i.e.,* wall heating and microwave heating have been illustrated in Fig. 30.

The thermal energy is produced due to dipole reorientation (polarization) [432]. Under this condition, atomic or electronic polarization, *i.e.,* displacement of electrons around atoms or nuclei occurs trillion times per second when polar molecules are exposed to microwave irradiations. Heat is generated as a result of friction between rotating molecules. The other two mechanisms for microwave heating are Maxwell-Wagner and conduction [432,433].

The best alcohol as acyl acceptor for microwave-assisted biodiesel production is methanol due to the presence of –OH group providing polar characteristics as well as anchoring behavior [434]. Consequently, more localized rotation of methanol molecules induces more superheating capability. This allows more rapid reaction with better performance and lower costs than other alcohols, for example ethanol [435]. The sustainability of microwave-assisted biodiesel production system was studied through comparison of the electrical energy demands of microwave generator and mixers during biodiesel production with the electricity generated through the combustion of the produced biodiesels [424]. Based on the reported findings, the microwave-assisted biodiesel production gen-

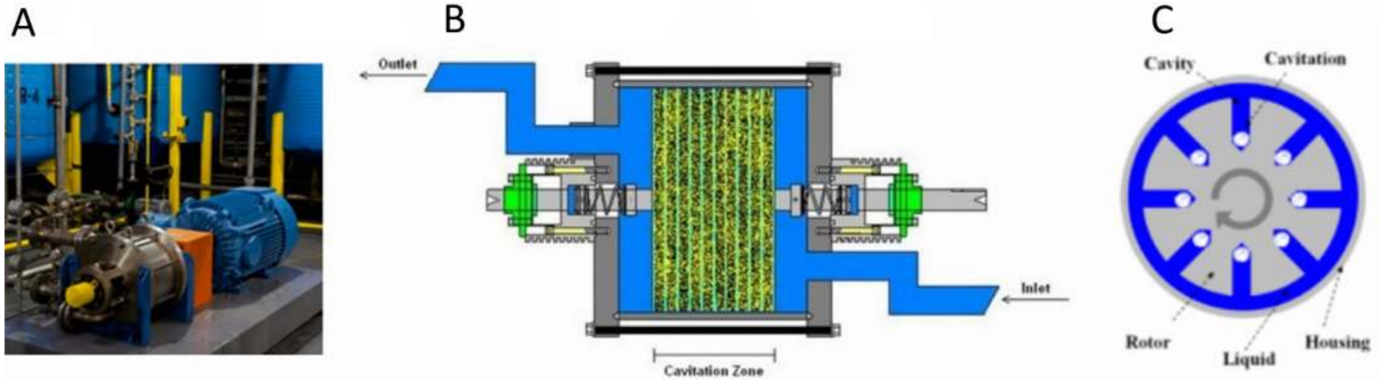

Fig. 29. A) Shockwave power reactor, B) Schematic of its working principle, and C) rotor with dead ended cavities. Courtesy of Hydro Dynamics, Inc. https://www.hydrodynamics.com.

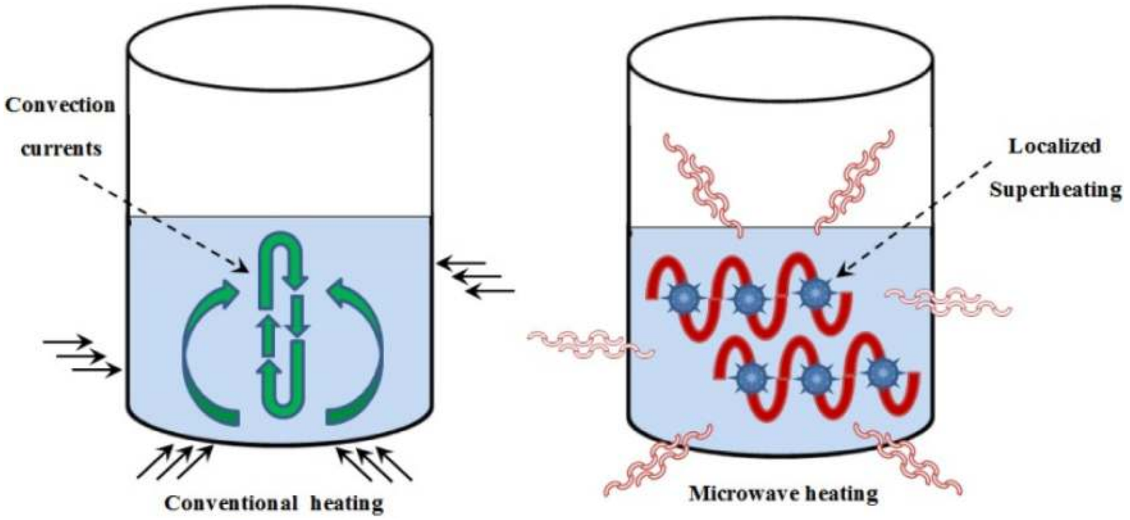

Fig. 30. Conventional wall heating *vs.* microwave heating [431].

erated an extra electrical energy of 1.66 kWh per kg of biodiesel after combustion.

Scares et al. [436] obtained an ethyl ester yield of 84% by transesterifying soybean oil in a continuous flow microwave reactor under optimum conditions (1 wt.% NaOH, 9:1 ethanol-to-oil molar ratio, 42.5 L/h flow rate, 56.4 °C, 33 s, 1000 W microwave power). Panadare and Rathod [437] also investigated the microwave-assisted enzymatic (lipase 435) synthesis of biodiesel from WCO and dimethyl carbonate. The reaction was completed in 4 h, resulting in a biodiesel yield of up to 94%. Milano et al. [158] successfully transesterified a mixture of *Calophyllum inophyllum* and WCO (yield of about 97%) using Anton Paar Monowave 400 high-performance microwave reactor (0.77 wt.% KOH, 59.6 vol.% methanol-to-oil ratio, 600 rpm, 100 °C, 7.15 min). Thirugnanasambandham and Sivakumar [438] also obtained a high conversion yield of 99.5% by transesterifying cotton seed oil in the presence of undetermined amount of KOH (17:1 ethanol-to-oil molar ratio, 70 °C, 380 rpm, 12 min, 270 W microwave power).

Microwave irradiation has also been used for *in situ* transesterification of microalgae in combination with ultrasound or ionic liquid (see Section 2.3.3) [172,439]. For instance, Ma et al. [439] directly transesterified *Chlorella vulgaris* microalgae in the presence of heterogeneous KF/CaO catalyst in a ultrasound-microwave-assisted process. A biodiesel yield of 93% was reached under the optimum conditions (12 wt.% catalyst, 8:1 methanol-to-oil molar ratio, 60 °C, 45 min).

4. Environmental sustainability, economic viability, and policy-making aspects of biodiesel

4.1. Economic aspects and impacts of biodiesel production

The total investment cost for any biodiesel production plants includes capital investment and operating costs. Briefly, the former could be estimated through different methods, *viz.*, class 1 (*i.e.*, detailed estimates), class 2 (*i.e.*, definitive estimates), class 3 (*i.e.*, preliminary estimates), class 4 (*i.e.*, study estimates), and class 5 (*i.e.*, order-of-magnitude estimates) [440,441]. Of these, study estimate is the most commonly applied approach for determination of the cost of capital investment for biodiesel production [440–443]. This approach is useful for preliminary feasibility assessment of different scenarios [440] with respect to the direct plant costs (*i.e.*, piping, instrumentation, electrical facilities, auxiliary facilities, equipment installation, and yard improvement) and equipment purchasing costs [441]. Therefore, the accuracy of this estimation greatly relies on the precise design of the complete process flow, selection of equipment type (their construction materials and size), considering their most updated and adjusted prices, and execution of energy and material balances [440,441,444].

Total equipment costs for biodiesel production have been estimated by different researchers [440,442]. For instances, Turton et al. [440] used the formula $C^{\circ}_{R} = 15{,}000\,V^{.55}$ (V is volume) for calculation of the fixed on board cost of each type of equipment investigated in the design whereas Haas et al. [442] developed an estimation method based on Chemcost Capital Cost and Profitability Analysis Software as well as Cost Data Online (*i.e.,* Richardson Construction Estimating Standards). In addition to the direct plant costs and equipment purchasing costs, other criteria determining the total investment cost include direct (*i.e.,* materials and labor for installation) and indirect (*i.e.,* purchased taxes, insurance and transportation, contractor fee, auxiliary facilities, and construction overhead) expenses. Therefore, following the screening of the alternative processes by study estimates, the capital cost required for a profitable process is estimated using preliminary estimates by incorporation of the mentioned criteria on the basis of percentage allocation of the total equipment purchasing cost [440,441]. For instances, a percentage allocation method has been used in Chilton and Holland methods for estimating direct plant costs for biodiesel production processes [445].

Another cost associated with any biodiesel production plants is the operating cost which includes costs of repairs, maintenance, labor, utilities, and raw materials. Of these, raw materials (*e.g.,* alcohol, oil, catalyst, wash water, *etc.*) constitute the largest fraction of the operating cost [441]. The cost of raw materials for any given plants could be estimated by knowing the capacity of the biodiesel production plant and the final proportions of these materials in the transesterification reaction. Moreover, utilities consumption could be estimated according to the energy balance of transesterification reaction and is dependent on size and type of equipment and the applied process [441,446]. As mentioned earlier, the current high cost of biodiesel is mainly due to the high cost of feedstock, which may hinder its large-scale production as well. As an example, the cost of feedstock for small and large scale biodiesel production plants contributed up to 75% and 90% of the total production cost, respectively [440,441]. In another study [442], soy feedstock cost amounted approximately to 88% of the total biodiesel production expenses scored. Typically, annual operating cost of a biodiesel plant is the sum of the costs of raw (i) material, (ii) utilities, (iii) miscellaneous materials (1% fixed capital investment, FCI), (iv) maintenance (10% FCI), (v) operating labor (manning estimates), (vi) labor (20% of operating labor), (vii) supervision (20% of operating labor), (viii) overheads (50% of operating labor), (ix) capital charges (15% FCI), and (x) insurance and taxes (4% FCI) [440,441]. The sum of items i-iii stands for variable cost, while the sum of items iv-x indicates fixed cost. The sum of these two costs (*i.e.,* variable and fixed costs) determines the direct production cost which is equal to annual production cost in biodiesel production plant without R&D. If R&D is considered, the annual production cost is increased by 5%. By dividing annual production cost by plant capacity, unit production cost is determined [440,441].

Overall, different technologies require different equipment and may consume different raw materials; therefore, result in different total cost of investment for biodiesel production. Nevertheless, the operational biodiesel production systems around the world cannot deliver a cost-competitive diesel fuel with the current technologies and feedstocks. Therefore, the present manufacturers of biodiesel have been incentivized by offering government supports ranging from subsidies and tax exemption to mandatory application of biodiesel as diesel extender and imposing taxes on petrodiesel. It is obvious that the proper production and consumption of biodiesel have obvious environmental benefits (*i.e.,* GHG emission reduction) and possible positive economic impacts (*i.e.,* job creation) on countries. For example, National Biodiesel Board [447] analyzed the US economy in 2013 with respect to biodiesel production (6435.2 million L). Accordingly, this production had an economic impact of \$16.8 billion, supported about 62 thousand jobs, and paid \$2.6 billion wages. In the same study [447], it was reported that production and consumption of 4277.5 million L of biodiesel could approximately abate 10 million metric tons of $CO_{2\text{-eq}}$ in the US.

It is worth to mention that the extension of biofuels (such as biodiesel) industry has indirect and direct economic impacts on the related markets such as energy, forestry, and agriculture [448–451]. For example, as a result of land-use change, over-zealous biodiesel production may have noticeable economic consequences on the prices of forest products, land values, agricultural commodities, fossil fuel energy, and food and feedstuffs [448]. Eventually, commercial production of biodiesel may economically influence country spending resulted from any biofuel competitiveness policy. The increase in government expenditures and decrease in its revenue may also negatively affect national development programs.

4.2. Biodiesel policies and mandates

As mentioned earlier, the current higher price of biodiesel compared with fossil-based diesel substantially impedes its widespread production and application by private sectors. More specifically, an individual might be a staunch supporter of biodiesel but they are not willing to pay a cent more for a liter of biodiesel. Regardless of price, the place of biodiesel as a fuel could negatively be under vigorous political pressure by oil-rich countries or oil companies. In another word, every liter of biodiesel sold is a liter of petrodiesel that is not (*i.e.,* the product of an oil company). On this basis, the biodiesel industry could not stand alone without a strong policy supporting it. It should be noted that a single policy on biodiesel industry could not be applied worldwide as efficiency and success of any legislated policy depends on various socio-economic criteria (*e.g.,* the energy state of country, population, economics, public acceptance, unemployment rate, *etc.,*) of the destination country. For example, the success of Brazilian biofuel policy could not be replicated in India owning to the frequent failures of monsoon and seasonal variations [452]. Therefore, National Biodiesel Mission was launched by government of India in 2003 based on the Committee on Development of Biofuel's report. The goal was the exploitation of 13.4 million ha wastelands for *Jatropha*-based biodiesel in two phases including experimentation and demonstration, and *Jatropha* cultivation, biodiesel production and marketing [452]. In 2006, the government mandated oil marketing companies for buying standard biodiesel at Rs. 26.5 (0.38 USD/L), including all taxes, in specific centers [452]. Despite these efforts, the National Biodiesel Mission put an end and up to this date, noticeable commercial production of biodiesel in India was unsuccessful [452]. These were due to unscientific cultivation and maintenance of *Jatropha* oil feedstock and lack of trust between industry players and farmers. Nevertheless, the main constraint was the price of biodiesel production which was 20–50% higher than the purchase price determined in the biodiesel purchase policy [452]. Consequently, National Policy on Biofuels was adopted by the government of India. According to its 2018 approved policy [453], the biofuel feedstocks were further expanded and farmers were allowed (with National Biofuel Coordination Committee's approval) to sell food feedstocks during the surplus production phase to biofuel companies. The policy supported the foundation of supply chain mechanisms for production of biodiesel from WCO, nonedible oilseeds, and short duration crops. Eventually, synergistic efforts were encouraged by defining responsibilities and roles of each department or ministry involved with respect to biofuels [453]. The expected outcome from such policy would be cleaner environment, health benefits, infrastructural investment in rural areas, employment rate improvement, increase in farmers' income, and decreased dependency on energy import [453].

On the other hand, the main justifications of the European Union for development and coordination of a mandatory biofuels policy at continental level have been environmental criteria (*e.g.,* at least 20% CO_2 abatement by 2020, compared with 1990) and fuel security [454]. The Directive on the promotion of the use of biofuels or other renewable fuels for transport was introduced in 2003, setting 2 and 5.75% of biofuel shares in transport fuel by 2005 and 2010, respectively [454]. In the same year, Member States were allowed for biofuels tax reductions and exemptions under certain conditions defined by the Energy Taxation Directive. Despite some success, the share of biofuel stood at 1.4% in 2005, 0.6% lower than the set point [454,455]. Therefore, “A European Union strategy for biofuels” was released by the European Commission in 2006 to facilitate biofuels developments by setting out seven strategic policy areas. This communication included “support to developing countries”; “research and development”; and “discussing the opportunities and biofuel demand improvements” [454]. In 2007, the Europe Union endorsed the “Renewable Energy Roadmap” for turning the Europe into a low-carbon and highly energy-efficient economy by increasing the share of renewable and sustainable energies up to 20% by 2020. In line with this, the minimum share of biofuels for phasing out diesel and petrol in the transport sector was targeted at 10% [454]. The endorsement was further supported with some legal measurements, *i.e.,* Climate and Energy Packages legislated and adopted in 2008 and 2009, respectively [456]. However, different stakeholders and Member States weakened the position of liquid biofuels in the transport sector in the original proposal during negotiations for legislation by stating that renewable resources (*i.e.,* bioelectricity, biohydrogen, biodiesel, *etc.*) must source 10% of the energy (*i.e.,* not only diesel and petrol) in the transport sector [454].

Recently, the energy and climate objectives for 2030 set in 2018 increased the share of renewable energies up to 32% of total energy consumption in all sectors with a minimum GHG emission reduction targeted at 40% [457,458]. More specifically, the exchange of the total transportation energy by renewable ones were agreed to be 14% with 3.5% share of advanced biofuels (such as WCO and/or animal fats derived biodiesel) [458]. It should be noted that in both 2020 and 2030 Renewable Energy Directives (REDs), the WCO and animal fats derived biofuels could count double towards the respective targets of 10% and 14% renewable energy sources. Marine and aviation sectors were exempted from these mandates; however, the application of each unit of biofuel in these sectors could be counted at 1.2 times of other transportation sector [458].

The encouraging mechanisms for biofuels production and consumption range from total or partial tax exemptions (or fossil fuels taxation) for making the price of biofuels lower than fossil fuels to force blending of biofuels. The latter mechanism was adopted by many European countries to avoid revenue losses by governments in expense of transport users [454,459]. An alternative mechanism was established by Fuel Quality Directives in which State Members were ordered to reduce their fossil fuel lifecycle emissions up to 6% of 2010 by 2020 while at the same time allowed the application of greater amounts of biofuels as petrol and diesel extenders. This mandate could motivate fuel suppliers for consuming more biofuels in their products as blends to decrease GHG emissions level [454,460]. The European Union farmers were also motivated by Common Agricultural Policy to grow energy crops by providing 45 €/ha subsidy (under Energy Crop Scheme) and by allowing the cultivation of these crops on set-aside lands (constituting 10% of a farmer land under European Union agricultural law), that were terminated in 2008 and 2010, respectively [454]. In 2015, the European Union Indirect LUC Directive made an amendment to RED transport target for encouraging the non-food-based-biofuels by capping the contribution of conventional feed- and food-based biofuels at 7% [458,461].

In 2008, Germany (2,477,983 toe), France (2,020,690 toe), and United Kingdom (691,335 toe) were the top three highest consumers of biodiesel in the European Union [462]. Germany, for example, has mandated the application of biofuel in rail and road transport since 2009 with a biofuel target of 6.25% [16,458]. In 2016, the contribution of biofuels to the transportation sector in Germany was up to 4.7% (with double counting) out of the 6.9% share of the renewable energies [458]. The two most widely applied biofuels were biodiesel and ethanol with 59% and 35% of all the biofuels consumed, respectively [458]. Germany plans to decrease its GHG emissions from fossil fuels in the transport sector up to 6% in 2020 and to maintain it at that level for 5 years (*i.e.,* until 2025) by blending the required amounts of biofuels (not from animal fats and oil) with no double-counting criteria [458]. Nevertheless, the application of conventional biofuels capped at 6.5% and the mandatory application of advanced biofuel will be in place in 2020 and will reach up to 0.5% in 2025. This plan clearly shows Germany‘s agenda shifting from an energy mandate to a GHG abatement since 2015. Parallel to this, the 1.55 €/L and 0.7 €/L penalties of diesel equivalent for violating fuel suppliers until 2014 were replaced by 470 €/t$CO_{2\text{-eq}}$ of GHG not saved [458].

Overall, regardless of the scope, the success of any sustainable biofuel policy program substantially depends on the strict legal obligations and effective implementation. Nevertheless, a supportive agricultural policy is also needed to improve the biofuel feedstock amount and cost.

4.3. Biodiesel tradeoffs and feedstock sustainability

Despite the substantial advantages of biodiesel, some negative impacts are also associated with its application including (i) net GHGs from direct or indirect land-use change (LUC), (ii) impacts on tropical forests and biodiversity, (iii) threat to food security and food price (*i.e.,* food *vs.* fuel debate), and (iv) competition for water resources (*i.e.,* drink *vs.* drive debate) [463]. Theses tradeoffs of biodiesel production/utilization can be at least minimized, if not eliminated, through observing sustainability criteria encompassing careful selection/evaluation of feedstock/technology used for sustainable biodiesel production as well as by the implementation of appropriate policies.

Among such criteria, those related to feedstock are of outmost importance given the fact that the majority of the above-mentioned disadvantages of biodiesel are attributed to this domain. Feedstock evaluations must be multi-criteria based considering the geographical as well as societal features of a given territory. Moreover, such evaluations should take into account carbon footprint, water footprint, impact on food/water security, economic feasibility (both cultivation and conversion processes), and quality attributes of respective biodiesel (*i.e.,* cloud point, flash point, pour point, calorific value, cetane number, *etc.*). It is also critical to consider highly diverse biodiesel feedstocks to prevent dependency on certain resources both regionally and globally [464]. In line with that, different oil feedstocks used for biodiesel production have been investigated with respect to oil yield as well as carbon and water footprints (Table 14) and the properties of the resultant fuels (Table 15).

4.3.1. Edible and non-edible oil crops

Further increases of the global biodiesel production capacity either requires more exploitation of non-agricultural lands such as forests for growing more biodiesel feedstock crops (*i.e.,* direct LUC) or increasing the diversion of already cultivated feed or food crops towards biodiesel industry (*i.e.,* indirect LUC). LUC could in general contribute to altered GHG emissions due to the following modifications in; the aboveground and underground biomass, the emission of N_2O from soil, and the soil carbon stocks [544]. These modifications may render biodiesel production not sustainable with respect to emission reduction of GHGs and carbon payback. For example, the conversion of peatland or natural rain forest for oil palm cultivation requires 320 or 57 years carbon payback by palm-based

Table 14
The comparison of sustainability aspects of different oil feedstocks for biodiesel production with respect to oil yield as well as carbon and water footprints.

Alternatives	Oil yield (kg oil/ha)	Oil content (%)	Carbon footprint[1] (g CO_2-eq/MJ)	GHG mitigation (%)[2]	Water footprint[3] (m^3/ton)	Ref.
Edible oils						
Canola oil (*Brassica napus* L.)	1094–1376	40–50	4.56	(+)51.6 (LUC included)	5846.5* 6666 (Australia)*	[465-469]
Coconut oil (*Cocos nucifera* L.)	2200–2925*	63–65	NA	NA	2671	[465, 470]
Olive oil (*Olea europaea* L.)	1432*	15–16	NA	NA	2969	[465, 470]
Palm oil (*Arecaceae*)	5000	30–60	51.53	(+)38–41	1057	[470-472]
Rapeseed oil (*Brassica napus* L.)	1000	38–46	58.91	(+)29.7–32.5	1935 1482 (Germany)	[465, 470, 473, 474]
Safflower (*Carthamus tinctorius* L.)	350–650	20–45	21.65	(+)78	6938	[465, 470, 475]
Sesame (*Sesamum indicum* L.)	256–310*	52–63	NA	NA	8969	[465, 470]
Soybean oil (*Glycine* max L.)	375	15–20	51.5	(+)45.4 (LUC included)	2107 1442 (Italy)	[465, 466, 470, 473]
Sunflower oil (*Helianthus annuus* L.)	305–696	25–42	NA	NA	3165	[470, 476]
Non-edible oils						
Camelina oil (*Camelina sativa* L.)	403–706*	30–45	18	(+)80 (LUC included)	NA	[477, 478]
Castor oil (*Ricinus communis* L.)	350–1200	40–45	22.145*	(+)75–90	9598	[470, 479, 480]
Cotton oil (*Gossypium* spp. L.)	320–640*	16	NA	NA	3589	[470, 481]
Croton oil (*Croton megalocarpus*)	1800	40–45	NA	NA	NA	[465, 482]
Field Pennycress oil (*Thlaspi arense* L.)	349.6–699.2*	53.6	13–41	(+)56–85	NA	[483, 484]
Jatropha oil (*Jatropha curcas* L.)	1590	35–40	23.5–44	(+)61.6–72	3222 (Brazil)	[465, 473, 485, 486]
Jojoba oil (*Simmondsia chinensis* L.)	1578	44–59	66 (combustion excluded)	NA	12,344	[465, 487-489]
Karanja (*Pongamia pinnata* L.)	225–2250	27–39	343.06	(-)22.5	1300	[465, 490, 491]
Linseed oil (*Linum usitatissimum* L.)	380–1320*	38–44	NA	NA	5005	[465, 470]
Mahua (*Madhuca indica/longifolia*)	2700	35	38.45	(+)87.57	NA	[465, 492, 493]
Moringa oil (*Moringa oleifera* L.)	681–1192*	38–40	18.61–21.07*	NA	NA	[465, 494, 495]
Patchouli oil (*Pogostemon cablin* L.)	99–124	2.5–3.5	NA	NA	NA	
Polanga oil (*Calophyllum inophyllum* L.)	~5000	65–75	NA	NA	NA	
Pranajiwa oil (*Sterculia foetida* L.)	350	34	NA	NA	NA	[496, 497]
Rubber oil (*Hevea brasiliensis* L.)	120	40–50	~15–45 (combustion excluded)	(+)70–86	13,325	[465, 470, 496, 498]
Waste oils						
WCOs	–	–	27.93–32.49	43–51	NA	[499]

NA: Not available.

[1] Well-to-wheel life cycle assessment (crop cultivation, biodiesel production, biodiesel combustion, *etc.*).

[2] Overall GHG mitigation relative to conventional petroleum diesel.

[3] The sum of global average blue and green virtual water.

* Values estimated in the present study using the available literatures.

Table 15
Fuel properties of biodiesel (B100) obtained from different oil feedstocks.

Alternatives	Cetane number	Flash point (°C)	Cloud point (°C)	Pour point (°C)	Calorific value (MJ/kg)	Carbon residue (wt.%)	Ref.
Edible oils							
Canola oil (*Brassica napus* L.)	61.5	182–186.5	−3	−9 to −8	39.5	NA	[500,501]
Coconut oil (*Cocos nucifera* L.)	51–57.4	100–118.5	0–1	−4 to −3	38.3	0.01	[500,502–504]
Olive oil (*Olea europaea* L.)	61	173.8	NA	NA	41.35	NA	[503,505]
Palm oil (*Arecaceae*)	52–62	164–214.5	13–15	14–15	40	0.03–0.07	[500,506-508]
Rapeseed oil (*Brassica napus* L.)	56	170–180	−4 to −2	−12	37	1.1	[506,507]
Safflower (*Carthamus tinctorius* L.)	49.8–53.14	166.8–187	−5	−24	40.3–41.3	NA	[503,505,509]
Soybean oil (*Glycine* max L.)	45–51.5	178–202.5	−5 to 1	−9 to 0	40	1.74	[500,507,510]
Sunflower oil (*Helianthus annuus* L.)	45.5–58	192–220	2	0	38.2–39.5	≤0.01	[503,511–513]
Sesame (*Sesamum indicum* L.)	40–53	110–185	−5	−18 to −8	34.6–40.9	NA	[471,505,514]
Non-edible oils							
Camelina oil (*Camelina sativa* L.)	46	>160	−2 to 3	−8 to −4	39.1	0.02	[464,515–517]
Castor oil (*Ricinus communis* L.)	43.7	160–260	−27.8 to −12	−45 to −30	37.9–39.8	0.028	[464,479,506,518–520]
Cotton oil (*Gossypium* spp. L.)	41.2–59.5	181.8–243	1.7	−15 to −10	39.5–40.3	0.42	[503,505,521,522]
Croton (*Croton megalocarpus*)	40.7–46.6	164–189	−4 to −3	−9 to −2	39.8	NA	[482,500,523]
Field Pennycress oil (*Thlaspi arense* L.)	59.8	NA	−10	−18	NA	NA	[483]
Jatropha oil (*Jatropha curcas* L.)	46–57.1	135–238	4–13	2–6	38.5–42	0.02	[464,500,507,508,522,524]
Jojoba oil (*Simmondsia chinensis* L.)	63.5	61–75	6–16	−6 to 6	42.8–47.4	NA	[464,522]
Karanja (*Pongamia pinnata* L.)	52–58	150–187	13–15	−3 to 5.1	35.6–38	0.15	[464,506,522,525,526]
Linseed oil (*Linum usitatissimum* L.)	28–35	108	1.7	−18 to −4	37.7–39.8	NA	[522]
Mahua (*Madhuca indica/longifolia*)	51–52	127–129	3–5	1–6	39.4–39.9	0.2	[464,522,526]
Moringa oil (*Moringa oleifera* L.)	67	162–176	17–21	17–19	40.1–43.28	NA	[494,500]
Patchouli oil(*Pogostemon cablin* L.)	NA	118.5	<−33	<−33	44.2	NA	[500]
Polanga oil (*Calophyllum inophyllum* L.)	56.2–57.3	140–170	−1 to 14	0–4.3	39.2–41.3	0.18	[500,508,522,526,527]
Pranajiwa oil (*Sterculia foetida* L.)	57.9	130.5–179	−3 to 3	−3 to 3	40.42	NA	[500,527,528]
Rubber oil (*Hevea brasiliensis* L.)	37–49	130–187	1–5	−8 to −2	36.5–41	0.126	[81,464,518,522,529,530]
Waste oils							
Animal waste fats	44–74	106–174	−5 to 14	−6 to 15	38.76–40.23	0.024–0.21	[531–538]
WCOs	50–54.43	120–235	−1 to 9	−16 to −3	38.2–40	4.0 wt.%	[67,499,539–543]

biodiesel, respectively [545]. While only eight years of palm-based biodiesel production could mitigate the carbon debt in the form of GHG emission from LUC of the logged-over forest [545]. It should be noted that the reduction of vegetation of managed and natural ecosystems as well as the organic carbon storehouses in the soils must be minimized in order to achieve a sustainable production of biodiesel in terms of GHGs mitigation. On the same basis, it is recommended to grow native perennial crops in abandoned agricultural or degraded lands for biodiesel production [546].

Microalgae have also been promoted as promising triglyceride source for sustainable biodiesel production, if their limitations to commercialization would be overcome. For instance, cheap concentrated CO_2 supply point together with other essential resources such as fertilizers are necessary for efficient cultivation of microalgae [27,547]. On this basis, nitrogen and phosphorous nutrients must be totally recycled back and ideally the system ability for nitrogen bio-fixation should be granted. Another constraint on the way of large-scale algal biodiesel is freshwater and its limited supply considerably reducing the yield of production [547]. These constraints make the near-future commercial application of algal biodiesel almost impossible. Therefore, in this section the main focus is placed on other viable feedstocks for biodiesel production, *i.e.,* animal fats and vegetable oils. The carbon footprint of any crop-based biodiesel could be estimated through an analysis known as life cycle assessment (LCA), involving all the stages from the production of a given feedstock to the combustion of its respective biodiesel and could be further completed by considering LUC [466,548,549]. LCA is in fact directly related to agricultural practice efficiency (field practices, yield, transportation, *etc.*) [550] as well as biodiesel production efficiency. It should be noted that in general, biodiesel combustion emits roughly equal GHG emissions to what fixed during the growth of its respective feedstock (biomass). However, the utilization of fossil fuels in various stages of crop cultivation and/or biodiesel production could lead to a final carbon debt. According to the European Union's policies and regulations, *i.e.*, RED, LCA of biodiesel from any given feedstock must confirm a minimal GHG-emissions reduction of 35%, compared with GHG emissions arisen from the synthesis and application of conventional fuels, to be considered as sustainable [551].

Four major biodiesel feedstocks include palm oil, rapeseed, soybean, and sunflower seed. Of these, rapeseed biodiesel is the most extensively used biodiesel; however, this crop is currently cultivated using an intense application of nitrogen-containing fertilizer. Up to 3–5% of the provided N_2 is emitted in the form of N_2O with a 296-time stronger global warming potential than CO_2 [552]. In contrast, soybean cultivation does not require any nitrogen-containing fertilizers, and hence, its cultivation is more favorable than rapeseed in terms of economic and GHGs emissions. The cultivations of palm and soybean are mostly concentrated in biodiversity hotspots [553]; therefore, any further expansions in their production may further jeopardize tropical forests and consequently threaten their associated native biodiversity [463]. Cerrado and the Amazon (in the case of soybean) in South America, and Indonesia's and Malaysia's rainforests (in the case of palm) in Southeast Asia are at the highest risk of the above-mentioned destructions [544,554].

On the other hand, a popular debate allegory, *i.e.,* food *vs.* fuel has also been raised due to increasing food prices in this millennium. More specifically, biodiesel production may decrease the availability of foods by either direct absorption of food/feed feedstocks and/or reducing the production of food/feed crops due to indirect LUC as well as soil depletion. In addition, increasing water demands for agricultural expansions as well as population growth have already raised severe water crisis worldwide [463]. As mentioned earlier, biodiesel production plants generate up to 1.2 L of wastewater per each liter of purified biodiesel during wet washing process. Although, this water consumption can be minimized (~20 mL/each liter of biodiesel) through adopting various advanced technologies, biodiesel production still require huge amounts of water for the cultivation of oil feedstocks. The latter water consumption has raised drink *vs.* drive arguments and is partially blamed for water crisis severity.

The water footprint of any crops can be calculated by considering their consumption of blue, green, and gray virtual-water [470]. The blue virtual-water content represent the amount of evaporated rainwater while the green virtual-water content stands for the amount of ground and surface water consumed during the cultivation process [470]. They all directly depend on irrigational, geographical, and climatic variables. The gray virtual-water of a crop refers to the amount of polluted water generated during the crop cultivation and is mainly related to agricultural practices [470]. In general, some oilseed crops yield appropriately under rain-fed conditions and require limited irrigation facilities at the critical growth points, *i.e.,* sowing, flowering, and seeding [555]. Such crops if indigenous to arid or semi-arid areas or genetically-modified to be so could serve as sustainable biodiesel feedstocks with respect to water footprint.

Table 14 presents the data on global average water footprint (blue and green) of some oil feedstocks used for biodiesel production [470]. It should be noted that the water footprints of these crops may vary in different parts of the world as evapotranspiration of crops could be affected by climatic conditions. For example, soybean consumes 602 m^3/ton (61 m^3/GJ) water in Brazil but its water consumption increases to 979 m^3/ton (99 m^3/GJ) and 1360 m^3/ton (138 m^3/GJ) under the climatic conditions present in the United States and Zimbabwe, respectively [556]. Therefore, the Brazilian priorities for biodiesel feedstocks (based on water footprint) would be coconut, 444 m^3/ton (49 m^3/GJ); groundnuts, 426 m^3/ton (51 m^3/GJ); sunflower, 972 m^3/ton (54 m^3/GJ); soybean, 602 m^3/ton (61 m^3/GJ), palm oil, 1502 m^3/ton (75 m^3/GJ), and rapeseed, 1460 m^3/ton (214 m^3/GJ) [556]. While based on the data provided by Berger et al. [557] on blue virtual-water footprint of some crops, the European priorities for biodiesel feedstocks would be rapeseed, soybean, and sunflower consuming 41.8, 302.3, and 426.2 million m^3 water for the production of about 6.17, 2.88, and 0.58 million L of biodiesel (each 31 L of biodiesel is equal to 1 GJ), respectively. Based on these results, it could be concluded that the application of irrigated sunflower for biodiesel synthesis is a total waste of water, particularly in Spain where 275.2 million m^3 water is used for the production of only 0.9% of the total European feedstock required for synthesis of 250.3×10^5 GJ biodiesel [557].

Overall, edible oils, despite their low FFA contents (*i.e.*, no esterification pretreatment requirement), could not be used for sustainable biodiesel production even if economically feasible, due to violently triggering food/water *vs.* fuel debates and threating biodiversity in some cases as well. Therefore, non-edible oils are arguably more agronomically-justified (*i.e.*, lower water, soil, fertilizer, pesticide requirements) and more environmentally-efficient (*i.e.,* less LUC, more CO_2 sequestration) feedstocks than edible ones as long as they are cultivated on marginal and waste lands, *i.e.,* lands that are poor for other crops [464,558–560]. A good example could be jatropha plant (life-cycle of 30–50 years) which efficiently grows and yields oil seeds (after 2–3 years) even in sandy and saline soils with 250 mm annual precipitations [506]. Castor shares similar ecological requirements with jatropha and could be intercropped with it to compensate for the low income of jatropha cultivation in its initial 2–3 years of plantation [506]. Castor biodiesel has one of the lowest cloud point (−12 to −27.8) and pour point (−32 to −45) amongst all the biodiesel produced ever (Table 15). Rubber plant is another non-edible oil seed producing tree that has been extensively studied as a biodiesel feedstock

[81,518,529]. Its oil-rich kernel (40–50% oil content) constitutes up to 50–60% of the seed and the extracted oil can be efficiently converted into biodiesel *via* one-step (*i.e.*, alkaline-catalyzed transesterification) or two-step process (*i.e.*, FFA esterification followed by alkaline-transesterification) [81,518,529].

Non-edible oil crops respond well to cultivation in rotation with food/feed crops, through converting fallow-crop system to crop-crop system, *i.e.*, more intensive cropping system. The latter system significantly improves agronomic and economic aspects [561], such as land availability, minimizing LUC and food insecurity. For instance, Chen et al. [561] studied a three-year replicated rotation system, in which *Camelina* and winter wheat were rotated in the Northern Great Plains. Compared with fallow-wheat system, 13% less wheat yield (365 kg/ha) were conveniently offset by the production of 907 kg/ha *Camelina* [561]. *Camelina* has a short life-cycle (2–3 months) and low requirement for water, delivering up to 45% non-edible oil (290–400 kg/ton) [561,562]. Fröhlich and Rice [515] reported relatively similar fuel economy for *Camelina*-based biodiesel and diesel oil based on vehicle trials. Niger seed oil (*Guizotia abyssinica* L.) is another non-edible crop option which is well-adapted to poor acidic soils. This oil crop matures within about four months and can be cultivated in rotation with some food crops such as maize and wheat [563]. A seed oil content of up to 30% can be delivered, whereas the remaining high protein meal could be used as animal feed [563]. Despite these advantages, biodiesel production from this oil crop seems unfeasible because of its low seed yield (5–10 kg/ha) as well as the application of whole seed as birds' food in many countries.

It is interesting to note that the production cost of non-edible oils for castor (1188 kg oil/ha), jatropha (1590 kg oil/ha), and karanja (225–2250 kg oil/ha) oils are estimated at 0.12, 0.39, and 0.25 USD/kg, respectively, whereas soybean oil (375 kg oil/ha) production costs 1.64 USD/kg [506,529,564]. Although palm oil (5000 kg oil/ha, 0.19 USD/kg) and rapeseed oil (1000 kg oil/ha, 0.34 USD/kg) could economically compete with the above-mentioned non-edible oils [506,565], they are associated with several shortcomings mentioned earlier. An untapped non-edible oil feedstock for biodiesel could be polanga (65–75% seed oil content) with an oil yield of about 5000 kg/ha, *i.e.*, equal to palm oil yield [508,566]. In a thorough investigation, Dinh et al. [507] compared algae, jatropha, palm oil, rapeseed, and soybean as biodiesel feedstock based on economical, sustainability (cultivation feasibility excluded), and technical criteria. According to the results of analytical hierarchy process technique, soybean was the most economic option but was interior from the environmental (GHG emissions, land usage, water consumption) and biodiesel quality (cetane number, cloud point, carbon residue) perspectives. Moreover, although palm oil was the best feedstock in term of biodiesel quality, it was only slightly better than soybean in terms of environmental aspects. Overall, algae followed by palm oil had the highest total ranks based on their suggested priority structure using the analytical hierarchy process technique. In a simulated study [567], jatropha biodiesel (USD 0.15/L) followed by WCO biodiesel (USD 0.23/L) had lower production costs compared with the other investigated oil feedstocks (*i.e.*, palm, microalgae, tallow). Overall, it could be deduced that non-edible oils would be better biodiesel feedstocks than edible oils. However, they also could lead to food/feed and water insecurity, to a much lesser extent than edible oil plants though. Therefore, full exploitation of non-edible oil as sustainable feedstocks for biodiesel production still requires some improvements with respect to agricultural practices, post-harvest technologies, and processing techniques [464,568].

Currently, biodiesel costs about 1.5–3 times higher than diesel, of which the price of oil feedstocks, as mentioned earlier, could contribute up to 70–95% of the production costs [67,543]. Unfortunately, for many entrepreneurs, economic aspects have the priority over both environmental and societal aspects. Therefore, it is the responsibility of those few companionate individuals to improve the former aspect of biodiesel production and application while making its production more environmentally sound. One approach is to force and encourage *via* legislations, subsidies, or their combinations defined by policy makers. Alternatively, the more interesting approach could be scientific solutions either by introducing novel economically-viable oil crops and/or by improving the characteristics of already-known oil crops. Both approaches require careful and comprehensive investigation with periodic updates on improvements in terms of alternative feedstocks, their cultivation practices, and their conversion into biodiesel. More specifically, the latter approach involves the presentation of some environmentally-friendly oil crop species with appropriate characteristics for biodiesel production, such as through identification of naturally drought- and pest-resistant, high oil-yield crops (preferably non-edible) that require minimum agricultural practices followed by the introduction of agronomic techniques and technologies to exploit the best out of their cultivations. Castor, karanja, jatropha, linseed, and polanga are some examples of this approach. Moreover, this approach could involve traits improvements (oil traits, agronomic traits) through natural selection or recombinant technology, the latter commonly referred to as genetically modified crops. This may even decrease the feedstock cost through co-production of high-value recombinant products [465]. For instance, a transgenic low-palmitic-acid (<5%) and high-oleic-acid (>85%) soybean was developed by Graef et al. [510] showing stability towards environmental stresses such as production on irrigation and non-irrigation schemes. Moreover, oil properties and consequently, fuel characteristics of the resultant biodiesel were also efficiently improved compared with the conventional soybean oil biodiesel, *i.e.*, cetane number (from 47.2 to 51.5), cloud point (from −1 to −5 °C), pour point (from 0 to −9 °C), and total glycerol (from 0.097 to 0.068 wt.%) [510].

4.3.2. Biodiesel production under biorefinery concept

Biodiesel could be produced in a sustainable way under recycling or biorefinery concept from residual oils or crops, such as oil refinery waste oil streams (acid oil, soapstock, fatty acid distillate, oil crop pomace) as well as other waste oil feedstocks (animal fats, WCO, brown or yellow grease, residual oil from food/fruit processing industry, *etc.*) (Table 16). Collection, transportation, and treatment mainly determine the cost of these promising feedstocks. For instance, leftover apricot or plum stone from fruit processing industry could provide low-cost oil feedstock for biodiesel production through either one-step process and/or two-step process as they contain 44.7–57.8 or 32–45.9% oil, respectively. Plum stone oil content is relatively similar to those of sunflower and rapeseed but about 1.6–3.1 times higher than that of soybean seeds [569]. The possibility of conducting one-step biodiesel production process from some of these oil feedstocks indicates their low acid value (FFA contents). Apricot kernel oil biodiesel has been synthesized by Wang [570] displaying a cetane number of 47.2–51.23 and flash point of 173 °C whereas that obtained from plum kernel oil by Kostić et al. [569] showed 57 and 155 °C, respectively. These studies found kernel oil, from the leftovers of fruit processing industry, promising biodiesel feedstocks as long as efficient oil recovery techniques are conducted. Nevertheless, appropriate genotype must be selected and established by agricultural studies as well as by cloning techniques to further improve both productivity and quality of these fruits including their kernel.

Soapstock is a by-product of oil refinery industry, produced when crude vegetable oil is refined from FFAs by agitation with alkali. The typical generation rate of soapstock is about 6% of the total crude oil input [580]. The high lipid content of soapstock, together with its low market value of about 0.11 USD/kg dried

Table 16
Some examples of biodiesel production under biorefinery concept with respect to feedstock, industries, and technologies involved as well as the generation of value-added products.

Feedstock	Integrated industries	Value-added products	Technologies involved	Ref.
Castor plant	Ethanol and biodiesel industries	–Ethanol -Biodiesel (149.6 g biodiesel and 30.1 g ethanol per each kg of biomass)	–Simultaneous saccharification and fermentation of residual castor plant -Ethanolic transesterification of castor oil	[571]
Saussurea heteromalla	Ethanol and biodiesel industries	–Ethanol -Biodiesel (112.2 g biodiesel and 42 g ethanol per each kg of biomass)	–Simultaneous saccharification and fermentation of residual biomass -Methanolic transesterification of *Saussurea heteromalla* oil	[572]
Oil feedstocks	Food, fuel, and cosmetic industries	–Biodiesel -Dihydroxyacetone -Hydroxypyruvic acid -Ethylene glycol –1,2-propanediol -Propanediols -Ethanol -Polyhydroxyalkanoates -Docosahexaenoic acid	–Transesterification of oil -Oxidation, hydrogenolysis, aqueous phase reforming, or fermentation of glycerol from biodiesel industry.	[573,574]
Olive oil residue	Vegetable oil refinery and biodiesel industry	–Edible olive oil -Biodiesel	–Oil extraction techniques -(Trans)esterification of residual olive oil wastes from oil refinery industry	[57]
Microalgae	Food and biofuels industries	–Pigments -Proteins -Vitamins -Biodiesel -Ethanol -Biogas	–Various extraction methods or biological processes -Transesterification of extracted oil -Fermentation of microalgae carbohydrate content -Anaerobic digestion of microalgae residues	[27,575,576]
Chlorella minutissima	Food and biodiesel industries	–Lutein -Biodiesel	–Ethanol-hexane based solvent extraction followed by parallel saponification and transesterification	[577]
Palm oil	(Bio) energy and agriculture industries	–Biodiesel -Electricity -Heat -Biofertilizer	NA[1]	[578]
Mucor circinelloides	Enzyme, biodiesel, ethanol, and food industries	–Hydrolytic enzyme -Biodiesel -Ethanol -Carotenoids -Nutritional biomass as food	NA	[579]

[1] Not available.

soapstock (20% of the crude soybean oil price) makes it an attractive feedstock for biodiesel production [581]. Once soapstock is H_2SO_4-treated, acid oil containing long-chain FFAs along with traces of other compounds are generated. Other by-product of oil refinery industry is fatty acid distillate generated in the final deodorization stage. All of these low-cost by-products can be converted into biodiesel. For example, Haas [581] successfully synthesized soybean soapstock methyl esters with promising fuel properties, *i.e.*, flash point of 169 °C, carbon residue of 0.01 wt.%, cetane number, 51.3, and cloud point of 6 °C. Moreover, biodiesel production cost was decreased by 23%, compared with soy-based biodiesel. Alternatively, the oil crop residues from oil refinery may also be further processed and used as biodiesel feedstock. For instance, olive pomace oil has been successfully converted into biodiesel reducing up to 43–51% GHG emissions relative to petroleum-based No. 2 diesel [499,582]. It has also been argued that the total carbon footprint of olive pomace oil biodiesel could be further decreased by improving agricultural practices as 48–60% of the emissions were attributed to these practices [499]. Residual olive oil has similarly been considered as biodiesel feedstock to increase the economic profitability of olive oil refinery plant [583].

Waste animal fats (WAFs) such as beef tallow, chicken fat, duck tallow, lard, mutton fat, *etc.* are another group of waste oils that can be used as biodiesel feedstock. A cheap by-product of meat industry is tallow, produced in a centralized manner in slaughtering houses, processing facilities or by rendering operations. Beef tallow, for example, can be divided into edible and non-edible fats and the latter is traditionally used as animal feed supplement (main market), soap, and lubricants [584]. In recent years, the trade of tallow as well as its shipment for the above-mentioned applications has been negatively affected by risk of transmission of bovine spongiform encephalopathy. However, these tallowate feedstocks can be safely converted into value-added product, *i.e.*, biodiesel costing about 0.38 USD/L [584]. It should be noted that higher transesterification reaction temperature is commonly required for the conversion of WAFs into biodiesel than vegetable oils due to high saturated fatty acid (SFA) content of WAFs (up to 61.1%) [538]. An exception is chicken fats (30–33% of SFA) that tend to be liquid or in semi-solid form. Chicken fat (*i.e.*, skin and visible fat) is another largely available leftover from the meat industry in leading poultry-producing countries, constituting up to 8–20% of chicken carcass weight and have direct relationship with chicken weight [585]. For example, considering Iran chicken production (2.5 million ton/annum) and Iranian people tendency to buy larger chickens, up to 500 ton/annum chicken fat is produced. The oil can be conventionally extracted from chicken fat by melting technique (90–100 °C) or by more recent techniques utilizing microwave heating or ultrasonic irradiations [586], followed by its one-step or two-step process conversion into biodiesel.

An alternative feedstock considered under the biorefinery concept is WCO whose conversion into biodiesel would provide a safe and economic disposal method for this waste as well. WCO is largely produced (11 million ton/annum in the US only) as a leftover from preparation or cooking of foods and is no longer suitable for the consumption by humans or animals [67]. WCOs may be divided into yellow and brown greases, typically containing less than and more than 15% FFAs, respectively. They could be considered as promising biodiesel feedstocks because they are cheap and readily available. For example, yellow grease of soybean oil is available at a market value of about 0.27 USD/L in 2018 [587] compared with virgin soybean oil price of about 0.67 USD/L in the same year. The production of biodiesel from WCO could be at very reasonable price even in oil-rich countries such as Iran (~0.61 USD/L biodiesel) [67].

WCO has relatively same physicochemical characteristics to those of virgin cooking oil but with higher FFAs and water content, requiring an appropriate pretreatment before alkaline-catalyzed transesterification reaction. Some pretreatment techniques for removing FFAs from WCO include (solid)acid-catalyzed trans(esterification), glycerolysis, silica gel pretreatment, and vacuum distillation [588–591]. Vacuum distillation is used to trap FFAs when their content is between 3 and 15%. Glycerolysis process involves the addition of glycerin to retrieve FFAs in the form of monoglycerides at ~204.5 °C [591]. Acid or solid acid is generally used for WCOs with higher than 15% FFAs content and converts FFAs to esters. The main advantage of solid acid over acid esterification is its immiscibility with oil, and hence, no purification step and consequently no wastewater treatment are required. It should be noted that even oil feedstocks with high FFAs (such as WCOs, non-edible oils) can be directly converted into biodiesel using supercritical method (see Section 2.3.3) for simultaneous conversion of FFAs and triglycerides into biodiesel. From the quality perspective, a proper pretreatment process guarantees similar characteristics of biodiesels produced from WCO and virgin cooking oil [588].

In an interesting study on the various aspects of WCO biodiesel using LCA, Moecke et al. [592] considered WCO-based biodiesel (200 L/day) production in a plant in the vicinity of Pinheira Beach (Santa Catarina, Brazil). They advocated the economic, environmental, and societal gains of the plant for the community. However, based on their results, oil collection was the most polluting stage of biodiesel production (92.1% contribution) in terms of total GHG emissions (2.23 $tCO_{2\text{-eq}}$/t biodiesel). This highlights that a well-managed collection system must be implemented to increase the carbon pay efficiency as well as economic profitability of the WCO-based biodiesel plants through reducing fuel consumption for feedstock collection. For example, total $CO_{2\text{-eq}}$ emission from biodiesel production could be decreased by up to 23% reaching 1.72 $tCO_{2\text{-eq}}$/t biodiesel in the same study [592] if fossil fuel (petroleum) was replaced by B50 (biodiesel 50%) in the WCO-vehicle collection system. Alternatively, centralized WCO-based biodiesel production plants could be by the decentralized ones to minimize the environmental and even economic burdens associated with waste collection and transportation [593].

An important consideration in further economizing any biodiesel production chains would be glycerol upgrading for production of value-added products and hence, reducing the biodiesel production cost. Crude glycerol (containing water, salts, alcohol, biodiesel, mono and diglycerides, FFAs, soap, *etc.*) generated during biodiesel production cannot be applied for cosmetic, food, and pharmaceutical industries unless it is purified. Nevertheless, the purification steps are highly expensive with respect to operation and equipment costs [574]. Alternatively, crude glycerol can be used as a feedstock for synthesis of a number of different chemicals through (i) reduction or oxidation process, or (ii) reaction with other chemicals, forming other three carbon molecules or new chemical species, respectively. The application of cheap oxidizing agents (*e.g.,* oxygen, air, bleach, hydrogen peroxide) for transforming glycerol allows inexpensive production and in turn, industrial application of some value-added products including, Glyceric, Hydroxypyruvic, Mesoxalic and Tartronic acids, and Dihydroxyacetone compounds [594,595] (Table 17). Additionally, aqueous phase reforming (*i.e.,* moderate pressure, low temperatures) could be applied for breaking glycerol into gaseous (*i.e.,* containing mainly H_2) and liquid (*i.e.,* acids, alcohols, aldehydes, esters, ketones, *etc.*) phases. Among them, 1,2-propanediol (Table 17) is used in synthesis of polyurethanes, polycarbonates, polyesters, resistant textile fibers and carpet, food products (*i.e.,* solvent for flavoring and coloring), emulsifiers, other solvents, and plasticizers [595,596]. Moreover, 1,2-propanediol is applied as component in cosmetics, lubricants, hydrolytic fluids, and anti-freezing agents [574]. Another group of compounds, *i.e.,* polyglycerols and their esters could be obtained through etherification of glycerol for application in cosmetics, food additives, and surfactants [594]. The halogenation of glycerol leads to production of epichlorohydrin (significant feedstock in papermaking industry) with 1,3-dichloropropanol as an intermediate, consuming hydrochloric acid (*i.e.,* chlorination agent) and lower water while generating lower chlorinated residues [597].

Anaerobic digestion, fermentation, pyrolysis, and gasification of glycerol are also possible [598]. The main product of anaerobic digestion of glycerol (or its co-digestion with other feedstocks) is CH_4 with acetate, butyrate, and propionate as major intermediates [599]. Whilst the fermentation of glycerol delivers some similar compounds to anaerobic digestion (*i.e.,* acetate, butyrate, and H_2), it also generates butanol, ethanol, and lactate [574]. The products of low temperature pyrolysis of glycerol mainly include acetaldehyde, formaldehyde, and acrolein whereas ethylene, H_2O, CO_2, and CH_4 are dominant at higher temperatures [574,594]. On the other hand, gasification process decomposes glycerol into H_2 and syngas which are suitable for energy application [600]. In addition to gasification and aqueous phase reforming, H_2 could be produced from glycerol (*i.e.,* in 4:1 ratio) by auto-thermal reforming and steam/water reforming processes [601,602]. Similarly, a number of different fuel additives could be formed from chemical modification of glycerol *via* acetalization, etherification, ketalization, or methylation process (Table 17). Ketal derivatives of glycerol could stabilize biodiesel with respect to oxidation, iodine, and viscosity while improving its cold-flow characteristics [603]. An engineered bacterium, *Escherichia coli* strain YL15 efficiently consumes glycerol to metabolize fatty acids forming glycerol esters with a yield of 813 mg/L [604]. Isobutylene and 1-butene could be used for etherification of glycerol for the production of some biodiesel additives including dibutoxy glycerol as well as propyl glycerol ethers and butyl glycerol ethers, respectively [605,606].

Overall, upgrading biodiesel-derived glycerol not only could economize the production of biodiesel but also could mitigate its environmental impacts. Table 17 tabulates some glycerol-based value-added products as well as their potential commercial applications.

4.4. Social acceptance of biodiesel

There have been significant efforts for the introduction of low-carbon biofuels such as biodiesel into the transport sector. The levels of success were different from country to country and even one community to another. Regardless of the cost, other social ac-

Table 17
Different glycerol upgrading methods for synthesis of value-added products with their potential industrial applications [574,594–596,607–611].

Conversion method	Value-added product	Application	Industry
Acetalization	–Monoacylglycerides –Diacylglycerides -Diacetin -Triacetin	Fuel additives	Fuel industry
Etherification	–Butyl glycerol ethers -Di-butoxy glycerol -Propyl glycerol ethers -Glycerol *tert*-butyl ethers		
Ketalization	−2-butanone-glycerol -Methyl hexonoate -Fatty acid formal glycerol ester -Solketal		
Methylation	–Glycerol dimethoxy ether -Glycerol tert-butyl ethers		
Oxidation	–Dihydroxyacetone	–Manufacturing of sunless tanning lotions -L, D-serine synthesis	Cosmetic and food industries
	–Hydroxypyruvic acid	–Flavoring agent in cheese -Synchronization of fruit maturation -L, D-serine synthesis	Food industry
	–Glyceric acid	–Skin disorder treatment	Pharmaceutical and detergent industries
	–Tartronic acid	-Production of biodegradable fabric softener –Adjuvant for tetracycline absorption in blood -Scavenging dissolved oxygen in alkaline water	Pharmaceutical and chemical industries
	–Mesoxalic acid	–Precursor in organic synthesis	Chemical industry
Hydrogenolysis	–Ethylene glycol	–Production of monobasic alcohols and alkanes	Various industries
Aqueous phase reforming with no hydrogen addition	−1,2-propanediol	–Production of various chemical species	Food, fuel, and cosmetic industries
Dehydration	–Acrolein	–Production of D/L-methionine, acrylic acid, acrylic acid esters, glutaraldehyde, detergents, and herbicides	Various industries
	−3-hydroxypropionaldehyde	–Healthcare diet for animals and human -Chemical fixation of biological tissues -Food preserving agent	Pharmaceutical, food, and chemical industries
Etherification	–Polyglycerols and polyglycerol esters	–Production of cosmetics, lubricants, food additives, and surfactants	Fuel, food, and cosmetics industries
	–Glucosyl glycerol	NA[1]	Food and cosmetics industries
	–Glycerol monoesters	–As nonionic surfactants and emulsifiers in dairy products, margarines, bakery products, and sauces -As texturing agent in lotions and creams -As plasticizing and lubricant agent in machinery oil formulation	Food, fuel, and cosmetic industries
	–Di and triglycerides	–Fuel additives	Fuel industry
Esterification or transesterification	–Glycerol acetates	–Monoacetin; production of cryogenics, biodegradable polyester, explosives, and (tanning) leather -Diacetin; printing ink, softening agents, plasticizer, and dye solvent -Triacetin; production of perfumes, and photographic films, and as viscosity and cold flow improver of biodiesel and antiknock additives for gasoline	Various industries
Transesterification	–Glycerol carbonate	–Efficient solvent for resins and plastics -Production of glycerol ethers by reacting with alcohols, phenols and carboxylic acids in presence of heat	Chemical industry
Halogenation	–Epichlorohydrin	Synthesis of elastomers, epoxide resins, and sizing agents	Paper industry

[1] Not available.

ceptance criteria (discussed hereafter) of any biofuels play decisive roles in its commercial feasibility.

Public awareness, opinion, and knowledge could contribute to the social acceptance of any biofuels including biodiesel. Moula et al. [612] studied the social acceptance of biofuels for transport in Finland. Interestingly, none of the respondents considered biofuels as the most ideal energy carrier. More specifically, up to 50% of the respondents raised fuel *vs.* food debate while others had either not enough information on biofuels or disappointed by their unavailability or high prices at fuel stations. Similar results (*i.e.*, availability at fuel stations and price) were obtained by Gracia et al. [613] who examined Spanish biodiesel market for identifying parameters influencing biodiesel acceptance in the transport sector. If these two parameters were comparable to those of diesel, about 50% of car drivers would definitely consume biodiesel. The number of biodiesel users would drop to 20% or 30% when only one of the mentioned factors were comparable to that of its fossil counterpart (*i.e.,* availability or price, respectively) [613]. Nevertheless, the study emphasized that the use of biodiesel was also avoided due to lack of knowledge (*i.e.,* only 20% of the car drivers surveyed knew what biodiesel was). Generally, higher degree of willingness-to-pay for renewable energy projects could be found in people (mainly younger females) with higher environmental awareness, and more income and education [613,614].

From a different viewpoint, Amin et al. [615] studied the social acceptance of biodiesel with respect to Malaysian stakeholders' willingness to commit palm-based biodiesel development and commercialization. Intriguingly, it was determined that perceived benefits (*e.g.*, health and social aspects) were the most significant direct predictor for stakeholders' attitude towards biodiesel. The other important interconnected determinants were willingness for engagement in biodiesel technology (*i.e.,* knowledge, awareness, *etc.*), trust in key players (*i.e.,* scientists, industry, and policy makers), attitude towards technology, and perceived risk (*e.g.,* environmental, human health, moral, and societal issues) [615].

In conclusion, the social acceptance must be improved in parallel to biodiesel development and commercialization. Whatever the reasons are behind social repellents of biodiesel (*i.e.,* lack of knowledge, perceived risks, negative attitude towards technology, biodiesel unavailability or high price, and lack of trust), they must be carefully assessed and addressed properly. It should also be noted that these concerns have different magnitudes of effect among people with different social status. Finally, whilst the concerns about price and availability could be partially removed through mandatory policies, these policies would be ineffective if the other above-mentioned social acceptance concerns were not sufficiently addressed.

5. Concluding remarks and future prospects

Different types of transesterification reactors (tubular/plug-flow reactors, rotating reactors, simultaneous reaction-separation reactors, cavitational reactors, and microwave reactors) employed for converting natural oils and fats into biodiesel as well as their limitations and deficiencies have been comprehensively reviewed in this article. In order to better understand the mechanisms behind each reactor technology, the effects of the main influential parameters on the transesterification process have also been discussed in detail. Biodiesel production has been scrutinized from the biofuel policies and mandates, economic aspects and impacts, and feedstock sustainability perspectives. Moreover, biodiesel production under biorefinery concept utilizing waste-oriented oils and glycerol upgrading to various value-added products have been elaborated as well. It is worth mentioning that the present article is the first to comprehensively review and discuss all the above-mentioned aspects as a whole (Table 18).

Overall, the economic profitability of biodiesel production *via* transesterification reaction markedly depends on various process parameters, *viz.* process intensification method, quantity and type of alcohol, quantity and type of catalyst, composition of oil, residence time, and temperature. Among acidic, basic, and enzymatic catalysts applied to speed up the transesterification process, basic catalysts are the most promising type tolerating harsh operating conditions while accelerating the reaction up to 4000 times. However, a high concentration of basic catalyst as well as the presence of water and free fatty acid decreases biodiesel yield by forming soap as side-product. Methanol is the most common type of alcohol for economic biodiesel production. Alcohol-to-oil molar ratios of above six are often used to induce the formation of biodiesel.

The most commonly used process mode for commercial production of biodiesel is still batch operation. However, continuous process mode requires lower space, capital, and operating cost while it also guarantees a product with uniform quality. This process mode is suitable for quick reaction and provides superior heat transfer and high selectivity compared with the batch process mode. Accordingly, the biodiesel industry is shifting toward the continuous process mode to address the drawbacks associated with the batch process operation.

It is clear that there is no perfect reactor technology for transesterifying natural oils and fats since each technology has its own pros and cons. In the majority of developed transesterification reactors, various process intensification techniques have been employed to improve the economic profitability of the process. In general, BSTRs have been extensively applied at industrial scale due to its simplicity and low-cost fabrication, even though they suffer from low efficiency and serious instability. It should be mentioned that ACCs, shockwave power reactor, STT reactor, and ultrasonic reactor have also been reached or applied at industrial scale to date for transesterification of natural oils and fats into biodiesel.

Tubular reactors provide a more efficient and economic platform for blending when quick mixing, short hold-ups, and low maintenance are desirable. Although tubular reactors require lower capital and space for construction, they have a limitation for Reynolds numbers. Moreover, these reactors experience significant temperature and pressure changes at different points between inlet and outlet, negatively affecting heat and mass transfer coefficients. In rotating reactors, intense mechanical agitation facilitates mass and heat transfer and decreases retention time of reactants and reagents. The main problems associated with these reactors are their lower efficiency as well as the difficulty of process control. Using reaction-separation reactors, better quality and higher yield of conversion could be achieved due to excellent mixing. Nevertheless, upscaling these reactors for commercial application is slightly difficult and complex. Cavitational reactors provide more narrowly dispersed and more stable emulsions than the conventional techniques, which in turn boost the reaction rate. These reactors require lower alcohol-to-oil molar ratios, lower catalyst concentrations, lower temperatures, and shorter residence times than the conventional STRs. However, complex scale up and cavitational blocking are the main disadvantages of these systems. Simple control, time and thermal efficiencies, clean products, and less downstream processing are the main advantages of microwave reactors. However, difficulty in controlling power and temperature and, thereby, low process reproducibility is the main problems associated with microwave reactors.

Generally speaking, the interest in advanced transesterification reactor is growing due to the need for reducing capital cost, energy and water consumption, space requirement, reaction time, waste streams, and environmental burdens while improving biodiesel quality and boosting conversion efficiency. Nevertheless, the main barriers for the commercial application of advanced transesterification reactors applied for converting natural oils and fats into biodiesel are their high construction costs and difficult scalability. Accordingly, it is vital to develop inexpensive and scalable versatile transesterification reactors that are applicable to various feedstocks with different qualities. In addition, emerging technologies have a chance to replace the traditional ones, if they are proved to be economically profitable and environmentally sustainable using advanced engineering approaches.

It should be noted that the appropriate selection of sustainable feedstock is the most crucial criterion in biodiesel production feasibility as feedstock makes up the majority of produc-

Table 18
Comparison of the present review article and the review papers published over the last 5 years (since 2014) on biodiesel production and processing technologies.

Ref.	Production methods	Process parameters for transesterification						A[1]	Reactor technologies	Sustainability/feasibility				B[2]
		C[3]	D[4]	E[5]	F[6]	G[7]	H[8]			I[9]	J[10]	K[11]	L[12]	
This Study	√	√	√	√	√	√	√	√	18 reactor types	√	√	√	√	✗
[616]	√	√	✗	✗	✗	✗	✗	✗	Short note on 3 reactor types	✗	✗	√	✗	✗
[617]	√	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	√
[618]	✗	✗	✗	✗	✗	✗	√	✗	✗	√	√	✗	✗	✗
[619]	✗	√	√	√	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
[620]	✗	✗	✗	✗	✗	✗	√	✗	1 reactor type	✗	✗	✗	√	✗
[621]	✗	✗	✗	✗	✗	✗	✗	√	✗	✗	✗	✗	✗	✗
[622]	✗	✗	✗	✗	✗	✗	✗	✗	✗	√	√	✗	√	✗
[623]	√	√	✗	✗	✗	✗	√	√	✗	√	✗	✗	✗	✗
[624]	✗	√	✗	✗	✗	✗	✗	√	✗	✗	✗	✗	✗	✗
[625]	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	√
[626]	✗	√	✗	✗	✗	✗	✗	√	1 reactor type	√	✗	✗	✗	✗
[627]	√	√	✗	✗	✗	✗	√	✗	✗	√	✗	✗	✗	✗
[628]	√	✗	✗	✗	✗	✗	✗	✗	✗	√	✗	✗	✗	√

[1] Mass-transfer intensification.
[2] Combustion, engine performance, and/or emission.
[3] Catalyst (types and concentration).
[4] Molar ratio.
[5] Temperature.
[6] Mixing.
[7] Residence time.
[8] Feedstock (oil) composition.
[9] Feedstock type.
[10] Feedstock sustainability.
[11] Economic feasibility and impact.
[12] Biodiesel policy.

tion cost. Apart from the economic considerations, any sustainable feedstock for biodiesel production must be classified as non-edible (*i.e.* not triggering food *vs.* fuel debate) while requiring low water footprint (*i.e.,* not triggering water *vs.* fuel debate) for its cultivation and oil extraction. Moreover, such a feedstock should confirm a minimal GHG-emissions mitigation of 35% in comparison with GHG emissions arisen from the synthesis and application of petroleum fuels. The production of biodiesel under biorefinery concept can also address some controversial issues associated with large-scale biodiesel production while providing some environmental and economic benefits. Biodiesel production from waste-oriented oils is a good example for this approach but requires an elaborated management for feedstock collection.

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