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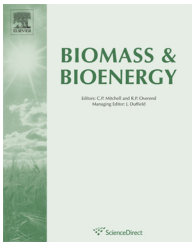

Review

A review of current technology for biodiesel production: State of the art

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ABSTRACT

This article reviews various technologies that have been used for biodiesel production till date, with a view to comparing commercial suitability of these methods on the basis of available feedstocks and associated challenges. This review shows that while emphasis is on the use of micro alga oil sources, the viability of the economics of the process is still in doubt. Homogenously catalyzed processes are the conventional technologies. However, their large-scale applicability is compromised due to their characteristic challenges. Batch processes and continuous processes are used for industrial purposes with typical capacity of 7.26–7.5 $\mathrm{Gg\,y^{-1}}$ and 8–125 $\mathrm{Gg\,y^{-1}}$ respectively, and heterogeneous catalysis may be sustainable for the continuous processes. Heterogeneous catalysts from renewable sources may be both environmentally and economically viable. Reactive distillation has the major advantage of combining the reaction and separation stages in a single unit, thereby significantly reducing capital costs and increasing opportunities for heat integration. This paper is a comprehensive overview of current technologies and appropriate options for scale-up development, providing the basis for a proposal for the exploitation of heterogeneous catalysts from natural sources to optimize biodiesel production.

1. Introduction

The consciousness of cleaner production technology is increasing globally. The need for an alternative to fossil fuels has engendered extensive research in recent years. Fossil fuels are non-renewable sources of energy which generate pollutants and are linked to global warming, climate change and even some incurable diseases. The impending challenges and the environmental implications of fossil fuels have been reviewed widely in the literature [1–3]. Biodiesel has been identified as one of the notable options for at least complementing conventional fuels. Its production from renewable biological sources such as vegetable oils and fats has been reviewed widely [4–7]. Its advantages over petroleum diesel cannot be overemphasized: it is safe, renewable, non-toxic, and biodegradable; it contains no sulphur; and it is a better lubricant. In addition, its use engenders numerous societal benefits: rural revitalization, creation of new jobs, and reduced global warming [8]. Its physical properties have been reviewed

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widely as well [4–6], some of which are dependent on the feedstock employed for its production. The flash point of biodiesel is significantly higher than that of petroleum diesel or gasoline, thus making it one of the safest fuels available. However, the calorific value of biodiesel (~37.27 MJ L^{-1}) is about ~9% lower than that of the regular petroleum diesel. The variations in the biodiesel energy density are more dependent on the fatty raw materials used than the production process [9].

There are several reports on biodiesel production from edible oils [5,10–12]; thus, its competition with food consumption has been a global concern. About 6.6 Tg (34%) of edible oil was estimated for worldwide biodiesel production from 2004 to 2007 [13], and biodiesel is projected to account for more than a third of the expected growth in edible oil use from 2005 to 2017 [13]. Consequently, employing waste and non-edible oils in biodiesel production would eliminate the competition with food consumption [9]; it will also allow for compliance with ecological and ethical requirements for biofuel. Algae are currently considered to be one of the most promising alternative sources of non-edible oils for biodiesel. Although full-scale commercialization of biodiesel from algae oil has not been launched, current research efforts have shown that algae are exceedingly fast growing and richer in oil (oil content in microalgae can exceed 80% by weight of dry biomass) [14] than the best oil crop. Biodiesel production from algae has been reviewed in detail elsewhere [14,15]. The fatty acids composition of some feedstocks used for biodiesel production has been reviewed by certain authors [4,7,16–19]. Comprehensive lists of the composition of various oils and fats have been compiled in this review (Tables 1a–f) to allow for comparison and easy choice of material. A high percentage of mono-unsaturation in fatty acid composition is a requirement for the choice of best oil for biodiesel production [4,20]. Tables 1a–f further reveal the percentage of saturated, monounsaturated, polyunsaturated and free fatty acid of each of the oil respectively. The acid values reported in g kg^{-1} of KOH are twice the free fatty acid values in percentage [21,22].

Various methods have been employed in the production of biodiesel from oils and fats feedstock [6,7,23]. A number of published articles investigated a simulated approach to evaluate some of these methods with a view to proposing cost-effective alternatives [24–26]. However, available simulated reports considered only pure materials as feedstocks. Pure feedstocks may not be realistic on a commercial scale. Preliminary review has shown that the '*one size fit all*' approach proposed by various authors may in fact not be achievable due to problems associated with the downstream processing. The use of a homogeneous catalyst also poses an environmental concern as the disposal of the resulting quantities of glycerol may be challenging [27,28] and not economically viable. Hence, the quest for more innovative and efficient processes is reflected in the number of publications on biodiesel production till date. Some advances in heterogeneous catalysis have also been reported [29,30]. Heterogeneous catalysts from natural resources or biomaterials may be useful alternatives to conventional catalysts in view of the economics of production on commercial scale.

This paper reviews various technologies that have been used for biodiesel production till date with a view to comparing commercial suitability of these methods on the

Table 1a – Edible oils with high mono-unsaturation values.

Fatty acid	Oil types						
	Groundnut oil (*Arachis hypogaea*)[a]	Sesame seed oil (*Sesamum indicum*)[b]	Hazelnut kernel oil (*Corylus avellana*)[b]	Almond kernel oil (*Prunus dulcis*)[b]	Olive kernel oil (*Olea europaea*)[b]	Moringa oil (*Moringa oleifera*)[c]	Canola oil (*Brassica campestris*)[d]
Caprylic 8:0	0.01	–	–	–	–	–	–
Capric 10:0	0.01	–	–	–	–	–	–
Lauric 12:0	0.28	–	–	–	–	–	–
Myristic 14:0	0.12	–	–	–	–	–	–
Palmitic 16:0	8.23	13.10	4.90	6.50	5.00	6.80	4.00
Palmitoleic 16:1	0.11	–	0.20	0.50	0.30	1.00	<1
Stearic 18:0	2.46	3.90	2.60	1.40	1.60	4.60	2.00
Oleic 18:1	58.69	52.80	83.60	70.70	74.70	77.50	62.00
Linoleic 18:2	21.77	30.20	8.50	20.00	17.60	0.30	20.00
Linolenic 18:3	0.34	–	0.20	–	–	–	9.00
Arachidic 20:0	1.83	–	–	–	–	–	–
Eicosenoic 20:1	–	–	–	–	–	–	2.00
Behenic 22:0	3.89	–	–	–	–	5.20	–
Erucic 22:1	–	–	–	–	–	–	<1
Lignoceric 24:0	–	–	–	–	–	0.30	
Saturated	16.82	17.00	7.50	7.90	6.60	16.90	6.00
Monounsaturated	58.79	52.80	83.80	71.20	75.00	78.50	65.00
Polyunsaturated	22.11	30.20	8.70	20.00	17.60	0.30	29.00
Acid values (g kg^{-1} KOH)	5.64	2.40–10.20	4.20	–	0.40–12.28	2.90	0.50

[a] Ref. [193].

[b] Ref. [10].

[c] Ref. [194].

[d] Ref. [195].

Table 1b – Edible oils with high poly-unsaturation values.

Fatty acid	Oil types							
	Sunflower oil (*Helianthus annuus*)[a]	Soybean oil (*Glycine max*)[a]	Cottonseed oil (*Gossypium* spp.)[b]	Corn oil (*Zea mays*)[c]	Poppy-seed oil (*Papaver somniferum*)[d]	Safflower seed oil (*Carthamus tinctorius*)[d]	Walnut kernel oil (*Juglans regia*)[d]	Chinese tallow tree oil (*Sapium sebiferum* L.)[e]
2,4-Decadienoate 10:2	–	–	–	–	–	–	–	3.21
Lauric 12:0	–	–	0.10	–	–	–	–	–
Myristic 14:0	–	0.10	0.70			–	–	Trace
Palmitic 16:0	–	11.00	20.10	11.67	12.60	7.30	–	5.45
Palmitoleic 16:1	–	–	–	–	0.10	–	7.20	3.71
Margaric 17:0	–	–	–			–	0.20	Trace
Stearic 18:0	4.50	4.00	2.60	1.85	4.00	1.90	–	2.13
Oleic 18:1	21.10	23.40	19.20	25.16	22.30	13.60	1.90	13.78
Linoleic 18:2	66.20	53.20	55.20	60.6	60.20	77.20	18.50	30.71
Linolenic 18:3	–	7.80	0.60	0.48	0.50	–	56.00	38.87
Arachidic 20:0	0.30	–	–	0.24	–	–	16.20	–
Eicosenoic 20:1	–	–	–	–	–	–	–	–
Saturated	11.30	15.10	23.50	13.76	16.60	9.20	–	7.58
Monounsaturated	21.10	23.40	19.20	25.16	22.40	13.60	–	17.49
Polyunsaturated	66.20	61.00	73.50	61.08	60.70	77.20	9.10	72.79
Acid values (g kg^{-1} KOH)	0.16	0.20	0.08	0.12	3.72–5.18	2.90	0.34	16.34

[a] Ref. [196].
[b] Ref. [23].
[c] Ref. [23].
[d] Ref. [10].
[e] Ref. [20].

basis of available feedstocks and associated challenges. The lessons gleaned from this review form the basis of a proposal for the exploitation of heterogeneous catalysts from natural sources to optimize biodiesel production, and to suggest an appropriate option for scale-up development.

2. Techniques for biodiesel production

The direct use of vegetable oils and its blends as fuel in diesel engines had been considered both unsatisfactory and impractical, primarily due to high viscosity, acid composition,

Table 1c – Edible oils with high saturation values.

Fatty acid	Oil types			
	Palm oil (*Elaeis guineensis*)[a]	Palm kernel oil (*Elaeis guineensis*)[a]	Coconut oil (*Cocos nucifera*)[b]	Bay laurel leaf oil (*Laurus nobilis*)[c]
Caproic 6:0	–	0.20	–	–
Caprylic 8:0	–	3.30		–
Capric 10:0	–	3.50	–	–
Lauric 12:0	0.20	47.80	46.50	26.50
Myristic 14:0	1.10	16.30	19.20	4.50
Palmitic 16:0	44.00	8.40	9.80	25.90
Palmitoleic 16:1	–	–	–	0.30
Margaric 17:0	–	–	–	–
Stearic 18:0	4.50	2.40	3.00	3.10
Oleic 18:1	39.20	15.40	6.90	10.80
Linoleic 18:2	10.10	2.40	2.20	11.30
Linolenic 18:3	0.40	–	–	17.60
Arachidic 20:0	–	0.10	–	–
Saturated	49.90	82.10	78.50	60.00
Monounsaturated	39.20	15.40	6.90	11.10
Polyunsaturated	10.50	2.40	2.20	28.90
Acid values (g kg^{-1} KOH)	6.90	5.20	11.60	-

[a] Ref. [196].
[b] Ref. [23].
[c] Ref. [10].

Table 1d – Non-edible oils with high mono-unsaturation values.

Fatty acid	Oil types									
	Jatropha curcas oil (*Jatropha curcas* L.)[a]	Neem oil (*Azadirachta indica*)[b]	Caper spurge oil (*Euphorbia lathyris* L.)[c]	Rice bran seed oil (*Oryza sativa*)[d]	Honge oil (*Pongamia pinnata*)[e]	Putranjiva oil (*Putranjiva roxburghii*)[e]	Yellow Oleander oil (*Thevetia peruviana* M.)[e]	Mahua oil (*Madhuca indica*)[e]	Tamanu oil (*Calophyllum inophyllum*)[e]	Crambe oil (*Crambe abyssinica* Hochst)[f]
Myristic 14:0	0.10	–	–	0.80	–	0.03	–	1.00	–	–
Palmitic 16:0	14.20	18.10	6.80	17.70	10.60	10.23	15.60	17.80	17.90	2.07
Palmitoleic 16:1	0.70	–	0.50	0.23	–	0.07	–	–	2.50	–
Margaric 17:0	0.10	–	–	–	–	0.07	–	–	–	–
Heptadecenoic 17:1	–	–	–	–	–	0.02	–	–	–	–
Stearic 18:0	7.00	18.10	1.98	2.20	6.80	10.63	10.50	14.00	18.50	0.70
Oleic 18:1	44.70	44.50	81.46	40.60	49.40	48.65	60.90	46.30	42.70	18.86
Linoleic 18:2	32.80	18.30	3.71	35.60	19.00	27.50	5.20	17.90	13.70	9.00
Linolenic 18:3	0.20	0.20	2.78	1.80	–	0.87	7.40	–	2.10	6.85
Arachidic 20:0	0.20	0.80	–	0.20	4.10	0.24	0.30	3.00	–	2.09
Eicosenoic 20:1				–	2.40	0.30	–	–	–	–
Behenic 22:0			–	0.30	5.30	0.24	0.10	–	–	0.80
Erucic 22:1			0.20	–	–	0.03	–	–	–	58.51
Lignoceric 24:0			–	0.60	2.40	0.31	–	–	2.60	1.12
Saturated	21.60	37.00	8.78	22.00	29.20	22.56	26.50	35.80	39.00	6.78
Monounsaturated	45.40	44.50	82.16	40.83	51.80	49.07	60.90	46.30	45.20	77.37
Polyunsaturated	33.00	18.50	6.49	37.40	19.00	28.37	12.60	17.90	15.80	15.85
Acid values (g kg^{-1} KOH)	35.80	32.64	25.18	13.20–49.00	40.00	3.56	1.24	42.00	44.00	0.36

[a] Ref. [196].
[b] Ref. [194].
[c] Ref. [20].
[d] Ref. [197].
[e] Ref. [18].
[f] Ref. [23].

Table 1e – Other non-edible oils.

Fatty acid	Oil types						
	Linseed oil (*Linum usitatissimum*)[a]	Castor oil (*Ricinus communis*)[a]	Rubber seed oil (*Hevea brasiliensis*)[b]	Tobacco seed oil (*Nicotina tabacum* L.)[c]	Argemone oil (*Argemone mexicana*)[d]	Azedarach oil (*Melia azedarach* L)[d]	Kusum oil (*Schleichera triguga*)[d]
Caprylic 8:0	–	–	–	<0.01	–	–	–
Capric 10:0	–	–	–	<0.01	–	–	–
Lauric 12:0	–	–	–	<0.01	–	–	0.31
Myristic 14:0	–			0.09	0.80	0.10	15.54
Palmitic 16:0	5.10	1.10	10.20	10.96	14.50	8.10	10.35
Palmitoleic 16:1	0.30	–	–	0.20	–	1.50	–
Margaric 17:0	–	–	–	0.10	–	–	–
Heptadecenoic 17:1				0.05	–	–	–
Stearic 18:0	2.50	3.10	8.70	3.34	3.80	1.20	11.11
Oleic 18:1	18.90	4.90	24.60	14.56	18.50	20.80	27.08
Linoleic 18:2	18.10	1.30	39.60	69.53	61.40	67.70	6.14
Linolenic 18:3	55.10	–	16.30	0.72	–	–	–
Arachidic 20:0	–	–	–	0.25	1.00	–	15.79
Eicosenoic 20:1		–	–	0.13	–	–	6.17
Behenic 22:0	–	–	–	0.12	–	–	0.01
Erucic 22:1	–	–	–	<0.01	–	–	–
Lignoceric 24:0	–	–	–	0.04	–	–	–
Ricinoleic		89.60	–	–	–	–	–
Saturated	7.60	4.20	18.90	14.90	20.10	9.40	53.11
Monounsaturated	19.20	4.90	24.60	14.92	18.50	22.30	33.25
Polyunsaturated	73.20	90.90	55.90	70.25	61.40	67.70	6.14
Acid values (g kg^{-1} KOH)	8.30	3.00	34.00	70.00	76.20	5.08	21.30

[a] Ref. [10].
[b] Ref. [21].
[c] Ref. [198].
[d] Ref. [18].

Table 1f – Animal fats.

Fatty acid	Oil types			
	Tallow oil[a]	Lard oil[a]	Poultry fat[b]	Fish oil[c]
Lauric 12:0	0.10	0.10	–	–
Myristic 14:0	2.80	1.40	–	–
Palmitic 16:0	23.30	23.60	22.20	10.10
Palmitoliec 16:1	–	–	8.40	0.10
Margaric 17:0	–	–	–	0.10
Stearic 18:0	19.40	14.20	5.10	4.40
Oleic 18:1	42.40	44.20	42.30	26.90
Linoleic 18:2	2.90	10.70	19.30	51.80
Linolenic 18:3	0.90	0.20	1.00	0.40
Arachidic 20:0	–	–	–	5.40
Eicosatrienoic 20:3	–	–	–	0.50
Erucic 22:1	–	–	–	0.30
Saturated	45.60	39.30	27.30	20.00
Monounsaturated	42.40	44.20	50.70	27.30
Polyunsaturated	3.80	10.90	20.30	52.70
Acid values (g kg^{-1} KOH)	27.60	14.58	3.04	3.00

[a] Ref. [23].
[b] Ref. [199].
[c] Ref. [200].

and free fatty acid content of such oils, as well as gum formation due to oxidation and polymerization during storage and combustion. Carbon deposits and lubricating oil thickening are two of the more obvious problems [27]. As a result of these problems, efforts have been undertaken to convert these vegetable oils to suitable and viable biodiesel fuels. Ma and Hanna [23] have reviewed the three well-established methods for biodiesel production, namely, microemulsion, thermal cracking and transesterification. Transesterification is the most popular and preferred, its preference having been clearly reported in detail [23].

Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. The reaction may be facilitated by catalyst using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms [10]. It should be noted that this equilibrium reaction needs greater amounts of alcohol to shift the reaction equilibrium forward to produce more methyl esters as the desired product. Although methanol and ethanol are most frequently used, ethanol is the preferred alcohol as it can be derived from agricultural products and is renewable and biologically less objectionable within the environment. However, methanol is mainly employed because of its low cost and its physical and chemical advantages [10]. The transesterification reaction can be catalyzed by alkali and acid [5,27,31,32]. Enzyme catalysis in transesterification reaction has also been reported [33]. Although transesterification reaction can be carried out in batch or continuous processes, batch operations are mainly reported. Additionally, it has been reported that the drawbacks associated with batch operation [34] can be addressed by a continuous mode of production. An example is the higher capital investment associated with the use of large reactors volumes [28]. The production capacities of batch and continuous processes are in the range of 7.26–7.5 Gg y^{-1} [35,36] and 8–125 Gg y^{-1} [36] respectively.

3. Transesterification of vegetable oil using homogeneous catalysts

This method involves the use of catalyst in liquid form, mainly acid and alkali catalysts. The basic factor in the acid catalysis is the protonation of the carbonyl group in triglycerides and the alcohol attacking the protonated carbon to create a tetrahedral intermediate. However, in a homogeneous-base catalyzed reaction, the important factor is to create nucleophilic alkoxide from the alcohol to attack the electrophilic part of the carbonyl group of the triglycerides [37]. The breakdown of triglyceride requires three steps: 1) the first step is to produce an intermediate tetrahedral as shown in the reaction mechanism (Fig. 1a and b); 2) the second step is the breakdown of the unstable intermediate tetrahedral into diglyceride ion and fatty acid ester; and 3) the final step is the recovery of the catalyst by proton transfer. These three mechanisms are repeated for cleavage of each fatty acid ester and then finally, three fatty acid esters and a glycerol are formed [38]. The use of homogeneous catalysts is the first conventional method applied in the biodiesel production industry. Although its industrial application has been decidedly proven, recent investigations are focussing on the application of heterogeneous catalysis with a view to improve productivity.

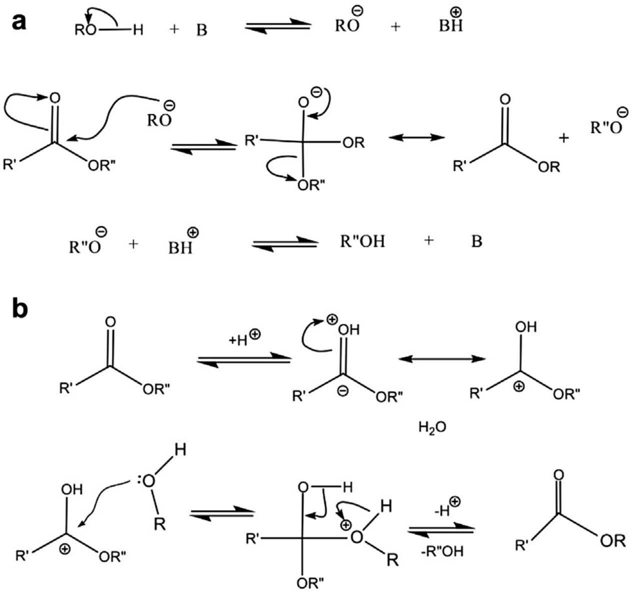

Fig. 1 – (a) Reaction mechanism of base-catalyzed transesterification reaction. (b) Reaction mechanism of acid catalyzed transesterification reaction.

3.1. *Acid catalyzed esterification process*

This method is more suitable for feedstocks with high FFAs, which may be of low grade and are less expensive [27,28]. The acid catalysts used include sulphuric, hydrochloric, sulfonic and phosphoric acids. This method has the advantage of producing tailored biofuel, as the biodiesel properties can be customized based on the fatty acids present in the feed and consequently the fatty esters obtained in the product [9]. However, this method is sensitive to the presence of water. Canakci and Gerpen [39] demonstrated that as little as 1 g kg^{-1} water in the reaction mixture was able to affect ester yields in transesterification of vegetable oil with methanol, with the reaction almost completely inhibited at 50 g kg^{-1} water concentration. Basu and Norris [40] also emphasized that the need to eliminate the water formed in FFA esterification still remains because the presence of water may favour ester saponification under alkaline conditions. The reaction is a slow one [10,27], usually performed at high oil to alcohol molar ratios, low to moderate temperatures and pressures, and high acid catalyst concentrations [41]. The separation and purification of the downstream process is tedious and capital intensive.

3.2. *Alkali-catalyzed transesterification process*

The homogeneous alkali-catalyzed transesterification has been the commonest method used at laboratory, pilot and industrial scale levels [42,43]. This process is catalyzed by alkaline metal hydroxides and alkoxides [44] as well as sodium or potassium carbonates [23]. The production cost of these catalysts is low and they show a very high performance when feedstocks (vegetable oils) with low free fatty acid are used. Also, this reaction leads to high conversion of triglycerides to their corresponding methyl esters in short reaction times [27]. However, this method also has its own shortcomings as it is energy intensive, recovery of glycerol is difficult, the catalyst has to be removed from the product, alkaline waste water requires treatment, free fatty acid and water interfere with the reaction, and low selectivity leads to undesirable side reactions [27,28,43].

3.3. *Two-step transesterification process*

This method is useful when dealing with feedstocks containing high free fatty acids (FFAs). It has been shown that alkaline catalysts cannot directly catalyze the transesterification of oils containing high FFAs save for FFA levels ranging from a mass fraction of 0.5% to less than 3% of the oil [45]. The transesterification of high FFA oils can be achieved by employing a two-step transesterification process. In this technique, the first step is an acid catalyzed process which involves esterification of the FFAs to FAMEs [4,46–48] as described in Section 3.1, followed by a second step, alkali-catalyzed transesterification, as described in Section 3.2. Various studies have been conducted using this technique with reported high yields of biodiesel [16,47,49–52]. Although a limit of <3% FFA level in oils has been reported as acceptable for homogeneous alkaline catalysis for biodiesel production without pretreatment, the FFA contents may extend beyond this limit, as it has been reported that a two-step process can also be achieved using alkaline catalysis in both steps to maximize overall yield [53] at room temperature. Ten percent increase in percentage yield was recorded using a two-step alkaline catalysis for a feedstock containing 4% FFAs [53].

4. Transesterification of vegetable oil using heterogeneous catalysts

The high production cost of biodiesel is due to both the cost of raw materials and processing costs. The application of heterogeneous (solid) catalysts in biodiesel production alleviates the problems associated with homogeneous catalysis. Heterogeneous catalysts can be recycled and re-used several times with better separation of the final product, minimizing material and processing cost. The process is environmentally benign and can be applied in either batch or continuous mode without the need for further purification steps [54,55].

According to Helwani et al. [41], heterogeneous catalyst is a spinel mixed oxide of two (non-noble) metals [41]; the acidic and basic characteristics of heterogeneous catalysts are important properties suited for use in transesterification of triglycerides just as homogeneous catalysis [54]. The reaction mechanisms have been reported showing some similarities to those of homogeneous catalysis, and these have also been reported in detail elsewhere [30,56]. These solid catalysts can be divided into two categories based on their catalytic temperature: high temperature catalysts and low temperature catalysts. According to Yan et al. [55], heterogeneous catalysis in biodiesel production, unlike homogeneous catalysis, removes the costly and time-consuming water washing and neutralization steps to separate and recover the spent catalyst. Also, contaminated water from homogeneous catalysis process is greatly reduced and the need for waste water treatment minimized [55]. The purity of methyl esters exceeds 99%, with yields close to 100%. In addition, the heterogeneous process produces glycerol as by-product with a purity of greater than 98% compared to about 80% from the homogeneous process [41]. It also has the ability to reduce the water content in the reaction medium to a value lower than the specified limit [57]. Heterogeneous catalysts can easily be tuned to include desired catalyst properties so that the presence of FFAs or water does not adversely affect the reaction steps during transesterification. Other advantages of the heterogeneous catalysts include its prolonged lifetime for fatty acid methyl ester (FAME) production and the fact that it is relatively cheap in comparison to homogeneous catalysts [55]. It has been shown that the mechanism of heterogeneous catalysis follows the principle of homogeneous catalysis of either acid or base systems [30,54]. The preparations of some selected heterogeneous catalysts are shown in Table 2.

4.1. *Heterogeneous acid transesterification*

Heterogeneous acid catalyst has the ability to catalyze both transesterification and esterification reactions simultaneously, which becomes quite important when using low quality feedstocks [28]. This catalyst is less corrosive, less toxic, and generates fewer environmental problems [58].

Industrially, heterogeneous acid catalysts have been determined to be useful because they contain a variety of acid sites with different strengths of Bronsted or Lewis acidity as compared to the homogeneous acid catalysts. Solid acid catalysts such as Nafion-NR50, sulphated zirconia and tungstated zirconia, were chosen to catalyze biodiesel-forming transesterification due to the presence of sufficient acid site strength [41]. The investigation of sulphur-based heterogeneous acid catalysts for converting acidic oils into biodiesel was studied by some researchers because sulphur-based acidic homogeneous catalysts such as H_2SO_4 showed a much higher tolerance to FFA and water than the basic homogeneous NaOH and KOH catalysts, suggesting that these catalysts may be more suited for processing acidic oils [55].

These heterogeneous acid catalysts could be either the low or high temperature type. Kiss et al. [59], in their study, used several low temperature heterogeneous acid catalysts – sulphated zirconia, zeolites, ion exchange resins and mixed metal oxides – in esterification reaction. The study revealed that sulphated zirconia was the most active heterogeneous catalyst for esterification. The transesterification of vegetable oil using sulphated zirconia as heterogeneous acid catalysts (SO_4^{2-}/ZrO_2) and tungstated zirconia (WO_3/ZrO_2) for successful conversion of the FFA to FAME prior to the biodiesel production was reported by Park et al. [60]. The pellet-type (WO_3/ZrO_2) was used for the reaction with longer time and it was determined that a 65% conversion could be maintained for up to 140 h at 75 °C. Other low temperature heterogeneous acid catalysts that have been used so far include heteropoly acid (HPAs) catalysts. The production of high-quality biodiesel fuel from low-cost *Eruca sativa* Gars oils using the solid heteropoly acid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was reported by Chai et al. [1]. The solid acid $Cs_{2.5}PW$ was shown to be an efficient catalyst for the production of environmentally compatible biodiesel fuel in high yields (99%) by using a low catalyst concentration (1.85×10^{-3}:1 weight ratio of catalyst to oil), a low methanol/oil ratio (5.3:1), and some co-solvent, THF, in a relatively short reaction time (45 min) at a low temperature (55 °C). Narasimharao et al. [61] investigated insoluble HPA salts of general formula $Cs_xH_{3-x}PW_{12}O_{40}$ ($x = 0.9–3$) for solid acid esterification and transesterification reactions. All samples with $x > 1$ were resistant to leaching, and insoluble HPA salts of general formula $Cs_xH_{3-x}PW_{12}O_{40}$ ($x = 0.9–3$) could be recycled without any major loss of activity. $Cs_{2.3}H_{0.7}PW_{12}O_{40}$ can be used in simultaneous esterification and transesterification reactions without loss of activity or selectivity. Zhang et al. [58] developed an efficient microwave-assisted transesterification (MAT) technique to prepare biodiesel from yellow horn (*Xanthoceras sorbifolia* Bunge) oil with a heteropoly acid (HPA) catalyst, namely $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. A study for optimizing the reaction conditions – reaction temperature, time, molar ratio of methanol/oil, catalyst amount, and recycle number of catalyst – was performed. The maximum yield of fatty acid methyl esters (FAMEs) reached 96.22% under optimal conditions of 60 °C, a reaction time of 10 min, molar ratio of methanol/oil 12:1, 1% $g\,g^{-1}$ of catalyst and minimum recycle number nine times.

The major drawbacks of some of the aforementioned catalysts, leaching and low surface areas, can be overcome by the use of organically-functionalized acid catalysts [55]. Some

Table 2 – Various heterogeneous catalysts and their preparation.

S/N	Heterogeneous catalysts	Catalysts' preparation
1	CaO solid base[a]	CaO powder was calcined at 1000 °C.
2	CaO solid base[b]	Calcium oxide (CaO) was prepared by decomposing pulverized $CaCO_3$ at 960 °C for 3.5 h.
2	$Ca(C_2H_3O_2)_2$/SBA-15 solid base[a]	The catalyst was prepared by an impregnation method of aqueous solution of calcium acetate on the support followed by calcination at 900 °C for 4 h.
3	$Ca(OCH_3)_2$ solid base[a]	Calcium methoxide was synthesized by a direct reaction of calcium and methanol at 65 °C for 4 h.
4	$CaTiO_3$ solid base catalyst[c]	For the synthesis of $CaTiO_3$, an equal molar mixture of TiO_2 and $CaCO_3$ was milled in an agate mortar. The mixed powder was calcined in air to 500 °C at a rate of 2 °C min^{-1} and then at 1050 °C for 2 h in an alumina crucible.
5	$Ca_2Fe_2O_5$[c]	For preparing $Ca_2Fe_2O_5$, a mixture containing a 1:2 molar ratio of Fe_2O_5 and $CaCO_3$ was milled and calcined in air to 900 °C at a rate of 2 °C min^{-1} and then at 1050 °C for 4 h.
4	SrO solid base[a]	SrO was prepared from calcination of strontium carbonate in a muffle furnace at 1200 °C for 5 h.
5	ZnO/$Sr(NO_3)_2$ solid base[a]	The aqueous solution of Sr $(NO_3)_2$ was loaded on ZnO by impregnation method and calcined at 600 °C for 5 h.
6	ZnO/Ba solid base[a]	The catalyst was prepared by an impregnation method using barium nitrate as precursor on ZnO. Dried overnight and calcined at 600 °C in air for 5 h.
7	ZnO/KF solid base[a]	The supported catalyst was prepared by impregnation method with an aqueous solution of KF. Afterwards was dried at 393 K and calcined at 600 °C in air for 5 h.
8	Al_2O_3/KI solid base[a]	The catalyst was prepared by an impregnation method from aqueous solution of potassium iodide, dried at 120 °C and activated at 500 °C for 3 h.
9	Al_2O_3/KNO_3 solid base[a]	KNO_3 was loaded on alumina by an impregnation method from aqueous solution, dried at 393 K for 16 h and finally calcined at 500 °C for 5 h.
10	Al_2O_3/Na/NaOH solid base[a]	The catalyst was prepared by mixing of γAl_2O_3, NaOH and metal sodium in a stainless steel reactor at 320 °C.
11	$VOPO_4 \cdot 2H_2O$ solid acid[a]	Vanadyl phosphate was obtained from the suspension of V_2O_5 in diluted phosphoric acid. Then activated at 500 °C.
12	ZnO solid	Pure metal oxide was used.
13	ZnO/I_2 solid acid[a]	The metal was prepared just by some treatment with distilled water and dilute HCl. Iodine was treated by sublimation.
14	ZrO_2/WO_3^{2-} solid acid[a]	The isopolytungstated zirconia was prepared by suspending a known amount of zirconium oxyhydroxide powder in an aqueous solution of ammonium metatungstate, finally calcined at 750 °C.
15	ZrO_2/SO_4^{2-} solid acid[a]	Zirconia powder were immersed in sulphuric acid solution, filtered, dried and calcined at 500 °C for 2 h.
16	TiO_2/SO_4^{2-} solid acid[a]	$TiO_2 \cdot nH_2O$ was prepared from precipitation of $TiCl_4$ using aqueous ammonia. Then immersed to sulphuric acid and finally calcined at 550 °C for 3 h to give $TiO_2–SO_4^{2-}$.
17	Al_2O_3/PO_4^{3-} solid acid[a]	Aluminium nitrate hydrated with nine moles of water dissolved in water and 85% orthophosphoric acid was added. The PH was controlled at 7 by aqueous solution of ammonia. The final precipitation was filtered out, washed, and dried at 383 K for 12 h, finally calcined at 400 °C for 3 h.
18	Al_2O_3/TiO_2/ZnO solid acid[a]	The catalyst was prepared by co-mixing of boehmite, titanium gel and zinc oxide in the presence of nitric acid and water. Calcined at 600 °C for 3 h.
19	$Al_2O_3/ZrO_2/WO_3$ solid acid[a]	The catalyst was prepared from mixture of hydrated zirconia, hydrated alumina and ammonium metatungstate and deionized water. Calcined at 900 °C for 1 h.
20	SBA-15-SO_3H-P123 sulphonic acid supported on mesoporous silica solid acid[a]	Tetraethoxysilane (TEOS) was used as silica source. 3-(mercaptopropyl)-trimethoxysilane was used as mesoporous silica modifier. Pluronic P123 (tri-block copolymer) used as surfactant. A co-condensation method was applied.
21	K/γAl_2O_3 catalyst[d]	A potassium catalyst supported on commercial γAl_2O_3 was prepared. The sample was prepared using the wet impregnation method with an aqueous solution of K_2CO_3
22	$Cs_{2.5}$PW catalyst[e]	This solid catalyst was prepared from a mixture of $H_3PW_{12}O_{40}$ and Cs_2CO_3. The compound was calcined at 573 K for 3 h in air.
23	Lithium doped calcium oxide (Li-CaO)[b]	Lithium doped calcium oxide (Li-CaO) was prepared by the incipient wetness or impregnation method: 7 g of LiNO3 was dissolved in water and 10 g of CaO was added and stirred by magnetic stirrer. The solution was dried in oven at 120 °C for 3 h and calcined at 550 °C for a duration of 3 h.
25	Lanthanum loaded on zinc oxide (La_2O_3-ZnO) supported on alumina (La_2O_3/Al_2O_3) catalysts[b]	Lanthanum loaded on zinc oxide (La_2O_3-ZnO) and supported on alumina (La_2O_3/Al_2O_3) catalysts were prepared using wetness impregnation followed by oven drying and calcination. A 10 g of La $(NO_3)_3 \cdot 6H_2O$ was dissolved in water and 7.5 g of ZnO was added to the solution. The solution was stirred and oven dried at 150 °C for 3 h. The catalyst was calcined at 470 °C for 3 h. La supported on alumina (Al_2O_3) was also prepared by the same method. A 5 g of $La(NO_3)_3 \cdot 6H_2O$ was dissolved in water and 20.3 g of Al_2O_3 was added and stirred using magnetic stirrer. The mixture was dried in oven at 150 °C for 3 h followed by calcination at 600 °C for 3 h.

(*continued on next page*)

Table 2 – (continued)

S/N	Heterogeneous catalysts	Catalysts' preparation
26	Anhydrous iron(III) sulphate ($Fe_2(SO_4)_3$) [b]	Anhydrous iron (III) sulphate ($Fe_2(SO_4)_3$) was dried in oven to remove any trace of moisture at 110 °C for 3 h prior to use as a catalyst.
27	$La_{0.1}Ca_{0.9}MnO_3$ catalyst[b]	$La_{0.1}Ca_{0.9}MnO_3$ catalyst was prepared by the precipitation method and was calcined at 650 °C.
28	Mg/Al hydrotalcites[f]	Hydrotalcites with various Mg/Al molar ratios were prepared by co-precipitation at high super-saturation. In the method, two solutions, A and B, were first heated to 40 °C, respectively. Then they were added simultaneously to a beaker under vigorous stirring. Solution A (200 ml) was prepared by mixing saturated solutions of Mg and Al metal nitrates in the desired molar ratios. Solution B was prepared by dissolving 14.0 g sodium hydroxide and 15.9 g sodium carbonate in 200 ml deionized water. After 2 h reaction, the precipitates were aged at 65 °C in a thermostatic bath. The resulting product was filtered, washed thoroughly with deionized water until the filtrate showed no presence of NaOH and subsequently dried at 90 °C for 24 h.

[a] Ref. [201].
[b] Ref. [54].
[c] Ref. [202].
[d] Ref. [203].
[e] Ref. [204].
[f] Ref. [130].

researchers have made attempts with the sulfonic acid ionic exchange resins, such as Poly (DVB) resin sulfonated with H_2SO_4, Amberlyst-35 (Rohm & Haas) [62], Amberlyst-15 (Rohm & Haas) [62], Amberlyst 15 DRY [63] and Nafion SAC-13 [64]. The only shortcoming of this type of catalyst is its functionality with very high ratio of oil to alcohol.

The high temperature heterogeneous acid catalysts have also been widely investigated. As found with low temperature heterogeneous acid catalysts, some sulphated salts and heteropoly acid catalysts are also present in the high temperature range. Solid super acid catalysts of sulphated tin and zirconium oxides and tungstated zirconia were prepared and evaluated in the transesterification of soybean oil with methanol at 200–300 °C and the esterification of *n*-octanoic acid with methanol at 175–200 °C, by Furuta et al. [65]. The tungstated zirconia-alumina was determined to be a useful catalyst for the production of biodiesel fuels from soybean oil because of its high performance in the conversions of over 90% for both esterification reactions.

Mittelbach et al. [66] reviewed transesterification of Triglyceride (TG) feedstocks using solid acid catalysts, and compared the activities of a series of layered alumino silicates with sulphuric acid for the transesterification of rapeseed oil. An initial molar ratio of 30:1 alcohol-to-oil and $5\%\ \mathrm{g\,g^{-1}}$ catalysts were used and among the catalysts tested: the ones activated by sulphuric acid impregnation showed the highest activity. The solid catalysts showed varied activities depending on reaction condition.

Activated montmorillonite KSF showed a 100% conversion after 4 h of reaction at 220 °C and $5.2 \times 10^{6}\ \mathrm{m^{-1}\,kg\,S^{-2}}$. However, leaching of sulphate species compromised the reusability of this clay. Thus, to maintain clay activity at constant values, sulphuric acid re-impregnation had to be carried out after each run. It was also likely that some degree of homogeneous catalysis was taking place due to sulphuric acid leaching.

4.2. Heterogeneous alkali transesterification

The use of heterogeneous alkali transesterification has been interesting in biodiesel production as a result of its simplification of production and purification processes, the decrease in the amount of basic waste water, the downsizing of process equipment, and the reduction of environmental impact and process costs [67]. Apart from ease of catalyst recovery, it has been shown that activity of a heterogeneous alkali

Table 3 – FAME yield using high temperature heterogeneous basic catalysts in methanol supercritical conditions.[a]

Oil	Catalyst	Reaction temp (°C)	Methanol/oil molar ratio	Reaction time (min)	Catalyst conc (% w/w)	FAME yield (%)
Sunflower	CaO	252	6.0:1	15	3.0	65
Sunflower	CaO	252	41.1:1	15	3.0	99
Soybean	CaO	300	39.3:1	10	0.58	97
Soybean	$CaCO_3$	250	39.3:1	10	1.14	87
Soybean	$CaCO_3$	300	39.3:1	10	0.67	99
Soybean	$Ca(OH)_2$	300	39.4:1	10	0.68	98
Soybean	MgO	300	39.6:1	10	1.29	91

[a] Di Serio et al. [30].

catalyst may resemble a homogeneous counterpart at the same operating condition [68]. According to Kim et al. [68], FAME yield during alkali heterogeneous catalyst, Na/NaOH/Al_2O_3, of soybean oil transesterification with methanol was found to have almost the same activity as homogeneous NaOH catalyst under optimized reaction conditions. Low tolerance to FFA and water in raw materials has been reported for heterogeneous alkali catalyst, and this has prevented their use for direct processing of crude oils with a high acid number [69]. Further, the problem of lixiviation of alkali catalyst components may be minimized by using alkaline earth metal oxide catalyst; this has been reviewed extensively elsewhere [55].

Brito et al. [70] investigated the transesterification of waste oil (used frying oil) with methanol using a high temperature heterogeneous alkali catalyst process in the presence of several Y-type zeolites with different Al_2O_3 content. Optimal reaction conversion for the transesterification of used frying oil with methanol could be achieved with zeolite Y530 at 466 °C, within a reaction time of 12.35 min, with a methanol/oil molar ratio of 6, and with zeolite Y756 at 476 °C, within reaction time 21.99 min, and the same feed mixture ratio. Demirbas [71] operated under supercritical methanol conditions using sunflower oil as feedstock. When the temperature was 252 °C, transesterification was completed within 15 min with 3% $g\,g^{-1}$ of CaO and 41:1 methanol/oil molar ratio. Other examples under these kinds of condition are shown in Table 3.

4.3. *Heterogeneous catalysts from natural sources*

Some biomass materials have been shown to possess catalytic properties that render them suitable for biodiesel production [29,72]. The application of these renewable feedstocks and heterogeneous catalysts from natural sources for biodiesel production will certainly lead to the development of a cost-effective process that is environmentally friendly. An eco-friendly process for biodiesel production can also be realized. According to Kotwal et al. [73], refined biodiesel and glycerol can be achieved, and the fact that the catalyst can be recycled will undoubtedly lower production costs. Although existing heterogeneous solid acid and solid base catalysts have been used for biodiesel production, these catalysts require a lengthy process of synthesis and may be complicated in some cases, requiring great expertise [72].

The catalytic activity of calcium containing natural and biological materials has been reported: namely, eggshell, limestone calcite, cuttlebone, dolomite and hydroxyapatite [74]. It has been shown that eggshell and dolomite can be used as catalysts in transesterification reactions yielding 95% and 98% biodiesel respectively [72,74]. The catalytic action of these materials can be attributed to the formation of calcium oxide during the calcination of these materials prior to transesterification. Fly ash-based catalysis has also been reported [73]. Babajide et al. [29] have reported an alternative route for the utilization of South African fly ash in transesterification reaction. A conversion of 86.13% can be obtained with fly ash loaded with 5% KNO_3 using sunflower oil at 160 °C. A problem of leaching was identified when sodium was impregnated unto zeolite, making potassium the metal of choice [29].

Solid catalysts derived from incomplete carbonization of carbohydrate materials followed by sulphonation have been reported to provide a high density of active SO_3H sites capable of converting waste cooking oils containing 27.8% $g\,g^{-1}$ high free fatty acids (FFAs) to biodiesel. In addition, the catalyst retained a remarkably high proportion of its original catalytic activity, even after 50 cycles of successive re-use, indicative of excellent operational stability. Evidently, solid catalysts derived from renewable and/or natural resources are effective for transesterification reactions; they are recyclable, eco-friendly and are highly suited for the production of biodiesel from oils containing high FFAs. The development of a suitable process that makes use of these catalysts would serve as a good alternative for the conventional heterogeneous catalyst of chemical origin. The aforementioned opportunities with natural and/or biological materials formed the basis of our argument for their application to heterogeneous catalysis with a view to optimizing biodiesel production by using appropriate option for scale-up development.

5. Supercritical fluid method

While the catalyzed route of production of biodiesel is the most common route used industrially, the major drawbacks of this method include the necessity of treating the free fatty acids and the triglycerides in different reaction stages, the negative effects of any water present in the mixture, catalyst consumption, the necessity of removing traces of the catalyst from the product mixture, the wastes produced, low glycerin purity, and generation of waste water. Any non-catalyzed route bears an inherent attraction associated with the absence of most of these disadvantages due to the absence of the catalyst. Production of biodiesel at supercritical conditions is one such method, where the reaction is carried out at supercritical conditions. Under such conditions, the mixture becomes homogeneous where both the esterification of free fatty acids and the transesterification of triglycerides occur without the need for a catalyst, rendering this method suitable for any type of raw material, especially those that are otherwise difficult to treat using conventional methods, such as animal fats and oils high in free fatty acids [75].

Most studies have focused on methanol and ethanol as the alcohols of choice. The key operating parameters, then, have been identified as the temperature, pressure, and methanol-to-oil ratio [76]. The typical range of operating conditions over the last decade have been temperatures of 280–400 °C and pressures of 10–30 MPa [77]. Earlier studies investigated pressures up to 45 MPa [76]. Though attractive for many reasons, the challenges regarding this method include the high alcohol-to-triglycerides molar ratios necessary to 42:1 in the case of methanol [77], and high operating temperatures and pressures.

Supercritical technology can be utilized at both the oil extraction and the esterification and transesterification reaction stages. An interesting combination of these two stages has attracted research interest recently, where simultaneous extraction and reaction from solid matrices is carried out using methanol with supercritical CO_2 as co-solvent. Each of these process types is discussed below.

5.1. *Sources of raw materials investigated with supercritical extraction*

Vegetable sources: Supercritical processes have been investigated using a wide range of both traditional and non-traditional sources of oil, with *Jatropha curcas* oil still attracting much interest, not least due to its abundance as well as its high free fatty acid content, making it particularly challenging to process. It also appears to be particularly suited for research into new processing techniques. A great deal of data on this oil is already available, making it easier to evaluate and compare new techniques against well-known processes. Thus, *J. curcas* oil is the oil of choice for researching new ideas such as reactive extraction [78–80], solubility measurements in CO_2 [81], oil extraction [82,83] and a range of combined processes [7,84–86].

Other oils of interest highlighted in recent literature have been oils of artichoke thistle [87], a range of other non-edible oils [88,89], waste vegetable oil [90–92], rice bran oil [93,94], corn oil [95,96], palm oil [97], coffee oil [98], microalgae [99–105], soybean [106], tea seed [107], grape seed [108] and rubber seed oil [109].

The cost of biodiesel is highly dependent on the cost of the raw material [110]. The range of various oils attracting research interest shows that the future of biodiesel production will be determined by a wide selection of vegetable sources depending on the economics of oil production in particular regions of the world. Also, as supercritical processes gain success, free fatty acid contents of oils, particularly of a non-edible nature, will become less of a hindrance in their conversion to the final product.

Animal sources: The use of waste animal fat for the production of biodiesel solves two problems – that of sourcing a cheap raw material from a renewable resource that does not compete with food, and that of tackling the waste management problems associated with meat production [75]. In addition, healthy, low fat meat is produced. Sources of these fats in the literature investigated have been from lamb [75,111], chicken [77] and leather [112].

As with vegetable oils, supercritical technology has been investigated at both the extraction stage and the reaction stage. Combining these two processes into a single integrated process significantly reduces processing costs [75], as the medium of extraction and reaction remain the same and high pumping costs are avoided.

The transesterification stage has likewise been carried out in a variety of ways, but predominantly catalyst free, and using methanol as the alcohol of choice [76,77,112,113]. Supercritical, enzymatic transesterification has also been investigated [75,111].

Earlier attempts to solve problems associated with catalyst separation and soap formation included the use of heterogeneous catalysts, for which immobilized enzymes were a promising alternative. These showed promising results, but with a major drawback – the immobilized catalyst was deactivated by short chain alcohols and the glycerin in the reaction mixture. This problem, though, was rectified by the use of organic solvents which dissolved both glycerol and methanol, resulting in increased yields and reaction rates, as well as the reusability of the catalyst. However, much as the use of such organic solvents would be even more necessary when animal fats are used, their use is unacceptable in meat processing. Supercritical CO_2 is an ideal replacement of organic solvents in this context. Another special challenge with the use of animal fat processing into biodiesel using the enzymatic process is the high melting point of the oil that is close to the denaturation temperature of the enzyme. However, supercritical CO_2 is a good solvent for triglycerides and offers processing temperatures that are well within the optimum conditions for lipase [75,111].

5.2. *Types of supercritical processes*

Supercritical fluid technology has been more extensively investigated for its application to the reaction stage of biodiesel production than for the extraction of oil. A survey of the literature reveals the following broad classifications of the research to date: classification based on 1) type of alcohol used (methanol or longer chain alcohols); 2) application as a catalyzed or non-catalyzed process; 3) whether or not it is used in combination with a different technology; and 4) oxidative stability and thermal decomposition of components in the reaction mixture.

5.2.1. *Alcohol type of supercritical processes*

The vast majority of investigations have focused on the use of methanol as the alcohol of choice. These investigations have looked mainly at process optimization [90,102,110,114,115] and the effects of free fatty acid content [116–121].

Shin et al. [110], using response surface methodology to investigate the influence of varying four parameters at the same time, found that for a non-catalyzed transesterification reaction of rapeseed oil in supercritical methanol, the optimum conditions were a temperature of 330 °C, pressure of 22 MPa, a molar ratio of methanol-to-oil of 50, and a process considered complete after 16 min. The content of FAME in the product was 93.6%. Lee et al. [114] investigated the same process using a much lower methanol-to-oil ratio, but allowing the reaction to proceed for much longer. It was found that the highest biodiesel yield was 102%; this was due to the reaction of methanol with glycerol, providing glycerol methyl ethers. This was a notable result as it showed that glycerol could be converted to other oxygenated and non-oxygenated compounds, enhancing the yield of this process.

Tan et al. [119] and Niza et al. [122] showed that the supercritical methanolysis reaction was highly tolerant to water and free fatty acid content, much unlike the base-catalyzed process. In fact, in both instances the yield benefitted from the presence of small amounts of water. These results represent the possibility of treating feed with rich in free fatty acids and water content without the need for pretreatment.

A few references indicate an interest in investigating other alcohols. Of these, ethanol dominates the literature. The attraction of the ethanolysis process over methanolysis lies in the fact that only the former can be 100% renewable since methanol is derived from fossil type sources. Certain physical properties of ethyl esters, like cloud point and pour point, are more desirable than those of methyl esters [123].

A direct comparison of supercritical methanolysis and ethanolysis using palm oil [124] showed that temperature was more significant factor in ethanolysis than methanolysis. At these conditions, supercritical methanolysis had a slightly higher optimum yield than ethanolysis (81.5% compared to 79.2%). This is an interesting result since the base-catalyzed processes used currently show a clear difference in favour of methanolysis over ethanolysis, mainly due to the fact that the emulsion formed by the reaction mixture when using ethanol makes the separation of the product very difficult [125]. Also, since the methoxide is more reactive than ethoxide, methanolysis results in a higher equilibrium conversion [126]. Supercritical conditions seem to eliminate these differences, making the prospect of fully renewable biodiesel more realizable.

Recently, methyl acetate transesterification was proposed [119], where methyl acetate is used in place of methanol, producing the FAME and triacetin instead of glycerol. Besides being a suitable component of the biodiesel fuel, triacetin can also be used in the cosmetic, food or petrochemical industries [127]. The results obtained using biocatalysts at ambient pressures showed long reaction times [128–130]. Under supercritical conditions without the use of a catalyst, high yield could be obtained within 45–59 min of reaction time [119]. Further, it was shown that under supercritical conditions, the free fatty acid content of the oil affects neither the kinetics of the process nor overall conversion. Complete conversion was achieved in 50 min at 345 °C, 20 MPa, at a methanol:oil ratio of 42:1 [127]. However, the theoretical amount of biodiesel expected from this process was somewhat lower than the theoretical amount expected due to the thermal decomposition of the triacetin.

5.2.2. *Application as a catalyzed or non-catalyzed of supercritical processes*

The non-catalytic processes have already been described above with respect to methanolysis, with the major drawback of this process being the high temperature required to achieve reasonable reaction rates at very high pressure [131]. The attraction to enzymatic-supercritical processes is the ability to achieve reasonable reaction rates at close to ambient temperatures. Carbon dioxide is the solvent of choice, since its critical temperature is low, at 31.1 °C, and its critical temperature is moderate, at 7.38 MPa.

It has been shown [131] that using the enzyme-catalyzed process to process edible and non-edible oils resulted in a maximum conversion of less than 70%, even after several hours. These were achieved at a temperature of 45 °C. The same oils, in a non-catalyzed process, achieved an almost complete conversion in less than 15 min. It was postulated that this was due to substrate and product inhibition of the catalyst.

A different approach to achieving high conversions in more moderate temperatures was demonstrated by combining the supercritical transesterification with use of a caesium-doped heteropoly acid catalyst near the critical point of methanol [132]. This approach combined the superior catalytic activity of heteropoly acids in acid catalyzed reactions such as esterification and transesterification, with the higher reaction rates in supercritical methanol. It was found that the use of supercritical methanol made up for the low reactivity of the acid catalyzed process, achieving 92% FAME content at 260 °C and 40 MPa in 40 min.

Other approaches have been employed to reduce the reaction temperatures and pressures required, including the use of co-solvents (for example carbon dioxide [106] and propane [106]) and also the use of inorganic heterogeneous catalysts [107].

5.2.3. *Combination with other technologies*

An important drawback of the supercritical methanolysis process is the fact that the harsh reaction conditions have been known to lead to the isomerization of the methyl esters, resulting in inferior flow properties of the product at ambient conditions [133]. The Saka–Dadan process [134,135] avoids this side reaction by carrying out hydrolysis of the triglycerides to obtain free fatty acids at subcritical conditions (7 MPa and 270 °C) prior to esterification with supercritical methanol. While avoiding the isomerization of methyl esters, this two-step process maintains all the advantages associated with the supercritical process [136].

The combination of oil extraction and simultaneous esterification/transesterification (reactive extraction) has been demonstrated [78–80,137]. Jatropha oil seeds were dried, ground, sieved and placed in a reactor together with methanol and *n*-hexane as co-solvent. A 100% oil extraction and 100% FAME yield were reported at temperatures not exceeding 300 °C, pressure not exceeding 240 MPa, and without catalyst [78]. Although the results were impressive, these conditions were considered too high. Further investigations were carried out to test the capability of different solvents in achieving the same results at lower temperature and pressure conditions [80]. The solvents selected as co-solvents for trials were pentane, heptane, toluene, THF, CO_2 and N_2. Results indicated that a co-solvent had a significant impact on the rate of extraction, as well as on conversion. CO_2 co-solvent enabled the process to be carried out at 280 °C and 4 L kg^{-1} of methanol, instead of 300 °C and 5 L kg^{-1}. Thus, reactive extraction of biodiesel from oil seeds has great potential.

5.2.4. *Oxidative stability and thermal decomposition of components*

The thermal stability of both the components and products of biodiesel is interesting since it poses a ceiling against which the temperatures at which the process can take place. Thus, studies concerning this topic have been quite extensive [122,133,138–140].

The fates of saturated and unsaturated fatty acids present in the feed were investigated in order to determine their thermal stability at temperatures ranging from 250 °C to 350 °C, pressures of 12–43 MPa, and reaction times of 15–90 min without the use of a catalyst. Methanol-to-oil ratio was maintained at 43:1 [139]. It was shown that even at the highest yield of methyl ester, unsaturated fatty acids with two or more double bonds were susceptible to thermal decomposition. This result was confirmed at slightly different reaction conditions [138]. For the methyl acetate process, the same result was confirmed [122], with the additional fact that the resultant triacetin was also thermally unstable at high temperatures, resulting in a reduced yield of biodiesel.

The thermal stability of the fatty acid methyl ester was also studied [133], with findings that all fatty acid methyl esters were stable at 270 °C. At 350 °C, isomerization reactions were evident, converting the molecules from the cis-type to the trans-type isomers. This, however, did not affect the flow properties of biodiesel. However, as in the investigations above, it was shown that polyunsaturated fatty acids decomposed at the higher temperature. Consequently, it was recommended that the supercritical methanolysis process should be carried out at temperatures lower than 300 °C, preferably at 270 °C, with a supercritical pressure of 8.09 MPa or higher.

The application of supercritical technology to biodiesel production is thus still in its infancy. Enormous potential has yet to be tapped through research and pilot plant experimentation. Results of the research published to date do show that it is likely to be a worthy competitor to the current production techniques.

6. Enzyme-catalyzed transesterification process

The search for a truly environmentally-friendly approach for biodiesel production has intensified research into the use of enzymes as catalysts. The challenges faced when conventional catalysts are employed – feedstock pretreatment, catalyst removal, waste water treatment and high-energy requirement – are alleviated in enzyme-catalyzed transesterification reactions. Biocatalysis is mediated by a group of enzymes called lipases (EC 3.1.1.3), produced by microorganisms, animals and plants [141,142]. There are two main groups of lipases: extracellular lipases and intracellular lipases. Intracellular lipases are usually employed in the whole-cell form, eliminating enzyme purification and separation processes [141]. In order to improve enzyme stability and reusability, lipases can be immobilized on several materials [141,143]. Biocatalysis is characterized by high selectivity and efficiency, consequent absence of side reactions, and high yield of methyl esters [27,43,144–148]. Further, glycerol recovery is easier and of high grade as compared to what is obtained in the alkaline process [27]. Unlike the conventional chemical catalytic routes, biocatalysis is applicable with a wide range of triglyceride sources, with FFA ranging from 0.5% to 80% [141,149]. Investigation of the kinetics of *Rhizopus oryzae* lipase indicated that free fatty acids (FFA) contained in waste oils and fats can be completely converted to alkyl esters at temperatures in the range 30–40 °C. On the other hand, alkali-catalyzed transesterification reactions, which are often carried out at temperatures in the range 60–70 °C, are characterized by significant reductions in ester yields in the presence of high FFAs [27,142]. Employing *R. oryzae* lipase in biodiesel production from soybean oil with methanol, in a solvent-free system, suggests that the process kinetics followed successive reaction mechanism [150]. Triglycerides and partial glycerides are first converted to partial glycerides and free fatty acids, respectively, after which methyl esters are synthesized from free fatty acids and methanol [150]. This implies that, as opposed to alkali-mediated transesterification where FFA composition hampers the process, FFA contained in oil can be converted to methyl esters via biocatalysis [150]. Extracellular lipase from *R. oryzae* catalyzed the conversion of feedstock with high water content (40–300 g kg^{-1}) [150]. Production of 67 mol % of methyl ester was obtained from 10 g soybean oil (containing 50 g kg^{-1} water) under optimized reaction conditions (1 h, 35 °C, 1:7.5 oil:methanol molar ratio, 475 mg enzyme) using immobilized *Pseudomonas cepacia* lipase enzyme [43].

While ethanol and methanol are commonly utilized as alcohol in most transesterification processes, Chen and Wu [151] have shown that these two alcohols have significant inhibitory effects on lipases. Their investigation revealed that enzyme deactivation increased with increasing carbon atoms of the alcohol. However, this inhibitory effect can be circumvented by employing stepwise addition of the alcohol [152]. A study by Du et al. [128] revealed that the utilization of 3:1, 4:1 and 5:1 alcohol:oil molar ratio in a solvent-free system catalyzed by *Thermomyces lanuginose* IM lipase reaction, resulted in 75, 92 and 80% FAME yields respectively. Conversely, the enzyme activity was significantly reduced to 10%, thus preventing reusability. While increasing the alcohol:oil molar ratio increases FAME yield, high values can inhibit lipases. An investigation by Shimada et al. [153] showed that the optimum methanol:oil ratio in solvent-free biocatalytic system was 1.5.

The use of organic solvents such as *n*-hexane, *n*-heptane, petroleum ether and cyclohexane is another certain factor that influences the efficiency of biocatalysis [154]. Reports have shown that comparable FAME yields are obtainable in the presence and absence of solvent [154,155]. However, reaction kinetics are enhanced in the presence of a solvent [156] due to the improved solubility of alcohol and protection of enzymes from inhibition [142].

In spite of the attractiveness of biocatalysis, its commercial application is hampered by certain demerits. These include: 1) high production cost of the lipase catalyst [27,28,157]; 2) higher reaction times as compared to base-catalyzed reaction systems [10]; and 3) regeneration and re-use of biocatalysts limited with a long operating time. As reported by Yücel [158], a 93% yield of biodiesel from pomace oil was achieved at a 24 h reaction time. Reaction times in the range of 3.5–90 h have also been reported using varying reactor types [145]. Further, potential hazard of explosion is associated with biocatalysis of biodiesel production from waste oil in an organic solvent system [153].

As shown in Table 4, the efficiency of biocatalyzed transesterification process is dependent on enzyme source and operational conditions. Additionally, there is interplay between the operational conditions and the catalytic properties of the enzymes.

7. Ultrasound assisted transesterification

The theory of ultrasonication and its application in many reacting systems has been widely reported as this provides the mechanical energy for mixing needed to initiate reaction [145]. In transesterification, it causes cavitation of bubbles near the phase boundary between the alcohol and oil phases leading to intensive mixing of the system. The cavitation leads to a localized increase in temperature, and due to the

Table 4 – Summary of enzymatic transesterification of *Jatropha curcas* oil.[a]

No.	Lipase	Time (h)	Reaction temp (°C)	Alcohol/oil molar ratio	Conv (%)	Remarks
1	*Pseudomonas cepacia* on Celite	8	50	4:1	98	Addition of 50 g kg^{-1} of water
	Free *Pseudomonas cepacia*	24	40	4:1	65	No solvent
	Pseudomonas cepacia on Celite	24	40	4:1	91	No solvent
2	*Candida antarctica* lipase B (Novozym 435)	24	45	5:1	98	A mixture of 25% pentanol and 75% iso-octane were used as solvent
	Thermomyces lanuginosus (Lipozyme)	24	45	5:1	77	
	Rhizomucor miehei (Lipozyme RMIM)	24	45	5:1	78	
3	*Enterobacter aurogenes* on activated silica 48 55 4:1 68 t	48	55	4:1	68	*t*-Butanol was used as solvent
4	*Rhizopus oryzae* on polyurethane foam	60	30	3:1	80	No Solvent
	Candida antarctica lipase B (Novozym 435)	90	30	3:1	75	No solvent

[a] Juan et al. [7].

formation of micro jets, neither agitation nor heating are required to produce biodiesel by ultrasound application [159]. As reviewed by Koh and Mohd. Ghazi [145], ultrasonication increases the chemical reaction speed, the efficient molar ratio of methanol-to-oil, and the transesterification yield of vegetable oils and animal fats into biodiesel. This method clearly works with less energy consumption compared to the conventional mechanical stirring method. Studies have shown that high yield biodiesel under the ultrasonic irradiation condition is attributable to the efficiency of cavitation which is dependent on irradiation frequency. This enhances the mass transfer between the reacting mixtures, thereby increasing the reaction rate [160]. In the transesterification of canola oil (*Brassica campestris*) with methanol by ultrasonic irradiation, conversion to fatty acid methyl esters was greater than 99% within the reaction time of 50 min [161].

The major problem associated with this method, however, is in the downstream processing. The amount of catalyst used in the process has a significant environmental impact. Large amounts of catalyst tend to produce a larger amount of soap (an undesired product) and part of the catalyst remains in the biodiesel, increasing its pH. After the completion of the transesterification reaction, biodiesel is separated from the alcohol phase and then is washed with water to remove excess catalyst, soap and glycerin, generating large amounts of waste water that should be treated [159]. This increases the purification cost, deterring the viability of the process.

8. Membrane technology of biodiesel production

A membrane reactor is a reaction system in which membranes and chemical reactions are combined. It is a device for carrying out a reaction and a membrane-based separation simultaneously in a particular physical enclosure or in close proximity. Membrane reactor technology has been successfully applied to many chemical reaction processes. The transesterification of lipids is a classic reversible chemical reaction that could also be combined with membrane reactor technology [162]. According to Dube et al. [163], the membrane can be either organic in nature (i.e. polymeric) or inorganic, with inorganic membranes being better than the former in terms of their excellent thermal stability. These membranes are very effective in removing the products as they are being formed [164]. Cao et al. [162] investigated the effects of the pore size of the membrane by using canola oil (*B. campestris*) for the biodiesel production. In their investigation, four carbon membranes having various pore sizes of 0.05, 0.2, 0.5, and 1.4 μm were tested. All the four membranes were found to retain canola oil (*B. campestris*) in the reactor, indicating that the oil droplets present in the reactor were larger than the entire pore sizes tested. A high purity of canola biodiesel was obtained.

This method has been decidedly advantageous over conventional means as it ends with a FAME-rich phase, a controlled contact of incompatible reactants, and an elimination of undesired side reactions. There is also an integration of reaction and separation into a single process, thereby reducing separation costs and recycle requirements, and an enhancement of thermodynamically limited or product-inhibited reactions resulting in higher conversions per pass [163]. The so-called ‘FAME-rich phase’ still contained, for the most part, FAME, methanol, glycerol and water [165]; therefore the problem of downstream processing in terms of separation still exists in this method.

9. Reactive distillation technology of biodiesel production

Reactive distillation (RD) is a promising multifunctional reactor to improve an ordinary process, as chemical reaction and thermodynamic separation are combined in a single unit [8]. As reviewed by Kiss et al. [8], reactive distillation is a valuable process intensification technique that can be applied successfully to the production of biodiesel since the reactions leading to the end-product are controlled by the chemical equilibrium. This is highly advantageous in esterification-type processes, when the feed has a high content of free fatty acids [166]. The use of excess methanol becomes unnecessary with this method as this can shift the reaction equilibrium towards the key product (ester) by continuous removal of by-product (water) [8]. An additional flash and a decanter are used to guarantee the high purity of the products. This is in agreement with the patent a work [167], that systems for producing a biodiesel product from multiple feedstocks may include a biodiesel reactor, a decanter, a flash evaporator and a distillation column. A reactive distillation column (RDC) consists of a core reactive zone completed by rectifying and stripping separation sections, whose extent depends on the separation behaviour of the reaction mixture. Since methanol and water are much more volatile than the fatty ester and acid, these will separate easily at the top [26].

Researchers have considered various aspects of this technique, including optimization of reaction conditions, heat integration, use of thermally-coupled distillation columns [168], dual reactive distillation [169] and catalysis [41].

Process simulation has played a central role in the exploration of various scenarios for heat integration. Cossio-Vargas [168] and Kiss [25,26] used free fatty acids as feedstock for their simulation. The former investigated sequencing of columns, specifically the advantages of a thermally-coupled distillation sequence that utilizes a side rectifier. It was noted that use of a solid acid catalyst further enhances the advantages already mentioned above by removing the necessity of separating the catalyst from the reaction mixture. Though a full economic analysis was not carried out, it was concluded that a complex distillation column with a side rectifier was capable of carrying out a reactive distillation process for the production of biodiesel.

Using pure free fatty acid as feedstock, Kiss [25,26] investigated the effect on energy saving by thermal integration of the feed and product streams on a process simulator. The data used as input to the simulator was based on reactive distillation column with a solid catalyst of sulphated zirconia. Plant-wide controllability and an economic analysis were also carried out. Energy savings of up to 45% were reported due to the heat integration alone, primarily because of the significant reduction in steam consumption in the raw material preheaters.

This process has several advantages over conventional biodiesel production processes [8]: 1) short reaction time and high unit productivity; 2) no excess alcohol requirements; 3) lower capital costs due to the small size of RDC and the lack of need for additional separation units; and 4) no neutralization and separation of the catalyst, as solid acids are used instead of homogeneous catalysts. It offers additional substantial advantages, such as higher reaction rate and selectivity, avoidance of azeotropes, and reduced energy consumption as well as solvent usage [69].

The clear advantages that reactive distillation has over other methods of processing make it particularly intriguing for further study, especially for continuous high volume production. It is clear that many researchers have opted to use process simulators to investigate reactive distillation as a method of production at a conceptual level. This has accelerated the selection of likely candidates for further exploration. Detailed economic studies, albeit using computer-aided economic analyses, as well as experimental work to support simulation studies, are still scarce in the literature.

10. Economic survey of the biodiesel industry

The major cost factor in the production of biodiesel is the cost of the raw material. Conversion costs account for about 10% in large facilities, and between 25% and 40% in small plants [170]. In recent years, the search for a cheaper product has therefore largely been a search for the cheapest raw material, together with a quest for the most economic processing method. While the variety of readily available oils have largely been studied to discover the optimum process conditions required to extract the maximum product yield, attention has now turned to the less traditional sources of triglycerides, such as algae and other lipids [76,102,171–174] from various sources. The research on processing methods has likewise broadened to include the use of heterogeneous bi-functional catalysts [175–177], the use of supercritical methods [116,127,178,179], and the integration of the biodiesel production process with other co-processes such as power co-generation and biogas production from the digestion of micro-algal waste [180]. The last few years have seen a promise of steady improvement of the economics of biodiesel production based on these research fronts. These are discussed in more detail below.

10.1. *Microalgae as a source of biodiesel feedstock*

Microalgae has many advantages over traditional sources, including soybeans [181], sunflower oil and maize oil. It is grown in open ponds, exerting zero demand on arable land. It has the potential for up to 100 times greater biodiesel yield than from soybeans [181]. It therefore presents an attractive option as a raw material source, if the cost of production of algae is favourable. However, several studies have demonstrated that at today's petroleum diesel prices, the commercialization of biodiesel from algae oil will actually be dependent on government subsidies [181]. Gallagher [182] reaches the same conclusion, adding that favourable economics is only possible if moderate algal oil yield are achieved and higher crude oil prices are reached (beyond $100 in 2008). Even then, accelerated depreciation allowances similar to agricultural start-ups are assumed. However, under conditions of high crude oil prices, in excess of $100 per barrel in real terms (based on the 2008 value), production of biodiesel from algae becomes very economically feasible, while becoming less and less sensitive to loss of government support or any increases in capital or operating costs. This also demonstrates that beyond ‘peak oil’, biodiesel from algae may well become an economic reality.

The objective in making biodiesel from algae cost competitive therefore lies in reducing the cost of production of the oil. Chisti [183] estimates the condition for the replacement of petroleum as a source of hydrocarbons to be an algal oil cost price per litre relating to the price of crude oil in $ per barrel to be:

$$C_{\text{algal oil}} = 6.9 \times 10^{-3} C_{\text{petroleum}}$$

Assuming a roughly 80% energy content of algae oil compared to crude oil.

Strategies for reducing production costs are employing genetic engineering to improve the oil production capacity of microalgae, and using an integrated bio-refinery based strategy whereby all components of the biomass are engaged in producing usable products.

10.2. *Small-scale biodiesel production*

Several publications discuss case studies of small-scale biodiesel manufacture [170,184–186]. Several notable factors differentiate small-scale production facilities from large-scale facilities. Whereas medium to large-scale facilities are more likely to be continuous operations, with feed sourced at market prices, small-scale production facilities, typically 10 Gg y^{-1}, are more likely to be batch processes, with on-farm or locally sourced raw materials required at relatively low levels. As such, their prices were insulated from sudden fluctuations in prices on the market [186], they could integrate feed production and biodiesel production [185], and the credit from the meal co-product could be accounted for. These factors had a significant impact on the economics of the operation.

For on-farm production facilities, Fore et al. [185] compared the economics of production of biodiesel from canola and from soybean oils in the United States. As expected, the viability of small-scale production was dependent on the price of petroleum diesel fuel. An important additional factor in this case was the price of protein livestock meal. The costing of the raw material, whether at market price or at production cost, also had a significant impact, particularly in the years when the difference between the two was large. Due to this factor alone, the feedstock of choice could vary from year to year. On the whole, under certain conditions, on-farm production of biodiesel was determined to be an efficient way to take advantage of the economics of integrating on-farm raw material production and biodiesel processing, while reducing reliance on off-farm energy and protein sources.

Similarly, Skarlis et al. [186] investigated the viability of a small-scale biodiesel production plant rated at 10 Gg y^{-1} in Greece. At a feed cost of 640 € Mg^{-1}, viability was guaranteed at a product cost of 780 € Mg^{-1} when the plant was running at two thirds of its annual capacity. The study provides excellent reference material for the methodology of economic evaluation of small-scale biodiesel production plants.

10.3. *Economic impact of catalyst type*

Studies comparing the economics of homogeneous and heterogeneously catalyzed processes are infrequent [36,187–189]. Sakai et al. [36] compare four processes: two homogeneous and two heterogeneous processes. Of each of these two groups, one had a hot water purification system and the other used vacuum distillation to purify the product. Basic designs for each of the four were done at four production capacities: 1.452, 2.904, 7.26 and 14.52 Gg y^{-1}. The results showed that at all production capacities, the heterogeneous process was economically superior on account of lower raw material costs (catalyst and fresh methanol), better by-product values for the water washed processes, and lower variable costs. The utilities costs were higher for the heterogeneous process, mainly due to higher steam costs.

The same conclusion was reached [188] when comparing four processes: two homogeneous, a heterogeneous and a supercritical process. The heterogeneous and supercritical processes were both superior economically, even though only the heterogeneous proved to have the only positive after tax rate of return.

Marchetti and Errazu [190] reach the same favourable conclusion with respect to heterogeneously catalyzed processes. This time the comparison was against two heterogeneous processes, one that included acid pretreatment.

10.4. *Other strategies for cost reduction*

Various strategies have been employed to reduce the production costs of biodiesel. These include use of waste or non-edible oils, integration of processes, optimization of feed combinations and development of novel processes, some of which have already been mentioned previously. A comprehensive review of many of these strategies is provided in Hasheminejad et al. [191].

The strategy to use low grade feedstock, high in FFA, has long been a priority of researchers. These include waste vegetable oils, animal fats and grease and inedible oils such as *J. curcas*. An overview of the production methods is given by Atadashi et al. [45]. Haas [173] showed that the quality of biodiesel obtained from a low value lipid soap stock was similar to any other.

Pinzi et al. [192] developed a method incorporating response surface methods to minimize the economics of a process by determining the optimum process conditions for a feed consisting of different vegetable oils.

Various integration strategies have been studied. Deshpande et al. [180] integrated a supercritical transesterification process with a heat and power generation system using part of the product as a fuel. It was found that biodiesel processing costs could be half that of conventional methods.

11. Conclusion

Various technologies employed to date for biodiesel production were described and reviewed in this paper. Membrane and reactive distillation technologies have the significant advantage of combining the reaction and separation stages in a single unit, thereby reducing capital costs in a continuous process. The latter has the further advantages of increasing opportunities for heat integration and having a purer FAME-rich phase, but it is still necessary to conduct detailed experimental and economic studies to garner support concerning the simulations done by researchers. Heterogeneous catalysts from biomass sources stand out as grossly underexplored on the basis of both environmental and economic viability.

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