Chapter 15
Intensive Technological Analysis for Biodiesel Production from a Variety of Feedstocks: State-of-the-Art

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Abstract The biodiesel industry depends on several unpredictable parameters like raw material availability, and due to this reason this industry has not spread to several countries as expected. Globally transesterification is the main technology used in the commercial production of biodiesel by reacting refined vegetable oils with methanol using homogeneous acid and alkaline catalysts depending on the quantity of the free fatty acid content present in the feedstock. During homogeneous catalyst-based process, large quantities of liquid effluents and salts result, which are responsible for environmental pollution. Due to this reason, several research groups are aiming to develop heterogeneous catalysts in place of homogeneous catalysts for developing green processes without generating effluents. These newer processes certainly help countries like India to handle the low-quality non-edible oils as feed stock. Heterogeneous catalysts provide high activity, high selectivity, and high water-tolerance properties, and these properties depend on the amount and strengths of active acid or basic sites present in these catalysts. In this direction, several heterogeneous metal-based catalysts, biomass-based carbon acid catalysts, enzyme-based catalysts are being employed by several researchers for the production of biodiesel from multi-feedstock including used cooking oils and animal fats.

Keywords Vegetable oils • Animal fat • Biodiesel • Glycerol • Homogeneous catalysts • Heterogeneous catalysts • Esterification • Transesterification

1 Introduction

Biodiesel has been focused as the most attractive alternate or complementing renewable fuel in the last two–three decades in place of petroleum fuels as the present engines need not require any modifications for biodiesel use [1]. Its

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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 provides numerous societal benefits: rural revitalization, creation of new jobs, and reduced global warming [2]. In addition the kinetic viscosity, combustion efficiency, cetane number and biodegradability of biodiesel prepared from any type of oils and fats are almost similar compared to petrodiesel. It is interesting to note that the concept of using vegetable oil as a fuel dates back to 1895 when Rudolf Diesel developed the first diesel engine to run on vegetable oil, and he has demonstrated his engine at the World Exhibition in Paris in 1900 using peanut oil as fuel [3]. The direct use of vegetable oils and its blends as fuel in diesel engines were found to be unsatisfactory and impractical, primarily due to high viscosity 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 [4]

As of now, majority of biodiesel industries are employing homogeneous catalysts for the commercial production of biodiesel from any type of feedstock. However, the use of homogeneous catalysts poses an environmental concern and also resulting with low-quality glycerol. Hence, the quest for more innovative and efficient processes employing variety of heterogeneous catalysts is being reflected in the form of several research publications on biodiesel production and some advances in this area have also been reported. This chapter reviews various newer alternative options reported for the preparation of biodiesel till date with a view to comparing commercial suitability of these methods on the basis of available feedstocks and associated challenges giving more thrust to Indian context.

2 Feedstocks Used for Biodiesel Production

Biodiesel is being produced globally from a variety of oils and fats of vegetable and animal origin, used oils, microbial oils, acid oil, fatty acid distillates [5]. However, the selection of feedstock generally depends on the availability and its commercial viability. Most of the industries in the United States of America produce biodiesel employing soybean, sunflower, and corn oils. Rapeseed/canola and sunflower oils are the major feedstocks in Europe and Canada. Few countries also employ used frying oils for the production of biodiesel. Palm oil and its fractions like palm stearin are used as the feedstock for the preparation of biodiesel in Malaysia, Indonesia, and some other Southeast Asian countries. Animal fats like tallow fats and lard and fish oil have also been used as feedstock in some of these countries for biodiesel preparation. Apart from all these traditional raw materials, some researchers have also evaluated various other vegetable oils like almond, babassu, camelina, coconut, piqui, poppy seed, sesame, tobacco, rice bran, castor cottonseed, groundnut, linseed, rubber seed, and mahua for their suitability as biodiesel feedstock [6].

The present biodiesel scenario clearly indicates that several edible oils are being used for biodiesel production and thus, its competition with food consumption has been a global concern. In addition, the range of feedstocks with different crop yields per hectare also creates lot of difference in production costs of biodiesel from country to country.

Apart from vegetable oils and animal fats, algal oil has also emerged as one of the most promising alternative feed stock. Algae can grow in municipal and industrial waste water ponds and near power-plant smokestacks by digesting the pollutants and produces triglyceride oil. It can also be grown in open ponds, exerting zero demand on arable land. Oil productivity of microalgae is several folds compared to the best producing oil crops with minimum use of land. Due to this reason, several global research organizations are investing more time and efforts into research for the development of appropriate and commercially viable processes for the production of algal oil.

2.1 Feedstock Options for India

India cannot afford to use the edible oils for the production of biodiesel as it is importing huge amounts of edible oils. In addition, during the last 5 years the imports are continuously increasing (Table 15.1) and during 2014–2015 about 14.2 million metric tons (MMT) of oils have been imported against the domestic production of 7.2 MMT [7].

Due to climatic advantages, India has a large number of oilseed-bearing trees in forests and isolated areas. However, the collection and extraction of oils from these sources are not yet carried out in a systematic manner for proper utilization. Hence there is lot of potential to exploit these cheaper minor oils as a possible feedstock for the production of biodiesel. The production of minor oils like sal, mahua, kusum, neem, and karanja is not being carried out in organized sectors and whatever the small quantities of oil produced in the country is being consumed either for edible or industrial applications. Hence, the Planning Commission of India had set an ambitious target of planting 11.2–13.4 million hectares for jatropha by the end of 11th Five Year Plan (by March 31, 2012). However, the Government

Table 15.1 Production and imports of vegetable oils in India

Year	Domestic edible oil production (in million metric tons)	Import of edible oils (in million metric tons)
2014–2015	7.20	14.42
2013–2014	8.62	11.61
2012–2013	8.08	10.38
2011–2012	8.15	9.98
2010–2011	8.52	8.37

Source: http://www.seaofindia.com/stats

of India's ambitious plan of producing sufficient biodiesel by 2012 to meet its mandate of 20% blending with diesel was unachievable mostly due to unavailability of sufficient feedstock (jatropha seeds) and lack of high-yielding drought-tolerant jatropha cultivars. In these circumstances, some state governments have also projected *Pongamia glabra* (karanja) in addition to jatropha as another major feedstock. Even though some state governments of India have initiated cultivation of both these crops, unfortunately, the reports related to these oil plantations are not really encouraging and karanja may have some potential in the coming few years compared to jatropha.

In these circumstances, Indian biodiesel industry presently employs very low-quality imported palm oil or its fractions like palm stearin, palm oil fatty acid distillates, acid oils, fish oil, used cooking oils, animal fats, available non-edible oils with higher content of free fatty acids (FFA), and small amounts of jatropha and karanja oils. According to GAIN Report of Indian Biofuels Annual [8], currently, India has 5–6 large capacity and few small-scale biodiesel plants with about 480,000 MT of total capacity. However, during 2014, these industries utilized only 28% of the installed capacity to produce about 140,000 MT of biodiesel from multiple feed-stocks. The biodiesel produced in the country is being sold to Indian Railways, small and medium enterprises, state and private transport and automobile organizations for carrying out experimental projects apart from minor sales to unorganized consumers such as cellular communication towers, brick kilns, progressive farmers, and to institutions that run diesel generators as source of power back-up. It is also interesting to note that recently Government of India has deregulated diesel price in line with petrol and following up, the Government has also allowed private biodiesel manufacturers, their authorized dealers and joint ventures of OMCs authorized by the Ministry of Petroleum and Natural Gas to sell biodiesel directly to consumers' subject to their product meeting prescribed BIS standards. These measures may encourage the biodiesel manufactures in the country in the coming years.

2.2 Selection of Appropriate Feedstock for Biodiesel

In the present scenario, it is little complex for any industry to choose the appropriate oil as they have to consider several issues like food versus fuel, economic feasibility, quality issues related to non-edible oils etc. The suitability of any uncommon feedstock oil for biodiesel production has to be critically evaluated based on their physico-chemical properties and fatty acid composition.

The appropriate physico-chemical properties and fatty acid profile are the crucial parameters for the selection of suitable feedstocks for the production of biodiesel. Comprehensive lists of the composition of various edible and non-edible oils and fats, their oil extraction techniques, technologies of biodiesel production have been compiled by several authors [9–11] and these publications will be useful as a good guide for choosing the appropriate oil.

Most of the seed oils usually comprise five major fatty acids namely palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2), and linolenic (18:3) with some exceptions like coconut oil [lauric (12:0) as major fatty acid], mustard [erucic (22:1) as major fatty acid], castor [ricinoleic (18:1) with hydroxy functionality at C12 position as major fatty acid] oils. Animal fat mostly contains palmitic, stearic and oleic acids as major fatty acids. Fish oil and some algal oils contain polyunsaturated rich fatty acids with more than 3 double bonds like eicosapentaenoic acid (20:5) and docosahexaenoic acids (22:6). Biodiesel produced from saturated fatty acid-rich oils like palm oil, palmolein, palm stearin and animal fat may not be suitable for use at cold places as it exists in semisolid or solid form at room temperature as its pour and cloud points are very high. A high percentage of mono-unsaturation in fatty acid composition may result biodiesel with better oxidative stability along with other required specifications. Even though there is no limit for a fatty acid containing two double bonds (linoleic acid), the content of methyl linolenate is restricted to a maximum limit of 12% by EN 14214 because of its tendency to oxidize. Similarly, the fish oil fatty acid esters are even more prone to oxidation than linolenic acid esters. In order to eliminate the use of fish oil or polyunsaturated fatty acid-rich oil as biodiesel feedstock, the FAME content with ≥ 3 double bonds have also been restricted to a maximum limit of 1% by EN 14214 specifications [12]. Hence one has to critically examine the fatty acid composition of any oil while choosing it as a feedstock for biodiesel production.

Kumar and Sharma [13] made a novel attempt to classify the 41 vegetable oils and 32 algal oils based on OSI as per ASTM D-6751 and EN 14214 biodiesel standards so that oils can be recommended for biodiesel which may or may not require fuel stabilization using additives. The proposed classification would help to select the oils, which can be suitably stabilized with/without antioxidants. However, no oil is found to have OSI exhibited more than 6 h as per EN 14214 biodiesel standard and therefore, all the oils/biodiesels would require stabilization using antioxidants.

3 Biodiesel Production Technologies

Several generally accepted technologies are well established for the production of biodiesel. The most common technology adopted for the preparation of biodiesel is transesterification of oils (triglycerides) with alcohol (methanol) which gives biodiesel (fatty acid methyl esters, FAME) as main product and glycerol as by-product. Transesterification works fine if the FFA and moisture contents of oil are in trace amounts. In case, the feed stock contains FFA, acid portion has to be removed from the oil by neutralization or esterification before transesterification. The most important operating variables affecting the transesterification process are reaction temperature, reaction time, reaction pressure, ratio of alcohol to oil, concentration and type of catalyst, mixing intensity and type of feedstock. Transesterification is an equilibrium reaction and needs larger amounts of alcohol to shift the reaction equilibrium forward to produce more methyl esters as the desired product. The transesterification reaction can be catalyzed by homogeneous catalysts like alkali and acid, variety of heterogeneous catalysts like metal oxides, mixed oxides, carbon catalysts, and enzymes. Certain pre-treatment methods like neutralization or esterification, degumming is also required for the smooth production of biodiesel. Several exhaustive reviews are available in the literature [4, 9, 14–23] describing various options of processing technologies for biodiesel production from clean oils, non-edible oils, used cooking oils, animal fats, and other minor feed stocks.

3.1 Pre-treatment Methods

The presence of free fatty acids, phospholipids, wax esters along with unsaponifiable matter in higher quantities in oils like jatropha oil, karanja oil, animal fats, fish oil, and used cooking oils normally create major processing problems during biodiesel preparation. Hence, pre-treatment protocols like degumming and also neutralization or esterification have to be performed before the transesterification reaction for the reduction of both phospholipids and fatty acids. Free fatty acid may not be present in case of clean oils like sunflower, soybean, and rapeseed, and hence a simple degumming process is sufficient before proceeding for transesterification.

The major component of gums is phospholipids, and these have to be removed during the degumming step as these have a tendency to form emulsion and cause problems in the separation of glycerol during the biodiesel preparation. Metal ions are also removed during the degumming step. Phospholipids present in any oils are classified into hydratable and non-hydratable phospholipids [24]. During normal water degumming, hydratable phospholipids are removed. Non-hydratable phospholipids contain calcium and magnesium salts of phosphatidic acid and phosphatidylethanolamine. They can be removed only with the help of citric or phosphoric acid after converting them into free form during acid degumming process as they do not hydrate in presence of normal water. Alcon process, dry degumming, acid degumming, super degumming, uni-degumming, special degumming, total degumming and enzymatic degumming are the commonly used degumming processes. Water and acid degumming processes are the most common processes employed by the industry. However, these methods are fine-tuned or changed as per the quality of the oil and technology used by the particular industry. Different pre-treatment methods employed before biodiesel preparation were reviewed by Chakrabarti and Prasad [9]. The phosphorus content must be <10 ppm in the biodiesel according to BIS and ASTM specifications and hence the degumming technique must be chosen for obtaining biodiesel with the required specification.

If the free fatty acid is $<2\%$ in the oil, it is generally removed through neutralization method by treating the oil with appropriate amounts of aqueous caustic alkali. The generated soap, which is sodium salts of fatty acids will be removed by centrifugation or settling down. In case, the oil is very dark, traditional bleaching operation is also employed for removing the pigments present in the oil. For oils having free fatty acid percentage more than 2%, esterification is generally carried out for converting the free fatty acids to methyl esters followed by transesterification reaction for converting triglycerides to biodiesel. Santoria et al. [25] in his review analyzed the industrial biodiesel production practice including the pre-treatment methods. However, industry has to take an appropriate decision, whether to employ neutralization initially or to convert the free fatty acid present in the oil to fatty acid methyl ester. The acid value of the biodiesel must be <0.5 as per the national and international specifications.

3.2 Homogenous Catalysts for Biodiesel Production

Homogenous catalytic methods involve the use of catalyst in liquid form, mainly acid and alkali catalysts. The use of homogeneous catalysts is the first conventional method applied in the biodiesel production industry. Homogeneous catalysts are less expensive and convert oils to biodiesel very fast.

Acid catalyzed esterification process is useful for the conversion of fatty acids and FFA present in oil to biodiesel. Most commonly employed acid catalysts are sulphuric, hydrochloric, sulfonic and phosphoric acids. Indirectly, this process can be considered as a pre-treatment process for converting FFA present in low-quality oils to biodiesel before alkali-catalyzed transesterification of triglycerides. Acid catalyzed esterification is slow and usually performed at high oil to alcohol molar ratios, low to moderate temperatures and high acid catalyst concentration. The liberated water during the esterification reaction has to be removed for enhancing the conversion of fatty acids to their respective esters. The separation and purification processes are tedious and generate effluents.

The homogeneous alkali-catalyzed transesterification reaction is the most common method being used at laboratory, pilot and industrial scale levels. This process is catalyzed by alkaline metal hydroxides and alkoxides as well as sodium or potassium carbonates. Sodium hydroxide or potassium hydroxide or corresponding alkoxides such as sodium methoxide or ethoxide are the most commonly used homogeneous alkali catalysts for transesterification of triglycerides to biodiesel. However, most popular alkaline catalyst is sodium hydroxide used as it is economically cheaper and easily available. Alkali is the commercially more viable catalyst compared to acid catalysts as the reactions very rapid [26]. At present, alkali-catalyzed transesterification is preferred globally due to lower catalyst costs and a very high reaction performance with higher yields in short reaction times when feedstocks with low FFA are used. Even though 1:3 stoichiometric ratio of triglyceride to methanol is sufficient for transesterification, 6–15 times alcohol molar proportions are generally employed to accelerate the equilibrium for getting yields of biodiesel at 60–65 °C temperature [27]. After the transesterification reaction, the glycerol is separated from biodiesel layer. The separated crude glycerol and biodiesel are purified as per the market specifications.

The process for the production of biodiesel from clean oils containing lower FFA is very easy as it involves only transesterification reaction. In case FFA is <2% in the crude feed stock, the FFA is removed as soap by alkali neutralization method followed by transesterification of triglycerides to biodiesel. Oil has to be free of moisture and FFA for alkali-catalyzed transesterification reaction as the resulting soap may create lot of problems including emulsion formation during the separation of glycerol. Salt formation is another challenge in case of homogenous acid catalyzed reactions employing catalysts like sulphuric acid while neutralizing the unreacted catalyst. Even though acid-assisted transesterification is a feasible process; the conversions are not very high like in the case of alkali-based reactions. Acid catalysts may not fully transesterify the triglyceride and this may result in low-quality biodiesel. Hence, two-step process is useful if the feedstocks contain more than 2% FFA as the alkaline catalysts may get consumed for the formation of soap without participating in transesterification reaction. Accordingly, the FFA will be converted to methyl ester in the first step employing acid catalyst followed by alkali-catalyst-based transesterification in the second step.

However, due to some issues like removal of the catalyst from the product, difficulties in the recovery and purification of glycerol, and generation waste water and its treatment and undesirable side reactions, industry is looking for alternative greener methods.

3.3 Heterogeneous Catalysts for Biodiesel Production

Biodiesel production technologies making use of homogeneous acid or base catalysts for both esterification and transesterification are quite matured and globally most of the industries are employing these catalysts. However, the major challenge during homogeneous catalyst-based technologies for biodiesel production is the generation of huge quantities of liquid effluents and salts. Biodiesel has to be washed by water after neutralization of the alkali followed by removal of moisture under reduced pressure. The industry using homogenous catalysts always face several environmental problems like corrosion, removal of catalyst residues and salts. The industry has also to take lot of care for the removal of residual catalysts from the by-product glycerol solution during the purification of glycerol. Hence, it is really necessary to introduce heterogeneous catalysts in place of homogenous catalysts to safeguard the environment in long run. During the last decade, several research groups are working in the area of heterogeneous catalysts for developing green processes for the preparation of biodiesel. The major advantage during the usage of heterogeneous catalyst is the recovery of glycerol as it does not contain water. The heterogeneous catalysts will have excellent economic advantage as these can be reused several times without losing their activity.

Heterogeneous acid catalysts will play a crucial role in the esterification of free fatty acids as low-cost oil feedstock contains high concentrations of FFA and if suitable, alkaline catalyst-based transesterification may be adopted after esterification of FFA. Several heterogeneous catalysts such as ion exchange resins, sulfated oxides, transition metal oxide and derivatives, boron group base heterogeneous catalysts, alkaline earth metal oxides and derivatives, mixed metal oxides and derivatives, alkali metal oxides and derivatives, hydrotalcites, zeolites, mesoporus silicas, heteropolyacids, waste material-based heterogeneous catalysts, carbon-based heterogeneous catalysts, biocatalysts like lipases reported for esterification, transesterification as well as simultaneous esterification and transesterification reactions and several exhaustive reviews are available in the literature describing the efforts of researchers on the development of heterogeneous catalysts for the preparation of biodiesel [16, 28–32]. It is clearly evident that heterogeneous catalysts have the ability to esterify and transesterify both fatty acids and triglycerides and hence these catalysts are more appropriate for the low-quality feedstocks which are being used for the biodiesel production in India. As of now, there are no serious reports about the commercial utilization of these heterogeneous catalysts and however, this is an exciting research area for making biodiesel industry eco-friendly. Some of the interesting aspects of heterogeneous catalysts are described here.

3.3.1 Metal-Based Heterogeneous Catalysts

Several metal oxides like barium, strontium, calcium, and magnesium oxides (BaO, SrO, CaO, MgO) were projected to have more potential for the preparation of biodiesel in quantitative yields due to their higher basicity and lower solubility in alcohols [33]. In spite of its better efficiency, Bao has not preferred over CaO due to its toxic nature and higher cost. Hence CaO has been widely used by several researchers for the transesterification of triglycerides. Some researchers also projected SrO as a potential transesterification catalyst for biodiesel preparation. All these oxides were extensively employed by several researchers for methanolysis of soybean, rapeseed, sunflower, palm, canola oils in addition to waste frying oils at 60–65 °C with 80–98% yields of biodiesel. Nanopowder calcium oxide (Nano CaO) was found to be more efficient compared to CaO for the biodiesel production from soybean oil with over 96% yields under microwave conditions [34]

Few researchers reported the use of oxides in combination of other materials for the production of biodiesel. KOH loaded on MgO, CaO supported on silicas, calcium oxide, solid super base prepared from CaO by dipping in ammonium carbonate solution, CaO impregnated with 10% $KNO_{3,}$ zirconia (ZrO_2) loaded with potassium bitartrate ($C_4H_4O_6HK$), Li, Na and K ion impregnated CaO, ZnO loaded with strontium nitrate followed by calcination were some of the modified catalysts for biodiesel production from soybean, canola, sunflower, castor, jatropha, cottonseed and rape seed oils. Eventhough the yields are very high in some cases, several issues like higher catalyst load, higher molar ratio of methanol, longer reaction times, leaching of catalysts, and problems in recycling of catalysts are some of the concerns for commercialization of these catalysts [35]

Several mixed oxides like Ca and Zn, CaO supported on zinc oxide, MgAl and MgCa oxides, $CaZrO_3$ and $CaO–CeO_2$, CaO and ZrO_2 mixed oxides, Nanocomposite mixed oxides of strontium-titanium (Sr-Ti), Aluminium oxide modified Mg–Zn, $CaTiO_3$, $CaMnO_3$, $CaZrO_3$, $Cao–CeO_2$, were employed by several researchers for the preparation of biodiesel from palm kernel oil, palmolein, soybean and sunflower oils, jatropha oil, waste cooking oils using higher equivalents of methanol to oil at varying temperatures to obtain 75–98% of yields [35]

Several base catalysts like potassium, sodium, barium and calcium, monolithic potassium, potassium hydroxide, sodium hydroxide, calcium oxide, magnesium oxide, barium oxide, potassium carbonate, Potassium nitrate (KNO_3), potassium fluoride, Eu_2O_3 were loaded on alumina and transesterified soybean, jatropha, cotton seed, rapeseed, canola, and sunflower oils and reported 63–99% yields by varying oil to methanol ratio (1:12–32) and temperature (50–70 °C). Eu_2O_3/Al_2O_3 yielded lowest yields (63%) and KF/Al_2O_3 and K/Al_2O_3 yielded 99% of biodiesel. However, most of these catalysts leached their active species into methanol and could not be recycled due to this reason [35].

Several types of hydrotalcites like Mg-Al hydrotalcites, cerium modified Mg-Al hydrotalcites, potassium loaded–calcined Mg-Al hydrotalcite, Mg-Al-CO_3 hydrotalcite, hydrotalcite-like compounds containing Mg^{2+}, Fe^{3+} and Al3+ (MgAlFe), Mg-Co-Al-La layered double hydroxide, calcinated Li-Al, Mg-Al and Mg-Fe layered double hydroxides, KF/Ca-Al hydrotalcite, KF/hydrotalcite, poly (vinyl alcohol) membranes loaded with hydrotalcite, lipase (*Saccharomyces cerevisiae*) immobilized on Mg-Al hydrotalcite were also employed for the preparation of biodiesel from soybean, rape seed, canola, cottonseed, and palm oils with 60–97% yields by varying oil to methanol ratio (1: 6–30) and temperature (60–100 °C) according to a review published by Kaki and Prasad [35]. Zeng et al. [36] employed Mg-Al hydrotalcite as a base for immobilization of *Saccharomyces cerevisiae* lipase and employed this successfully as a transesterification catalyst for the preparation of biodiesel from rapeseed oil with 96% yields.

Heteropolyacids (HPAs) have been the subject of recent attention as a result of their excellent water tolerance, superacidity, and porous architecture. In their native form, heteropolyacids are unsuitable as heterogeneous catalysts for biodiesel applications due to their high solubility in polar media [37]. Ion-exchanging larger cations into Keggin type phospho- and silicotungstic acids could able to increase their chemical stability. For example, Cs salts of phosphotungstic acid $Cs_xH_{(3-x)}$ $PW_{12}O_{40}$ and $Cs_yH_{(4-y)}$ $SiW_{12}O_{40}$ are virtually insoluble in water, with proton substitution accompanied by a dramatic increase in surface area of the resulting crystallites [38, 39]. As a consequence of these enhanced structural properties, albeit at the expense of losing acidic protons, both $Cs_xH_{(3-x)}$ $PW_{12}O_{40}$ and $Cs_yH_{(y\_x)}$ $SiW_{12}O_{40}$ are active for palmitic acid esterification to methyl palmitate and tributyrin transesterification. Most of the studies carried out using HPAs as catalysts are dedicated to the esterification of fatty acids or transesterification of short chain triglycerides.

Zeolites are flexible and versatile catalytic materials, whose acidity and/or basicity can be modulated by appropriate doping. As generally recognized, the versatile catalysis ability of zeolites results from their chemical composition, pore size distribution, and ion-exchange abilities. A microporus inorganic lithium containing zeolite has been shown to be a new generation solid base catalyst for transesterification [16]. Most of these catalysts contain the basic sites (cation) generated by thermal decomposition of the supported salt. Among zeolite family Zeolite-X, titanosilicates and mesoporus zeolites have attracted the most research attention for biodiesel preparation [40]. The acidic properties of zeolites are usually improved by protonation, that is, by exchange of the cations contained in the positively charged aluminosilicate cage with protons. It is also possible to induce some hydrophobicity of zeolites by the elimination of water of hydration [21]. Several studies have been reported for the preparation of biodiesel from variety of feedstocks employing different types of zeolites.

3.3.2 Carbon-Based Heterogeneous Catalysts

Heterogeneous catalysts were also prepared from unusual natural materials like waste egg shell, snail shell, shrimp shell, and cocoa pod husks derived Na-X zeolite by varying methods like calcination, partial carbonization and employed for production of biodiesel from soya, sunflower and rapeseed oils [35] with 83–99% yields by varying oil to methanol ratio (1:6–12) and temperature (60–80 °C).

Several carbon-based sulfonated catalysts (CBSC) have been reported in recent years with extraordinary stability and several strong protonic acid sites from renewable sources such as biomass. These catalysts are being developed from number of inexpensive biomasses like sugars, glycerol, lignin, corncobs, palm shell, and oilseed cakes and a detailed review on latest developments in biodiesel production using carbon-based catalysts by Konwar et al. [41] has been published recently. Carbon-based materials are considered as ideal catalysts due to desirable features such as low material cost, high surface area and thermal stability. They are easily prepared by functionalizing carbon surface with acids or bases and in other cases carbon material was reported to be used as support. In addition, due to structural resemblance of these activated carbons with graphite or grapheme sheets, it is possible to attach different acidic or basic functional groups to the carbon material. This paves a way for creating a diverse class of new catalysts from these carbon materials with unique structural features and catalytic properties depending upon the nature of attached groups for use in biodiesel preparation. Tada's group was the first research group to report the carbon catalyst containing polycyclic aromatic carbon rings from sucrose and D-glucose by partial carbonization followed by creating sulphonite ($–SO_3H$) groups by reacting the incomplete carbonized material with sulphuric acid. This acidic catalyst is very attractive for the conversion of fatty acids into fatty acid methyl esters [42]. The analysis confirmed that this catalyst consists of sheets of amorphous carbon bearing hydroxyl and carboxyl (–OH and –COOH) groups and high densities of $–SO_3H$ groups.

Carbon catalyst prepared from crude glycerol was another innovation by reacting with sulphuric acid by in situ partial carbonization and sulfonation

[43]. The researchers claimed that this is a single pot reaction and any type of crude glycerol obtained either from biodiesel process or glycerol pitch resulted from fat splitting process can be used for the preparation of this catalyst. This novel invention was aimed to develop alternate applications to crude glycerol and also make use of the catalyst for esterification of fatty acid in place of homogenous catalysts like sulphuric acid for the preparation of biodiesel [43]. The researchers further converted this glycerol-based carbon acid catalyst into base catalyst with transesterification activity by reacting with sodium hydroxide in specific reaction conditions [44]. Several vegetable oils like palm, sunflower, soya, rice bran, high oleic sunflower and castor were converted to biodiesel with quantitative yields employing this base catalyst. These glycerol-based carbon acid and base catalysts exhibited very good catalytic activity with excellent reusability along with moisture tolerant property with the capability to replace the traditional homogenous alkali and base catalysts. Rao et al. [45] also reported a similar type of carbon catalyst with acidic sulfonated groups from deoiled canola meal by partial carbonization followed by steam activation and treatment with sulphuric acid and this catalyst also exhibited esterification activity. The initial reports on carbon catalysts are very attractive from different angles and however, it may take some time to commercialize these catalysts.

3.3.3 Biocatalysts

The biocatalyst-mediated processes for biodiesel production have not yet reached a stage to claim as commercially feasible. However, the search for a truly environmentally friendly approach for biodiesel production has intensified the research into the use of enzymes as catalysts and a number of studies have been reported in the literature. The reported literature on biocatalysts reveals that lipases certainly compete alternative to the existing chemical catalysts. Significant data related to lipases and immobilized lipases used and their ratios to feedstocks, molar ratios of substrates, effect of solvent on the reaction, reaction conditions like time and temperature, and variation in acyl donors has been reported in the literature. Lipases are generally more effective over chemical catalyst as they exhibit substrate specificity, functional group specificity, and stereo specificity and hence industrial applications of the lipases in the oleochemical industry are becoming more attractive. The enzymatic preparation of biodiesel from different feed stocks employing lipases as alternative catalysts solves several disadvantages caused by chemical catalysts. There are several advantages for lipases as they are stable, do not require co-enzymes and tolerate organic solvents even though these catalysts cannot be commercially competitive as of now in comparison to existing base catalysts for transesterification. A large number of research communications are available in the literature employing lipases either in free from or in immobilized state for this purpose; however, the reaction times are longer compared to the alkali-catalyzed processes. Immobilized *Thermomyces lanuginosus, Candida antarctica, C. rugosa, Pseudomonas fluorescens*, *Rhizopus oryzae*, *P. cepacia* were some of the lipases extensively used at laboratory scale for the preparation of biodiesel from different oils, fats, and fatty acids [46].

The main advantage of lipases is that it can simultaneously esterify FFA and transesterify triacylglycerols and can be reused several times and hence these can be employed for the production of biodiesel from high FFA oils, acid oils, used oils, and low-quality oils extracted from spent bleaching earth. However, it is mandatory to remove the phospholipids, pigments, and other impurities from the oils and fats employing necessary pre-treatment methods like degumming and bleaching for safeguarding the activity of lipases and enhancing the biodiesel yields. In spite of all these problems, lipase-based reactions yield high-quality glycerol with minimum impurities like water and salts. A detailed overview on the use of biocatalysts for the production of biodiesel and the methodologies for enhancing the yields are reported in the literature [47].

Several studies revealed that glycerol reduces the activity of lipase by forming a coating over the lipase and blocks the active sites. Hence, glycerol has to be continuously removed from the reaction system. The lipase-catalyzed alcoholysis of oil can be achieved with and without the solvent medium. There are several initial studies reported in the literature for the transesterification of a variety of oils like sunflower, soybean, rapeseed, olive, jatropha, castor with methanol employing lipases like *Pseudomonas fluorescens, Mucor miehei, C. antarctica, Chromobacterium viscosum, C. rugosa,* and porcine pancreas for the preparation of biodiesel. The reactions were carried out directly or in the presence of solvents like hexane, and the reactions carried out in solvent medium resulted with better yields. In some cases, the biodiesel yields were improved using higher dosage of the enzyme, i.e., up to 30% based on the oil. The enzymes are reported to be unstable in the short chain alcohols like methanol in general, and the lower yields of the methanolysis could be due to the irreversible inactivation of lipase caused by the contact between the lipase and the insoluble methanol that existed as drop in the oil. These findings motivated the researchers to switch over to step-wise incremental addition of methanol to safeguard the lipase. Several findings in this direction resulted with higher yields more than 98% employing soybean, rapeseed, sunflower oils and enhancing the stability of the lipase for recycling several times immobilized *P. fluorescens and Rhizomucor miehei, C. antarctica, C. rugosa, P. cepacia* [48–50].

Several attempts were made by researchers for stabilizing the lipase by treating with glutaraldehyde or immobilizing employing various types of materials like macro porous acrylic resin, phyllosilicate, sol-gel polymer matrix and biomass support particles etc., Low-quality acid oil of the corn, rape and sunflower oils and the residual oil present in the spent bleaching earth obtained from the soya, rapeseed and palm oil contain large amounts of free fatty acids and these oils were converted to biodiesel employing *C. antarctica* and *R. oryzae* lipase-mediated esterification and transesterification and the resultant biodiesel could not be obtained in high quality. However, the lipases could able to recycle several times without loosing its activity [45, 51, 52].

Due to the high cost of lipases, it is always advantageous to commercialize lipase-based reactions employing fixed bed reactor employing immobilized lipases.

There were some isolated attempts in this direction for the preparation of biodiesel employing immobilized *C. antarctica* and *Burkholderia cepacia* lipases for the preparation of biodiesel from soybean, rapeseed and yellow grease in 90–100% yields and it was found that the activity of lipase continued for five cycles. As indicated earlier, the short-chain alcohols such as the methanol and ethanol are commonly used as acyl acceptors for the biodiesel production and however, the use of the excess alcohols and also by-product glycerol would lead to inactivation of the lipase. Novel acyl acceptors such as methyl acetate, ethyl acetate and propan-2-ol were reported recently for the successful interesterification of various oils into the biodiesel. Soybean oil was converted to biodiesel in presence of methyl acetate employing Novozyme *435* and the by-product triacetin obtained during the interesterification did not deactivate the enzyme and the enzyme could be reused continuously for 100 batches with about 92% yields [53, 54]. Ethyl acetate was also used as the acyl acceptor for the production of the biodiesel from the crude oils of jatropha, karanja, and sunflower using Novozyme 435 and the yields of ethyl esters were 91.3, 90.0, and 92.7%, respectively [55]. In a similar way, propan-2-ol was also used as an acyl acceptor for the production of biodiesel from crude jatropha, karanja, and sunflower oils with good yields employing Novozyme 435 [56].

In spite of significant number of research communications, the higher price of lipase compared to inorganic catalysts may be the real challenge to make the biodiesel production commercially viable employing biocatalysts. However, due to several advantages over the traditional catalysts, there is lot of scope for developing commercially viable biocatalysts in the area of biodiesel in the coming years.

3.4 Supercritical Fluid Methods for Biodiesel Production

The application of supercritical technology to biodiesel production is still in its infancy. Efforts have to be made through research and pilot plant experimentation for establishing this technology, and initial studies published to date do show that it is likely to be a worthy competitor to the current production techniques [57]. Under supercritical conditions, the mixture of oil and methanol becomes homogeneous where both the esterification of free fatty acids and the transesterification of triglycerides occur without the need for a catalyst. This method is suitable for any type of raw material including animal fats and high free fatty acid containing oils and also tolerant to moisture content in the feedstock [58]. The typical range of operating conditions tried over for the preparation of biodiesel have been temperatures of 280–400 °C and pressures of 10–30 MPa. However, the main challenges for this method include the high temperature and pressures in addition to the high methanol-to-triglycerides molar ratios of over 42:1 [59]. The major advantage of supercritical technology is that both the oil extraction and the preparation of biodiesel can be carried out in a single stage in the same vessel [17].

3.5 Ultrasonic Methods for Biodiesel Production

Ultrasonication provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction. 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 formation of micro jets, neither agitation nor heating are required to produce biodiesel by ultrasound application [60]. Ultrasonication increases the chemical reaction speed and yield of the transesterification of vegetable oils/animal fats. A number of oils like soybean, palm, jatropha, sunflower, canola, tung, rapeseed, fish and waster cooking oils, beef tallow were subjected to ultrasonic-assisted transesterification reactions under different process conditions of varying temperatures (25–65C), oil to alcohol ratio (1:3–12), time (5–180 min), and Ultrasonic frequency (20–40 kHz) in presence to homogeneous and heterogeneous catalysts and obtained yields upto 99% [10, 61, 62]. However, due to problems in downstream processing, a lot of efforts are required for making this process commercially viable [17].

3.6 Process Intensification Technologies in Biodiesel Production

The majority of commercial plants are producing biodiesel employing transesterification or esterification followed by transesterification reactions in stirred tank reactors in the presence of acid/base catalyst. The industry is facing several practical problems due to longer reaction times, high molar ratio of alcohol to oil and catalyst concentration, immiscible nature of oils and alcohol, reversible transesterification reaction, high operation cost etc. Hence, some researchers developed process intensification technologies and applied to improve mixing and mass/heat transfer between the two liquid phases of oil and alcohol to improve production efficiency and reduce operating cost of the process. Qiu et al. [15] summarized the process intensification technologies which enhance physical processes including heat, mass, and momentum transfer in the context of biodiesel system. The review article provided a rudimentary assessment of reaction time, energy efficiency, operating/capital cost, the difficulty of temperature control, and current status in a very detailed manner on several novel reactors like static mixers, micro-channel reactors, oscillatory flow reactors, cavitational reactors, rotating/spinning tube reactors, microwave reactors. Data was also analyzed related to the reaction/separation coupled technologies employing membrane reactors, reactive distillation and centrifugal contactors and the studies revealed that these reactors require less downstream processing steps. Some of these process intensification technologies offer the flexibility to process a variety of feedstocks. The data revealed that most of these reactors or process technologies have potential to increase the rate of reaction by intensifying transport process and mixing between alcohol and oil. The common characteristic of process intensification technologies is the small "footprint" required compared to conventional equipment as small size of reactors and less processing processes reduce the cost of construction and maintenance. Some of these technologies have also been scaled-up and commercialized successfully.

4 Conclusions

At present about 30 billion liters per year of biodiesel is being produced globally. Some of the countries namely USA, Brazil, Germany and other European countries, Indonesia, Argentina, Canada, and Malaysia are producing biodiesel from edible oils like soybean, sunflower, corn, rapeseed/canola, palm oils along with animal fat, and used cooking oils. India cannot afford to use any edible oil for the production of biodiesel, as the country is importing huge quantities of edible oil for human consumption. Hence, Indian biodiesel industry is presently employing very low-quality imported palm oil or its fractions like palm stearin, palm oil fatty acid distillates, acids oils, fish oil, used cooking oils, animal fats, available non-edible oils with higher content of free fatty acids and small amounts of jatropha and karanja oils accounting to not more than 140,000 MT of biodiesel per year. Several organizations like ASTM, European Union, and BIS have formulated specifications for B100 for ensuring that no operational problems will be encountered for the engines when the biodiesel is blended with petrodiesel. The biodiesel business worldwide is a complex phenomenon and depends on many issues that cannot be controlled so easily. Globally most of the countries are using clean edible oils for the production of biodiesel employing homogeneous catalysts like sodium hydroxide, potassium hydroxide or their corresponding alkoxides for transesterification reaction. Esterification step is also necessary in case of FFA containing oils as the fatty acids have to be initially converted into fatty acid methyl esters employing acid catalyst like sulphuric acid followed by transesterification using homogeneous alkaline catalyst. During homogeneous catalyst-based processes, large quantities of wash water and salts are formed which are responsible for environmental issues. Due to these reasons, efforts are being made to substitute homogenous catalysts with heterogeneous catalysts to counter the pollution problems. The heterogeneous process will be economically superior on account of lower raw material costs (catalyst and fresh methanol), better by-product values, and lower variable costs. Several research groups are working in this direction to develop commercially feasible heterogeneous catalysts for reducing the effluent loads from biodiesel industry which are using different types of low-quality vegetable oils. Even though significant number of research studies have been reported employing metal-based and other type of heterogeneous catalysts, several efforts are being made in recent years to utilize low-cost biomass like carbohydrates, glycerol, and oilseed cakes for the preparation of carbon-based catalysts. Biocatalysts have the capability to convert both FFA and triglycerides to biodiesel with good yields and, however, the expensive lipases and other issues related to inactivation of lipase during the reaction in presence of methanol and glycerol are still the major bottleneck to commercialize the enzyme-catalyzed technology for the biodiesel production. Some researchers developed process intensification technologies and applied to improve mixing and mass/heat transfer between the two liquid phases of oil and alcohol to improve production efficiency and reduce operating cost of the process. Hence, there are lot of challenges and opportunities for the development of newer approaches for the preparation of biodiesel for the countries like India, where low-quality oils are being used as feedstocks.

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