Biofuels are attractive alternatives to petroleum diesel. They are renewable, non-toxic, biodegradable, carbon neutral and lead to reduced tailpipe emissions. This article presents the current state-of-art processes of their production and discusses the opportunities and future challenges in this area of research.

Keywords: Biodiesel, Biofuels, Renewable fuels, Solid catalysts, Transesterification (fatty acid glycerides), Deoxygenation, Hydrodeoxygenation, Vegetable oils/fats

Presently, most of our energy needs are being met from fossil fuels. These sources of energy are non-renewable and are getting exhausted at an unprecedented rate. Moreover, the demand for energy is also increasing at a rate higher than ever. In view of this widening gap between demand and supply of energy and the increasing awareness of the pollution problems caused by the fossil fuels, it has become necessary to develop alternative/renewable fuels. The alternate fuel should be technically feasible, environmentally acceptable, readily available and economically viable to be of any practical application. Based on these criteria, vegetable oil-based biomass (triglycerides) proves to be a good source of renewable, alternative fuel. While this source alone cannot meet the entire global fuel requirement, it can, to some extent, supplement the demands. This report is not an exhaustive review but provides a brief update on various catalysts and available technologies for production of fatty acid ester-based (biodiesel) and hydrocarbon-based (biofuel) fuels from vegetable oils and fats. It also highlights the challenges and opportunities in these catalytic transformations.

Processes for Converting Vegetable Oils into Fuels

The idea of using vegetable oils as fuel for diesel engines is more than 100 years old. Rudolf Diesel ran the diesel engine on peanut oil at World Exhibition in Paris during 1900. However, the availability of low cost petroleum-based hydrocarbon fuels left no interest in plant oils. After 1970s, worldwide oil crisis and growing ecological awareness led to the rediscovery of vegetable oils as possible alternatives to fossil fuels. There are several hurdles in using vegetable oils as a fuel. Vegetable oils possess viscosities 10 to 20 times higher than the viscosity of fossil fuel. This leads to poor fuel atomization and results in incomplete combustion. Extremely high flash points of vegetable oils and their tendency towards thermal and oxidative polymerization aggravate the situation, leading to the formation of deposits on the injector nozzles, a gradual dilution and degradation of lubricating oil, and sticking of the piston ring. These problems can be solved by either adapting the engine to fuel or the fuel to the engine. The first strategy led to the development of vegetable oil engines which are not commercially relevant today. The later strategy is aimed at modifying vegetable oils by various technologies to produce fuels which approximate the properties and performance of fossil diesel. The possible methods for converting vegetable oils into biofuels for use in diesel engines are shown in Fig. 1.

Fig. 1 – Processes for converting vegetable oils into biofuels.
Vegetable oils can be blended with petroleum-diesel, but this blending is generally considered to be not satisfactory and impractical due to the high viscosity, free fatty acid content, gum formation due to oxidation and polymerization during storage. The problem of the high viscosity of vegetable oils can be solved by forming micro-emulsions with solvents such as methanol, ethanol and 1-butanol. These can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. Micro-emulsions of aqueous ethanol in soybean oil were nearly as good as No. 2 diesel, in spite of lower cetane number and energy content. Vegetable oils or animal fats can be converted to smaller molecules by means of heat/heat and catalyst. The fuel obtained through this process is called “diesel-like fuel” since there are a variety of components such as olefins and paraffin which are similar to the petroleum-based diesel. However, this pyrolysis/cat-cracking process requires high temperature between 573 and 773 K and characterization is difficult due to a variety of reaction products. The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. While the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produces some low value materials and, sometimes, more gasoline than diesel fuel.

Alcoholysis of vegetable oils is one of the most practiced commercial methods to produce biodiesel. The process involves a reaction between ester (here triglyceride) and alcohol to form a new ester (biodiesel) and alcohol (glycerol) (Fig. 2). Different types of alcohols such as methanol, ethanol, propanol and butanol have been used. However, methanol and ethanol are the most widely used, particularly methanol owing to its low price and availability.

Fatty acid methyl/ethyl esters, commonly referred to as biodiesel, are promising candidates as alternative diesel fuel. This transesterification process has been widely used to reduce the high viscosity of triglycerides. If methanol is used in this process, it is called methanolysis. The name biodiesel (Greek, bio—means life and diesel from Rudolf diesel/petrodiesel) has been given to the transesterified vegetable oil to describe its use as a diesel fuel and renewable nature.

In hydrotreatment, oxygen found in vegetable oils and fats is removed by treatment with hydrogen. It involves deoxygenation and decarboxylation, and is mostly accompanied by cracking. It is a direct route to the hydrocarbon chains of the fatty components of the triglycerides and is the ideal and also the shortest route to produce hydrocarbon-based biofuel that will have properties identical with those of conventional diesel fuels. However, this route has issues relating to process selectivity and economics. The processes commonly employed for obtaining deoxygenated biofuels from triglycerides include thermal and catalytic pyrolysis, but recently hydrotreating and deoxygenation are receiving increasing research attention.

Sources of Biofuels: Vegetable Oils and Animal Fats

Chemically, oils and fats are known as triacylglycerol or triglycerides (TG), i.e., triester of fatty acids with glycerol. Chemical and physical properties of oils and fats depend on the composition of their fatty acids. The composition of oils is reported in terms of the fatty acid profile of the oil or fat. For example, fatty acid profile of a representative soybean oil is palmitic acid (12 wt%), stearic acid (3 wt%), oleic acid (27 wt%), linoleic acid (52 wt%) and linolenic acid (6 wt%). The transesterification reaction of an oil or fat with alcohol leads to biodiesel which is a mixture of fatty esters with each ester component contributing to the properties of the fuel. Therefore, it is important and
crucial to have the knowledge of fatty acid profile of oil and fat and their properties. References 11 to 13 may be consulted for the fatty acid profiles and some physical properties of common fatty acids occurring in natural oils and fats. Fatty acids are classified into the following three categories on the basis of number of double bonds they contain.

1. Saturated fatty acids: stearic acid [C18:0], palmitic acid [C16:0], myristic acid [C14:0], lauric acid [C12:0]

2. Mono-unsaturated fatty acids: oleic acid [C18:1], palmitoleic acid [C16:1]

3. Poly-unsaturated fatty acids: linoleic acid [C18:2], linolenic acid [C18:3]

While the suitability of any material as fuel, including biodiesel, can be influenced by contaminants arising from the production or other sources, the nature of the fuel components ultimately determines the fuel properties. Some of the properties included as specifications in standards can be traced to the structure of the fatty esters (biodiesel) formed from the fatty acids of the parent oil or fat. Originally, the term “fatty acids” was applied only to carboxylic acids separated from animal and vegetable fats. Today, it includes all saturated and unsaturated aliphatic carboxylic acids with carbon chain lengths in the range of C6-C24.

Biodiesel can be produced from a variety of feedstocks. These feedstock include most common vegetable oils (e.g. soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, etc.) and animal fats (usually tallow, chicken fat, fish oils, etc) as well as waste cooking oil and grease. It can be produced either by transesterification of triglycerides or by esterification of fatty acids separated from animal and vegetable fats. Today, it includes all saturated and unsaturated aliphatic carboxylic acids with carbon chain lengths in the range of C6-C24.

Biodiesel is renewable as it is produced from oils from plant which can be cultivated again in a short span of time. Animal fats are produced when the animal consumes plant oils and other fats which are renewable. It is biodegradable and non-toxic. CO2 from the air is absorbed by plants and when the extracted oil is converted into biodiesel and burnt, the produced CO2 and other emissions are returned to the atmosphere. This cycle does not add to the net CO2 concentration in the air because the next soybean crop will reuse the CO2 in order to grow. Hence, it is referred to as ‘carbon neutral’. When fossil fuels are burned, 100% of the CO2 released add to the CO2 concentration levels in the air. When blends are used, the recycling of CO2 is not 100%; B20 reduces CO2 by 16%16,17. It reduces tailpipe particulate matter (PM), hydrocarbon (HC), and carbon monoxide (CO) emissions from most modern four-stroke CI engines. These benefits occur because the fuel (B100) contains 11% oxygen by weight. The presence of fuel oxygen allows the fuel to burn more completely, resulting in fewer unburnt fuel emissions. The same phenomenon reduces air toxics, which are associated with the

<table>
<thead>
<tr>
<th>Property</th>
<th>Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>ASTM D975</td>
<td>ASTM D6751</td>
</tr>
<tr>
<td>Composition</td>
<td>HCb (C10–C21)</td>
<td>FAMEc (C12–C22)</td>
</tr>
<tr>
<td>Kin. viscosity (mm²/s) at 313 K</td>
<td>1.9–4.1</td>
<td>1.9–6.0</td>
</tr>
<tr>
<td>Specific gravity (g/mL)</td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td>Flash point (K)</td>
<td>333–453</td>
<td>373–443</td>
</tr>
<tr>
<td>Cloud point (K)</td>
<td>258–278</td>
<td>270–285</td>
</tr>
<tr>
<td>Pour point (K)</td>
<td>238–258</td>
<td>258–289</td>
</tr>
<tr>
<td>Water (vol.%)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon (wt.%)</td>
<td>87</td>
<td>77</td>
</tr>
<tr>
<td>Hydrogen (wt.%)</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Oxygen (wt.%)</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Sulfur (wt.%)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cetane number</td>
<td>40–55</td>
<td>48–60</td>
</tr>
<tr>
<td>HFRR (microns)</td>
<td>685</td>
<td>314</td>
</tr>
<tr>
<td>BOCLE scuff (g)</td>
<td>3,600</td>
<td>47,000</td>
</tr>
</tbody>
</table>

a Reproduced from Ref. 15 with permission from American Chemical Society, Washington DC, USA.
bHydrocarbons; cFatty acid methyl esters; dHigh frequency reciprocating rig; eBall-on-cylinder lubricity evaluator.
unburnt or partially burnt HC and PM emissions. Testing has shown that PM, HC, and CO reductions are independent of the feedstock used to make biodiesel. However, an increase in NO\textsubscript{x} is observed due to higher combustion engine temperature because of 11% oxygen content in biodiesel. Various gas emissions are compared in Table 2. Due to environmental concerns, diesel is subjected to hydodesulfurization process that leads to removal of compounds like dibenzothiophenes with alkyl (usually methyl) substituents, which provide lubricity to the diesel fuel, and hence, ultra low sulphur diesel (ULSD) fuels possess poor lubricity. Adding biodiesel at levels of 2% or above restores lubricity. The presence of the ester moiety causes biodiesel to possess inherent lubricity\textsuperscript{6}. Biodiesel has a high cetane number (60 as compared to the value of 40 for petroleum diesel). This parameter is related to ignition quality and hence, biodiesel will allow cold starts and less idle noise. Also, higher flash point makes it safer in handling\textsuperscript{18}.

There are some disadvantages associated with biodiesel. Biodiesel contains 8% less energy per gallon than typical diesel. The difference between these two measurements is because biodiesel is slightly denser than diesel fuel. All biodiesel, regardless of its feedstock, provides about the same amount of energy. A further drawback to biodiesel use is its less favourable cold-flow properties compared to conventional diesel. Unlike gasoline, biodiesel starts to freeze or gel as the temperature gets colder. If the fuel begins to gel, it can clog filters and eventually become too thick to be pumped from the fuel tank to the engine. The presence of higher amounts of saturated fatty esters is one of the causes of cold-flow problems\textsuperscript{18}. The presence of polyunsaturated fatty esters causes oxidative stability problems with biodiesel. Less expensive feedstock (waste and inedible oil) and subsidies from governments can bring down the high cost of biodiesel and make it more viable.

### Methods of Biodiesel Production

There are two main factors that affect the cost of biodiesel production: the cost of raw materials (feedstock) and the cost of processing, though the commercialization of resultant glycerol (by-product) can share the production costs with biodiesel, improving the overall process profitability. Most of the biodiesel is produced from costly edible oils like soybean oil, sunflower oil, rapeseed/canola oil, palm oil, etc. However, the use of edible oils for fuel production has also led to a dilemma regarding the risk of diverting farm land or edible oil crops to biofuel production at the cost of food supply on a global scale which is commonly referred to as the ‘food versus fuel’ problem. This has led researchers to search for alternative sources such as non-edible oils derived from Jatropha curcas (Ratanjyot), Pongamia pinnatta (Karanja), Calophyllum inophyllum (Nagchampa), Hevea brasiliensis (Rubber), Madhuca indica (Mahua), used cooking oils, etc\textsuperscript{19}. The disadvantages of these oils are that they contain a large amount of free fatty acids which affect the activity of the catalysts used and hence, the rate of transesterification reactions especially in the case of homogeneous base catalyst. Depending on the quality of feedstock there are different routes used to produce biodiesel. Important routes (transesterification, esterification-cum-transesterification and hydrolysis-cum-esterification) for biodiesel production from edible and non-edible feedstock are shown in Fig. 3.

### Transesterification

This is the most common method for the production of biodiesel (Fig. 2). While homogeneous alkali catalysts are more commonly used for transesterification reactions, heterogeneous catalysts and enzymes have also been reported in the literature.

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**Table 2 – Average emissions from biodiesel compared to petroleum diesel**

<table>
<thead>
<tr>
<th>Emission type</th>
<th>B20 (%)</th>
<th>B100 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total unburned hydrocarbons</td>
<td>-20</td>
<td>-67</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>-12</td>
<td>-48</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>-16</td>
<td>-79</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>-12</td>
<td>-47</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>+2</td>
<td>+10</td>
</tr>
<tr>
<td>Sulfates</td>
<td>-20</td>
<td>-100</td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons</td>
<td>-13</td>
<td>-80</td>
</tr>
<tr>
<td>Nitrated polycyclic aromatic</td>
<td>-50</td>
<td>-90</td>
</tr>
<tr>
<td>hydrocarbons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozone potential of speicated HC</td>
<td>-10</td>
<td>-50</td>
</tr>
</tbody>
</table>
As base catalyst is mostly used for transesterification reaction, fats and oil used for it must be free from fatty acids, i.e., it requires good quality feedstock. Acid-catalyzed process, although slow and requiring higher temperature, can be used with any type of feedstock. It is mostly used for transesterification of high FFA-containing feedstock such as yellow grease, crude palm oil, karanja, etc., as in these cases base catalyst cannot be used. Figures 4 and 5 show the process flow sheets for the base and acid catalyzed processes.

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Fig. 4 – Flow diagram for a homogeneous base-catalyzed process for biodiesel production. [Reproduced from Ref. 22 with permission from Royal Society of Chemistry, London, UK].

Fig. 5 – Flow diagram for a homogeneous acid-catalyzed process for biodiesel production. [Reproduced from Ref. 22 with permission from Royal Society of Chemistry, London, UK].
Esterification followed by transesterification²²,²⁵

To reduce the cost of biodiesel production one option is to use low quality feedstock since 70-80% of the cost of biodiesel mostly depends on the cost of the feedstock. Low quality feedstocks include non-edible vegetable oils, animal fats, waste cooking oils, grease, etc. These feedstocks contain significant amount of free fatty acids (FFA). When FFAs are present, base catalyst cannot be used due to soap formation. Acid catalysts work 4000 times slower than base catalyst in transesterification reaction. To avoid corrosion, expensive acid resistant reactors have to be used. Therefore, instead of converting FFAs containing triglycerides directly into biodiesel using acid catalyst, first FFAs are esterified with methanol in the presence of an acid catalyst to obtain FAME and triglyceride mixture (Fig. 6) which then, in the second step is transesterified with methanol to obtain biodiesel and glycerol. Esterification step is sometimes also termed as the pre-treatment step as it is carried out to esterify only free fatty acids present before the main part of oil (triglycerides) is converted to fatty acid methyl ester by transesterification (Fig. 6).

Hydrolysis followed by esterification

This route is used for the production of biodiesel from low quality feedstocks. In this alternate route, biodiesel is prepared by the hydrolysis of waste oils/fats to fatty acids (Fig. 3)²⁶ followed by their esterification with alcohol to FAME. In this route, as both steps contain fatty acids (FA), base catalyst cannot be used due to soap formation. In the hydrolysis step, water and fats/oils are immiscible and water is used as a reactant, while in esterification, water is formed as a product; therefore, catalyst should be acidic²⁷. Besides biodiesel production, fatty acids are major components used in the preparation of a wide variety of products, such as soaps, surfactants, lubricants, plasticizers, paints and coatings, pharmaceuticals, foods and agricultural, industrial and personal care products²⁸.

Solid Catalysts for Biodiesel Production

A variety of catalysts have been used for the production of biodiesel. Conventionally most of the biodiesel is produced using homogeneous alkaline catalysts such as NaOH, KOH, Na₂CO₃, K₂CO₃, sodium and potassium alkoxides of methanol, ethanol, propanol and butanol or homogeneous acid catalyst such as sulphuric acid, hydrochloric acid, phosphoric acid, organic sulfonic acids if the feedstock is low-grade and contains free fatty acids (FFAs)²⁹-³². Base-catalyzed transesterification is many times faster than the acid-catalyzed reaction but cannot be used with low quality non-edible feedstock due to saponification. In addition to the saponification issue,
homogeneously catalyzed transesterification, whether an acid or base catalyst is used, suffers from some drawbacks in terms of process integrity. The first drawback is the corrosion of the reactor and pipelines by the dissolved acid/base species, which inevitably raises the material cost in process construction. The second is the difficulty in catalyst recovery from the reactant-product mixture. Disposing of used catalyst and waste water generated in removing the catalyst at the end of the reaction raise problems of environmental pollution. A drawback of homogeneously catalyzed transesterification is the limitation in establishing a continuous process. In order to overcome these disadvantages of the homogeneous catalysts, significant amount of work has been done and is still in progress for the development of a heterogeneous catalyst for biodiesel production. Both base and acid heterogeneous catalysts have been prepared and tested. The most recognized problem with the heterogeneous catalysts is its slow rate of reaction as compared to the homogeneous catalysts. For this reason, the reaction conditions of heterogeneous catalysis are intensified to enhance its sluggish reaction rates by increasing reaction temperature (373–523 K), catalyst amount (3–10 wt%) and methanol/oil molar ratio (10–50). Another problem with heterogeneous process is the leaching and deactivation of the catalysts which are important features of a catalyst for its continuous use. Table 3 gives the broad classification and lists the solid acid and base catalysts used for the production of biodiesel by transesterification.

Non-catalytic transesterification reaction is slow and normally needs high pressures and temperatures to be completed. Saka and Danton subjected rapeseed oil to transesterification process in supercritical methanol in the absence of catalyst and found that the amount of water in the reaction does not affect the conversion of oil. Conversely, the presence of some amount of water increases the formation of methyl esters and esterification of free fatty acids takes place simultaneously. Although the products can be easily separated since there is no base or acid catalyst, the supercritical process needs to be carried out at high temperatures (523–673 K) and pressure (35–60 MPa). The high temperatures bring along proportionally high heating and cooling costs. Also, high methanol:oil ratios (usually set at 42) involve high costs for the evaporation of the unreacted methanol. Additionally, the process as reported to date does not explain how to reduce free glycerol to less than 0.02% as suggested in the ASTM D6584 or other equivalent international standards.

<table>
<thead>
<tr>
<th>Catagory</th>
<th>Catalyst</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acid catalysts</strong></td>
<td>Zeolites</td>
<td>Y, β, ZSM-5, MOR, MFI, FAU</td>
</tr>
<tr>
<td>Metal oxides (mixed &amp; supported)</td>
<td>WO3–ZrO2/Al2O3, TiO2–ZrO2/Al2O3</td>
<td>38,39</td>
</tr>
<tr>
<td>Heteropolyacids</td>
<td>H3PW12O40, Cs2.5H0.5PW12O40</td>
<td>47,44</td>
</tr>
<tr>
<td>Resins</td>
<td>Amberlyst-15, Nafion-1 series, Nafion NR50</td>
<td>18,48-50</td>
</tr>
<tr>
<td>Metal complex</td>
<td>Fe-Zn DMC</td>
<td>51</td>
</tr>
<tr>
<td><strong>Base catalysts</strong></td>
<td>Zeolites</td>
<td>Zeolite X exchanged with Na, K and Cs, 10%KOH-zeolite-X, ETS-10</td>
</tr>
<tr>
<td>Basic oxides</td>
<td>MgO, CaO, La2O3, ZnO, SrO, BaO, Mg-La mixed oxide, CaCeO3, CaMnO3, CaZrO3, CaO/MgO</td>
<td>56-63</td>
</tr>
<tr>
<td>Modified catalysts (oxides, supports, mesoporous catalysts)</td>
<td>Alkali ion supported on Al2O3, ZnO, BaO and MgO, KF/KI-Al2O3, K2CO3-Al2O3, MgO-SBA-15, CaO-SBA-15, CaO-MCM-41, Eu2O3/Al2O3</td>
<td>64-73</td>
</tr>
<tr>
<td>Hydrotalcites and other basic clay</td>
<td>Crystotile, Sepiolite, hydrotalcite</td>
<td>74-76</td>
</tr>
<tr>
<td>Organic solid base</td>
<td>Guanidine [C(NH)(NH2)2] (amine), TBD (Triazo BicycloDecane), TBD-MCM-41, Zinc-Arginate (amino acid salt)</td>
<td>77-79</td>
</tr>
<tr>
<td><strong>Enzyme catalysts</strong></td>
<td>Lipases</td>
<td><em>Candida antartica</em>, Novazyme 435 (immobilized)</td>
</tr>
</tbody>
</table>

*Reproduced from Ref. 20 with permission from Springer, The Netherlands.
Solid acids contain a variety of acid sites with different strengths of Brønsted or Lewis acidity compared to the homogenous acid catalysts. Despite the fact that a wide range of solid catalysts is available for the transesterification and esterification reactions, most of them suffer from one or the other drawbacks. For example, zeolites are stable, robust and have good acidity but their small pore size causes diffusional limitation resulting in slow rates. Amberlyst-15 or -70, Nafion and resin-based catalyst possess high acidity and pore size but have to operate under mild reaction conditions to avoid catalyst degradation due to their polymeric matrix structure. In addition, when using an organic catalyst, the swelling capacity becomes a critical issue since it dictates a substrate’s accessibility to the acid sites. Unfortunately, TG is not a good swelling agent due to lengthy alkyl tails of substantial hydrophobicity, disfavouring the promise of organic resins as biodiesel catalysts. In this case, inorganic solid acid catalysts are more desirable where high reaction temperatures are necessitated to enhance the catalyst performance. The inorganic acid catalysts operate at higher reaction temperatures than base catalysts because of their lower activity for transesterification.

Solid acid catalysts have the potential to replace strong liquid acids to eliminate the corrosion problems and consequent environmental hazards posed by the liquid acids. However, the efforts at exploiting solid acid catalysts for transesterification are limited due to the pessimistic expectations of the possibility of low reaction rates and adverse side reactions. The factors governing the reactivity of solid catalysts have not been fully understood. For example, simple correlations between acid strength and activity of the catalyst have not been clearly formulated. Secondly, due to diffusional restrictions the catalyst must have a porous system with interconnecting pores, so that the entire surface of the solid is available for promoting the transesterification reaction. Even though it is possible to generate these features in solids, it is not yet routinely possible to obtain uniform pore architecture with absolute control over size or radius or geometry of the pores as well as the stability of the solid in the system. Recently, an increasing number of researchers have paid attention to the use of TG model compounds, e.g. triacetin and tricaprylin, for biodiesel formation reactions in order to develop a better fundamental understanding relevant to catalyst activation and deactivation. By understanding catalyst deactivation, one should be able to design catalysts and catalytic systems which are more resistant to deactivation. Keeping the above discussion in mind, an ideal solid acid catalyst should have the following characteristics:

1. Interconnected system of large pores to minimize diffusional problems of molecules having long alkyl chains,
2. High surface area,
3. High concentration of moderate to strong acid sites to promote the transesterification/esterification reaction with significant rates,
4. High thermal stability of acid sites, and,
5. Hydrophobic surface to promote the preferential adsorption of oily hydrophobic species on the catalyst surface and avoid possible deactivation of catalytic sites by strong adsorption of polar compounds such as water and glycerol.

**Solid Catalyst-based Processes in Commercial/ Pilot Plant Stage**

**Esterfip-H process**

The Institüt Français du Pétrole’s (IFP) wholly owned subsidiary, Axens, has pushed forward commercialisation of IFP’s R&D and has concluded licensing contracts with producers. Axens’ first breakthrough was a solid catalyst transesterification process known as Esterfip-H, which uses a combination of metal oxides, primarily zinc and aluminium, extruded into pellets. The main advantages are higher yield (nearly 100%) than with homogeneous catalysts, no side reactions producing soap, and, the catalyst remains stable for many years, keeping the catalyst cost below €4 per tonne of fuel produced.

**ENSEL process**

Benefuel Inc., USA has two catalysts, one of which is a hydrophobic double-metal cyanide (DMC), and the other, a metal oxide catalyst developed by NCL, Pune. Benefuel Inc.’s catalysts are produced in powder or extruded forms: extrusions for fixed-bed continuous processing reactors and powders for use in batch processing. There is a less pre-treatment requirement. Washing or glycerine treatment plant is not needed. Three factors favoring the ENSEL process include higher glycerin quality, low water consumption and lesser oil refining costs. The ENSEL catalysts are able to convert lower grade (less refined) oils. Higher FFA levels and water have no impact on ENSEL catalysts’ capacity for transesterification. Even palm distillate having 85% FFA can be
converted to biodiesel. Glycerin from the ENSEL process contains only traces of water and the purity ranges from 95 to 97%.

Catilin’s process

Catilin, USA, has commercialized the new catalyst developed at Iowa State University in Ames and the U.S. DOE’s Ames Laboratory. The T300 heterogeneous catalyst is non-toxic and can be a direct replacement for conventional catalysts used in biodiesel production. The drop-in solid catalyst operates at industry standard pressures and temperatures and is removed with filtration. As a result, current producers can retrofit their plants in a matter of days at very low cost. Another key advantage is that the glycerin co-product has purity greater than 98% and qualifies as technical grade, which significantly enhances its overall value. Catilin is currently running a batch production pilot plant in Ames, Iowa, which will be modified to a continuous process.

Nippon’s process

Nippon Shokubai Co. Ltd., has developed a new catalyst and therewith a new process for simultaneous production of biodiesel fuel and glycerin from vegetable oils. This process based on a new technology is a landmark and is cost competitive. It generates almost no waste and offers reductions of about 10 and 15 percent in equipment and variable costs respectively, compared to the conventional process. It can utilize all sorts of vegetable oils and yield biodiesel (3% higher) and high quality glycerin (98%).

Endicott process

Endicott Biofuels, Texas, USA, produces biofuels based in part on a license from Davy Process Technology Ltd. (Davy). This technology is an integral proven element of Davy’s industry leading Natural Detergent Alcohol Process in which methanol vapour passes counter current to the fatty acid over solid esterification catalyst (ion exchange resin containing sulfonic/carboxylic groups) ensuring almost complete conversion of the fatty acids to methyl esters. Endicott’s production technology enables the conversion of any fat/oil or fatty acid feedstock, up to 100% fatty acids, to high quality biodiesel. Endicott can also switch from one blend of low cost feedstock to another while online and producing at full capacity. Endicott’s production technology is also ready to process future feedstock under development today including algae oil and lipids from cell ethanol production. The ability to process any lipid regardless of whether it is neutral or acidic gives future feedstock developers more freedom to operate.

Despite having the various advantages over homogeneous process, only 10% of the total biodiesel is produced by heterogeneous catalysts and around 90% by using homogeneous catalysts – more than 80% of this quantity is made with methylates, the rest with hydroxides. Though still in infancy, biofuels is a fast-moving industry. Several companies have shown that solid catalysts can work on a commercial scale and with rising transport costs, increasing fuel prices and environmental concerns, the importance and market for biofuels is expected to grow.

Hydrocarbon-based Biofuels

An alternative method of converting triglycerides into hydrocarbon-based diesel fuel is through a hydrotreating process (Fig. 7). The hydrotreating

![Fig. 7 – Hydrotreatment of vegetable. [Reproduced from Ref. 94 with permission from Elsevier, UK.]}
process requires hydrogen gas to selectively eliminate the linkage oxygen as water and carbon dioxide. The resulting products are the respective diesel-like hydrocarbons. Paraffin-like liquid fuel obtained by hydrotreating vegetable oil and fats is sometimes termed as second generation biodiesel or green diesel. Unlike the first generation (ester-based biodiesel), this new generation of biodiesel (hydrocarbons) is more favorable for industrial applications, being compatible with the current engines and even avoiding the need to be blended with petrol fuels if isomerized. In hydrotreating, removal of oxygen is accomplished through hydrodeoxygenation (HDO) and other direct mechanisms such as hydrodecarbonylation (HDCN), hydrodecarboxylation (HDCX) and hydrogenation. These processes can be performed using existing petroleum refineries. Hydrotreating is used in thepetroleumrefinery to remove S, N and metals from petroleum-derived feedstocks including heavy gas-oil or vacuum gas-oil.

Deoxygenation provides straight chain hydrocarbons, which are isomerized to branched isomers to decrease the pour point of the paraffins obtained. Green diesel has a high cetane value and good cold-flow properties. It also has excellent storage stability and is completely compatible for blending with the standard mix of petroleum-derived diesel fuels. In contrast to fatty acid methyl esters, green diesel’s properties do not depend on feed origin. Table 4 compares the properties of this second-generation diesel (green diesel) with biodiesel. The cold-flow properties of the fuel can be adjusted in the process to meet climate-specific cloud point in either neat or blended forms. Diesel yields vary from 88-99 vol.% depending upon the level of hydroisomerisation and cloud point specification. Recently, several studies for conversion of different fatty acids and their esters (triglycerides and methyl ester) into a mixture of hydrocarbons have been published (Table 5). The light paraffin by-products are valuable hydrocarbons that can be used in a variety of ways including as a feedstock to an olefins plant or a hydrogen plant. In some cases where a convenient supply of hydrogen is not available, an integrated hydrogen production facility can be used to supply all of the hydrogen needed in the process. This hydrotreating process for biofuels has been commercially available since 2007, produced by Neste Oil in Porvoo, Finland and UOP-Eni since 2009. A number of manufacturers including ConocoPhillips (USA, Ireland), Petrobras (Brazil), Syntroleum (USA) are also developing hydrodeoxygenation derived renewable biodiesel (2nd generation biodiesel) processes. This process utilizes supported metal catalysts like Ni/silica, Ni-Mo/γ-alumina, Pd/C, Co-Mo/alumina etc. One of the challenges in the HDRD process is to convert the deoxygenation and hydroisomerisation steps into a single step-process.

### Conclusions and Future Perspectives

Biofuels represent an increasingly important alternative to petrodiesel. However, the biofuels will not be able to completely replace fossil fuels, given the current worldwide demand for the energy. Most likely, biofuels will find widespread use in the form of blends with the conventional diesel as is currently found in some countries in Europe. The conventional
biodiesel technologies using homogeneous catalysts are simple and operator-friendly. However, very high quality feedstock is needed which makes the diesel production costs very high and non-competitive. The integrated, two-step, homogeneous acid-base processes can handle low quality feedstocks but these technologies require even more catalyst, processing steps, thereby eliminating some of the gains of their application. Replacement of homogeneous catalysts by solid catalysts enables a cost efficient process. Although some of the catalysts reported here show good promise, they do so at the expense of high temperatures and pressures. Development of a more efficient solid acid catalyst that can work at mild to moderate reactions conditions and can handle low-grade feed stock in a continuous flow operation is desirable. Such solid catalyst should have large pores, hydrophobic surface and high density of medium to strong acid sites. Value addition to the glycerin by-product in the biodiesel production would lower the biofuel costs considerably. The hydrocarbon-based fuels produced via hydrotreating can be used as blends or as such. However, development of stable and selective catalysts and processes that could minimize or eliminate the use of hydrogen in their production are desirable. There is a large scope for the conversion of lignocellulosic biomass into fuels via thermochemical and biochemical means. Identification of suitable and stable catalysts and development of continuous processes are the challenging tasks.

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