Biofuels and Their Production Through Different Catalytic Routes

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This paper presents a review of the literature available on biofuels production through different chemical catalytic routes. Biofuels are promising alternative to the fast-depleting fossil fuel and oil reserves. In consideration of the existing environmental issues, such as greenhouse effect and global warming, researchers are now interested in biofuels production from biomass. Biofuels are produced from renewable and sustainable bioresources, which are available globally in the form of residual agricultural biomass and wastes. However, the biofuels production process through chemical transformation could be very expensive and uneconomical for large-scale commercial supply. Hence, there is a continuous need for improvisation on the research on this topic. This review broadly describes the different types of biofuels and the processes for their production through catalytic routes.

Key words:
biofuels, biomass, catalysis, bioresources, fossil fuels

Introduction

Prior to the discovery of fossil fuel, the energy demand was mostly dependent on biomass resources, consisting of wood, log residues, agricultural wastes, water hyacinth, algae etc. Biomass-based fuels known as biofuels which are renewable and sustainable in nature. Basically, there are two types of biofuels based on the presence of oxygen molecule; 1. Hydrocarbon-nonoxygenated biofuels consist of syngas, biogas, and solid biofuels 2. Hydrocarbon-oxygenated biofuels consist of butanol, ethanol and biodiesel. Different biofuels require different catalytic processes for their production. This review describes different types of biofuels and their production processes. Among the existing biomass, the most abundant and cheapest feedstock is lignocellulose (or cellulose). The production of biofuels from lignocellulose involves removal of some oxygen as CO_2 or H_2O, and conversion into high-density fuels. This can be done through three primary routes. One of these routes is the gasification of cellulosic biomass for the production of syngas, consisting of a mixture of CO and H_2, which is used to produce hydrocarbon (diesel or gasoline, methanol and other fuels) by Fischer-Tropsch synthesis. Another added chain process for syngas includes methanol production by methanol synthesis. The second route is thermo chemical liquefaction, which includes the production of liquid alkane fuels, while the third route includes pyrolysis for bio-oil production and acid hydrolysis for sugar production[1].

Types and sources of biofuels

Biogas

Biogas is methane, produced from biodegradable waste materials by the process of anaerobic digestion of organic material. The digested solid by-product can also be used as a biofuel or fertilizer. Biogas can be recovered from mechanical biological treatment waste processing systems. The anaerobic biological conversion or digestion of organic matter occurs in three steps. The first step is called hydrolysis, which involves enzyme-mediated transformation through microbial route of insoluble organic material into soluble organic material. The second step is acidogenesis and fermentation, which involves the production of hydrogen, carbon dioxide, and other lower weight volatile organic acids. In the third step, the products of the second step are converted into a mixture of methane and carbon dioxide by methanogenic bacteria[2].

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Syngas

Syngas is a mixture of carbon monoxide, hydrogen, and other hydrocarbons, produced by partial combustion of biomass. Prior to partial combustion, the biomass is dried and sometimes pyrolysed. The resulting gas mixture, syngas, is more efficient than direct combustion of the original biofuel, since it contains more energy. Syngas may be burned directly in internal combustion engines, turbines or high-temperature fuel cells. Syngas can be used to produce methanol, DME and hydrogen, a diesel substitute and/or a mixture of alcohols via the Fischer-Tropsch process[3].

Solid biofuels

Solid biofuels include everything from wood, dried plants, bagasse, seeds to garbage, agricultural waste and manure. Manure has low CO_2 emissions, but high nitrate emissions. Carbon, hydrogen and oxygen are the main components of solid biofuels, and of special relevance for the gross calorific value. Fuel containing nitrogen is responsible for NO_x formation. NO_x emissions belong to the main environmental impact factors of solid biofuel combustion. Chlorine and sulfur are responsible for deposit formation and corrosion. Since chlorine causes HCl emissions and sulfur causes SO_x emissions, these elements are involved in the formation of aerosols (submicron particle emissions). The ash content influences the choice of the appropriate combustion technology and deposit formation, fly ash emissions and the logistics concerning ash storage, as well as ash utilization/disposal. Major ash forming elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) are of relevance for the ash melting behavior, deposit formation and corrosion. In addition, volatile elements such as Na and K are the main constituents of aerosols. Volatile minor elements (As, Cd, Hg, Pb, Zn) play a major role in gaseous and especially aerosol emissions, as well as in deposit formation, corrosion and ash utilization/disposal. Either partly or non-volatile minor elements (Ba, Co, Cr, Cu, Mo, Mn, V) are of special relevance for ash utilization[4].

Ethanol

Ethanol fuel is the most common biofuel, produced by the fermentation of sugars derived from wheat, corn, sugar beets, sugarcane, molasses, potato and fruit wastes. Currently, bioethanol is produced primarily, from sugarcane, maize (corn) and sugar. Ethanol production involves enzyme digestion (to release sugars from stored starches), fermentation of the sugars, distillation and drying. Ethanol is used in petrol engines as a replacement for gasoline because it mixes well with gasoline in any percentage. Most existing car petrol engines can run on blends of up to 15 % bioethanol with petroleum/gasoline. Ethanol has a lower energy density than that of gasoline which means it takes more fuel (volume and mass) to produce the same amount of work. An octane rating of ethanol is higher than ethanol-free gasoline which means higher engine compression ratio for increase in thermal efficiency[5].

Methanol

Methanol is another oxygenated biofuel. Initially, it was known as wood alcohol because of its production mainly as a byproduct of the destructive distillation of wood. It is also produced from syngas and methane itself, and is part of natural gas as well. Methanol is used as antifreeze, solvent, fuel and denaturant for ethanol. Its most common use is in biodiesel production via the transesterification process. Methanol has attracted attention as an alternative transport fuel blended in various proportions. Methanol is used as a transport fuel in many countries. From the thermodynamic point of view, utilization of methanol in internal combustion engines could bring some advantages as an increase in power (due to the increase in the engine compression rate) and in energy efficiency, besides reducing the emission of pollutants. For example, in the United States, methanol has been used as a fuel in certain vehicles (e.g. race cars) either alone (100 %) or blended since the 1970s, and in 1993[6].

Butanol

Butanol is used as a solvent in cosmetics, hydraulic fluids, detergent formulations, drugs, antibiotics, hormones, vitamins and as a chemical intermediate. Butanol is also used as a fuel due to its specific characteristics. Butanol, as compared to ethanol, is less volatile and explosive, has a higher flash point and lower vapor pressure, which makes it safer to handle[7]. It contains more energy as it has a higher number of carbon atoms. It is less hygroscopic and easily miscible with gasoline in any proportion. In addition, the air to fuel ratio and the energy content of butanol are close to gasoline. Butanol can be used directly or blended with gasoline or diesel without vehicle retrofit, and supplied through the existing gasoline pipes. Butanol as a fuel, contributes to the formation of photochemical smog when it reacts with other volatile organic compounds in the atmosphere. Butanol is flammable and causes irritation of the eyes, nose and throat in humans. Since it can also be produced from biomass (fermentation of biomass in A.B.E. process), it is considered a biofuel and called biobutanol. The properties of biobutanol are quite similar to those of petro-butanol[8].

Vegetable oil

Triglycerides are moieties extracted from plants. Vegetable oils are used for producing biodiesel in the transesterification process. Initially, vegetable oil was used as fuel; in fact, Rudolf Diesel ran his engine with peanut oil. However, this practice was abandoned later because of the high density and viscosity of vegetable oil. High viscosity of vegetable oil causes coke deposition in engines. Vegetable oils can be used as fuels with upgradation techniques, such as transesterification, hydrogenation and pyrolysis.

Bio-oil

Bio-oils are produced by the thermochemical treatment of biomass. The process conditions favoring liquid products include short residence times, fast heating rates, and moderate temperatures. Liquefaction and pyrolysis are the two major technologies for the production of bio-oils. Pyrolysis oils are miscible with water and have higher oxygen content than liquefaction oils. Liquefaction occurs at 50-200 atm and 250–325 °C, whereas pyrolysis occurs at 1–5 atm and 375–525 °C. Pyrolysis has a lower capital cost as compared to liquefaction, and many pyrolysis technologies are currently being used commercially. A number of catalysts and solvents have been used for liquefaction including alkali (from the alkaline ash components in wood, alkaline oxides, carbonates, and bicarbonate), metals such as nickel, zinc, copper and nickel, iodine, cobalt sulfide, zinc chloride, ferric hydroxide, and Ru-based heterogeneous catalysts preferentially for hydrogenation. Water (the most common solvent), creosote oil, ethylene glycol, methanol, and recycled bio-oil have been used to increase product selectively[9].

Biodiesel

Biodiesel is fatty acid methyl ester (FAME), produced by the transesterification of vegetable oil with methanol in the presence of catalysts. Other alcohols can also be used for the production of biodiesel; however, methanol is the commonly used alcohol because of its low cost. Biodiesel is meant to be used in standard diesel engines, and thus unlike vegetable and/or waste oils, is used as fuel in converted diesel engines. Biodiesel can be used alone or blended with petro-diesel.

Processing of biomass

Biomass gasification

Gasification is a process in which solid or liquid carbonaceous material, such as biomass, coal, or oil, reacts with air, oxygen, and/or steam to produce a gas product called syngas or producer gas containing CO, H_2, CO_2, CH_4, and N_2 in various proportions. The principle difference between producer and syngas is that air is used to make producer gas, which has higher levels of N_2 and lower concentrations of CO, H_2, CO_2, and CH_4 than syngas. Producer gas is usually combusted to produce electricity and/or heat, while syngas is used for the production of fuels and chemicals. Many industrial routes are there for the utilization of syngas including, the production of H_2 by the water gas shift reaction, diesel fuel by Fischer-Tropsch synthesis (FTS), methanol by methanol synthesis, and methanol-derived fuels[10].

The chemistry of gasification is complex and it could be pyrolysis, partial oxidation and steam oxidation. Pyrolysis is the thermal decomposition of the feedstock in the absence of air or steam[11]. Partial oxidation processes use less than the stoichiometric amount of oxygen required for complete combustion of biomass. Steam oxidation involves the reaction of water with the biomass-derived feedstock to produce CO, CO_2, and H_2. The water-gas shift (WGS) reaction (water and CO react to form H_2 and CO_2) and methanation (CO and H_2 react to form CH_4 and H_2O) are another two important reactions that occur during gasification.

Syngas production

Syngas is a mixture of carbon monoxide and hydrogen, which can be prepared from biomass gasification. It can be used for the production of transportation fuels as well as chemical products such as hydrogen by the water gas shift reaction (WGS), alkanes by Fisher-Tropsch synthesis (FTS), synthesis of isobutane and isobutene by isosynthesis, and ethanol by fermentation.

Production of hydrogen

Hydrogen can be harvested from biomass by various biological and thermal processing techniques. Biological conversion methods, such as microbial conversion and fermentation, are less energy-intensive than thermal processing, but yield significantly less hydrogen. Catalytic steam gasification has been shown to produce the most hydrogen per kilogram of biomass feedstock.

The dominant technology for hydrogen production is currently steam methane reforming. Four steps are involved here: (a) Feed pretreatment, (b) steam reforming, (c) CO shift conversion and (d) hydrogen purification. The only pretreatment required is desulfurization because sulfur acts as a poison for the catalyst, which usually consists of a hydrogenator followed by a zinc oxide bed. After pretreatment, natural gas is fed into a reformer reac-

tor, where it produces CO, CO_2, and H_2 through the reforming and water gas shift reaction with steam. Conventionally used steam reforming catalysts are nickel-based catalysts on a mineral support (alumina, cement, or magnesia). Heavy feedstock tends to form coke on the catalyst surface but promoters (potassium, lanthanum, ruthenium, and cerium) are used to avoid this problem. These promoters increase steam gasification of solid carbon reducing coke formation, which in turn increases the reforming activity of the catalyst. For feedstocks heavier than naphtha, nickel-free catalysts containing primarily strontium, aluminum, and calcium oxides, are successfully tested. Uranium oxide and chromium oxide are used as promoters for the tolerance to sulfur poisoning. Natural gas usually contains only small amounts of sulfur compounds generally in the form of hydrogen peroxide (H_2S).

Fischer-Tropsch synthesis

Fischer-Tropsch synthesis (FTS) is known for the production of a wide range of hydrocarbon products (olefins, paraffin, and oxygenated products). Because of the highly exothermic reaction, a large amount of heat is evolved. Product distributions depend on temperature, feed gas composition (H_2/CO), pressure, catalyst type, and catalyst composition. Similar to hydrogen production, here also are involved four main steps: (a) syngas generation, (b) gas purification, (c) FT synthesis, and (d) product upgrading. Depending on the types and quantities of FT products desired, either low (200–240 °C) or high temperature (300–350 °C) synthesis is used. Group VIII transition metal oxides are generally regarded as good catalysts used for FTS. In decreasing order of activity: Ru > Fe > Ni > Co > Rh > Pd > Pt. These metal oxides suffer from deactivation process also; the reasons are conversion of the active metal oxide to an inactive oxide, carbon deposition on active sites and chemical poisoning due to coke deposit. Sulfur compounds are poison for both iron and cobalt catalysts. Sulfur is present in both natural gas and coal. It converts primarily to H_2S plus other organic sulfur compounds during steam reforming or gasification. Again, ZnO is used for desulfurization of catalyst[11].

Isosynthesis

In the isosynthesis reaction, syngas converts to isobutene and isobutene over a thorium or zirconium-based catalyst at relatively extreme (150–1000 atm and 450 °C) conditions. In this reaction, the main focus is to optimize isobutane production for use in high-octane gasoline. At lower temperatures, alcohols and other oxygenates are formed, whereas at higher temperatures, methane and aromatics are formed. The isosynthesis mechanism is related to higher alcohol synthesis. It involves two chain-growth mechanisms a step-wise CO insertion reaction, and a condensation reaction mechanism involving surface-adsorbed oxygenates. The precursor to the oxygenate products has been identified as a surface-adsorbed methoxide species. The oxygenates, alcohols and ethers undergo dehydration and hydrogenation to form the isoalkenes and branched alkanes. Thorium- and zirconium-based catalysts are used in isosynthesis. Thorium-based catalysts are good alcohol dehydration catalysts and, in turn, are the most active isosynthesis catalysts. Promoters such as Zn, Cr and alkali metals are used. The lifetimes of these metals are very long, and as a result, they can be regenerated by oxidizing the accumulated coke that deposits on the surface and are also sulfur-tolerant. Zirconium-based catalysts also have high activity for isosynthesis. Unpromoted zirconium catalysts have demonstrated 32 % CO conversion at 150 atm and 450 °C with much higher selectivity to isobutene as compared to the thorium-based catalysts. The overall activity of ZrO_2-based catalysts for isosynthesis is lower compared to ThO_2-based catalysts. Various promoters have been investigated to improve the activity and selectivity of ThO_2 and ZrO_2 catalysts[12].

Methanol to gasoline

The methanol to gasoline (MTG) process involves the conversion of methanol to hydrocarbons over zeolite catalysts. The MTG process occurs in two steps. Initially, crude methanol (17 % water) is super-heated to 300 °C and partially dehydrated over an alumina catalyst at 27 atm to yield an equilibrium mixture of methanol, dimethyl ether, and water (75 % of the methanol is converted). This effluent is then mixed with heated recycled syngas and introduced into a reactor containing ZSM-5 zeolite catalyst at 350–366 °C and 19–23 atm to produce hydrocarbons (44 %) and water (56 %).

Bio-oil production from biomass

In addition to producing gases, thermochemical treatment of biomass can also produce liquids and solids. The process conditions that favor liquid products are short residence times, fast heating rates, and moderate temperatures. Liquefaction and pyrolysis are the two major technologies for the production of bio-oils[13].

Triglycerides and vegetable oils

There are plants that produce triglycerides (TGA) which are high energy density liquid molecules and can be used to make liquid fuels. The TGA or fats and oils consist of water insoluble, hy-

drophobic substances that are made up of one mole of glycerol and three moles of fatty acids forming ester bond, mainly used for cooking and food purposes. All triglycerides can be broken into one glycerol molecule and three fatty acid molecules upon hydrolysis. The carbon chain length and number of double bonds in the fatty acids vary, depending on the source of the vegetable oil. Triglycerides are the major component of vegetable oils and animal fats. Vegetable oils can be used directly in diesel engines; however; there are number of disadvantages of using these oils in engines, including high viscosity, low volatility, and some engine problems, such as coking on the injectors, carbon deposits, oil ring sticking, and thickening of lubricating oils. If vegetable oil is to be used as a fuel, it requires upgrading. The most common way of upgrading vegetable oils to a fuel is transesterification of triglycerides into alkyl-fatty esters, and the product is called biodiesel. Waste vegetable oils, like frying oils, can also be used as feedstock; however, changes in the process need to be made as waste vegetable oils contain free fatty acid (FFA) and water impurities. Vegetable oils can also be blended with diesel fuel or upgraded by other methods, including zeolite upgrading, pyrolysis and hydrogenation.

Transesterification is the reaction of triglycerides (or other esters) with alcohols to produce alkyl esters (biodiesel) and glycerol. Methanol, due to its low cost, is the alcohol most commonly used. Alkyl esters can be blended with traditional diesel fuel in up to 20 vol. %, with no engine modification because biodiesel is soluble in petroleum diesel in all proportions. The transesterification reaction of oil consists of a number of consecutive, reversible reactions, with diglycerides and monoglycerides as intermediates. The first step in transesterification is the production of diglycerides and alkyl esters, followed by monoglycerides and alkyl esters, and finally alkyl esters and glycerol. Overall transesterification reactions shown in Figure 1 are reversible, and the excess alcohol solvent is used to drive the reaction to completion. Pyrolysis of vegetable oil can be used to produce a liquid fuel that contains linear and cyclic paraffins, olefins, aldehydes, ketones, and carboxylic acids. The pyrolysis reaction

can be conducted with or without a catalyst, and a number of catalysts have been tested including HZSM-5, α-zeolite, and USY. Studies have shown that zeolite upgrading is a nonselective process producing a range of compounds and undesired coke and lighter alkanes from oils[14].

Vegetable oils can also be hydrotreated to produce straight chained and high cetane numbered (55–65) alkanes ranging from C_{12} to C_{18}. Sulfided $NiMo/Al_2O_3$ catalysts are promising candidates for hydrotreatment at 350–450 °C and 40–150 atm. Further alkanes can also isomerize using molecular sieve or zeolite catalysts. Vegetable oils can also be mixed with any hydrotreated petroleum heated oil[14]. A summary of all routes for production of liquid fuels from biomass is given in Figure 2, e.g., sugarcane gives sucrose and glucose which can be converted to C_1-C_6 hydrocarbons, ethanol, aromatics and hydrogen, while baggasse produces feedstock which can be gasified, pyrolysed, or liquefied to produce syngas or bio-oils which can be converted into gasoline, aromatics, and larger hydrocarbons. The sugar from corn and sugarcane yield C_1-C_5, hydrogen and hydrofuels.

Biofuels production

Most of the literature is available on the fatty acids and the vegetable oils for the production of biofuel through different approaches. The palladium and platinum catalysts are most extensively used, as reported in the literature. Non-noble metals such as nickel, iron and molybdenum are also used as second good option for biofuel production.

Murzin *et al.*[15] carried out deoxygenation of dodecanoic (lauric) acid in an inert atmosphere using a laboratory-scale fixed-bed reactor. They reported undecane and undecene as the main reaction products. Undecane and undecene were formed by decarboxylation and decarbonylation reaction, respectively, the catalyst being palladium (Pd) supported on mesoporous carbon. They found that the Pd catalyst had deactivated due to coke deposition as the reaction progressed. The liquid-phase deoxygenation of stearic, oleic, and linoleic acids with 5 wt. % Pd/C catalyst was investigated by Lamb *et al.*[16]
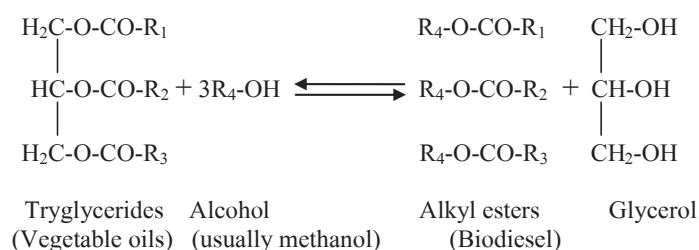
$$
\begin{array}{cc}
H_2C\text{-}O\text{-}CO\text{-}R_1 & R_4\text{-}O\text{-}CO\text{-}R_1 \quad CH_2\text{-}OH \\
| & | \\
HC\text{-}O\text{-}CO\text{-}R_2 + 3R_4\text{-}OH \rightleftharpoons R_4\text{-}O\text{-}CO\text{-}R_2 + CH\text{-}OH \\
| & | \\
H_2C\text{-}O\text{-}CO\text{-}R_3 & R_4\text{-}O\text{-}CO\text{-}R_3 \quad CH_2\text{-}OH \\
\end{array}
$$

Tryglycerides   Alcohol   Alkyl esters   Glycerol
(Vegetable oils) (usually methanol) (Biodiesel)

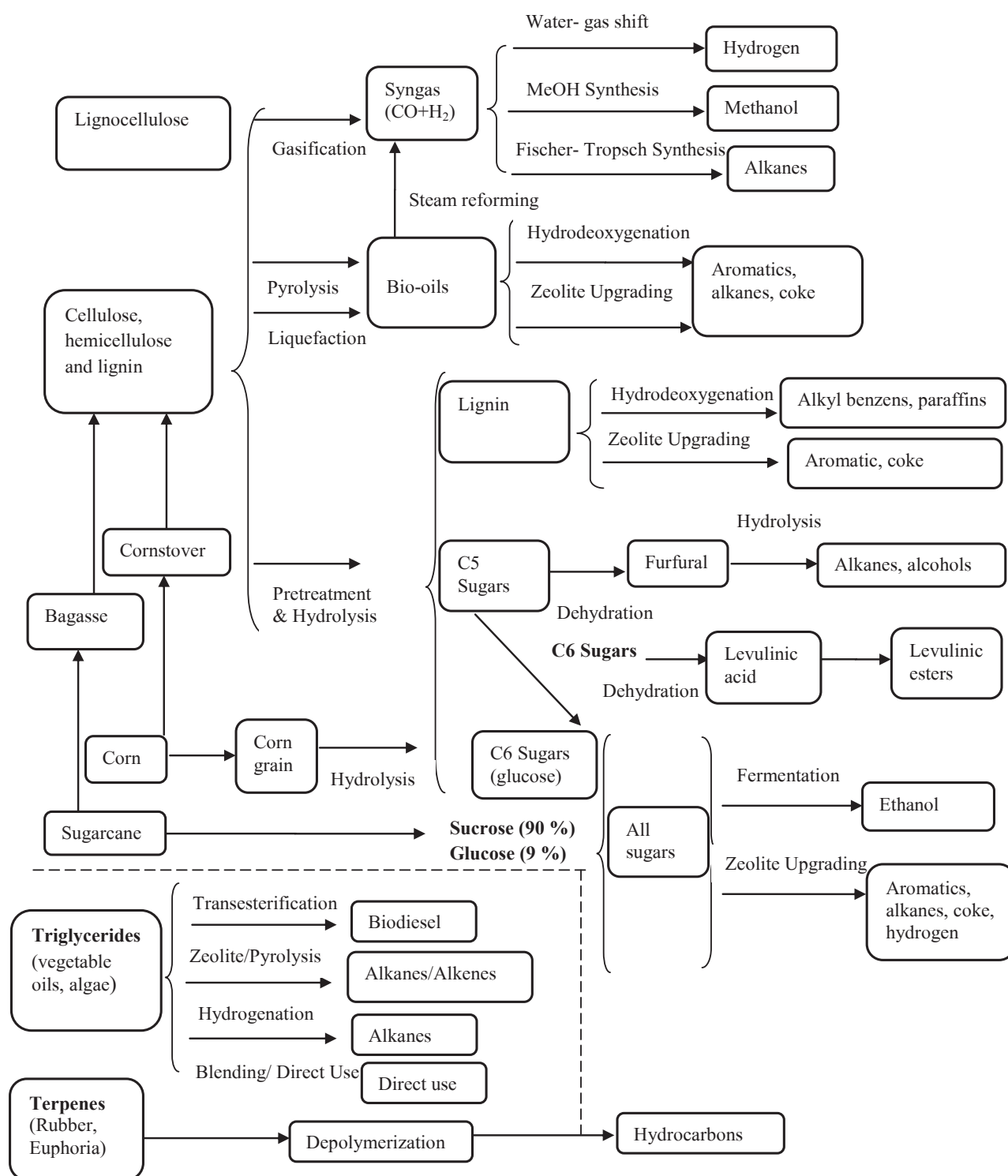F i g. 1 – *Transesterification of triglycerides*

F i g . 2 – *Known routes for the production of liquid fuels from biomass[14]*

On-line quadrupole mass spectrometry (QMS) was used to detect the reaction product. They reported n-heptadecane and n-heptadecene as the main products. The authors suggested that the unsaturated C_{18} free fatty acids, oleic and linoleic must be hydrogenated to stearic acid before decarboxylation. They also reported that decarboxylation kinetics and product yields were not affected by the initial unsat-

uration of the reactant. Catalytic decarboxylation of stearic acid was studied by Jones *et al.*[17] using highly dispersed palladium nanoparticles on ultra-porous silica mesocellular foam at 300 °C. The conversion of stearic acid was varied in the range of 80–90 %. n-Heptadecane was reported as the main product. Kaluza and Kubicka[18] reported deoxygenation of vegetable oils for the production of biofuels

over Ni, Mo, and Ni-Mosulfided catalysts prepared by impregnation methods. The reaction was carried out using rapeseed oil as feedstock at 260–280 °C, 3.5 MPa, and 0.25–4 h^{-1} liquid hourly space velocities in a fixed-bed reactor. The activity of the catalysts decreased in the following order: NiMo/Al$_2$O$_3$> Mo/Al$_2$O$_3$> Ni/Al$_2$O$_3$. The study revealed that the bimetallic NiMo catalysts showed higher yields of hydrocarbons than the monometallic catalysts at a given conversion. Low-pressure catalytic co-conversion of biogenic waste (rapeseed cake) and vegetable oil was carried out at temperatures of 350 and 400 ºC, respectively. The authors reported that the yields and compositions of the product mixtures were very much dependent on the nature of the catalyst as well as the process temperatures. The produced organic phases consisted mainly of hydrocarbons, fatty acids and nitriles[19]. Simakova et al.[20] studied fatty acid decarboxylation in a semi-batch reactor over 1 wt.% Pd/C Sibunit (a class of porous carbon-carbon composite materials combining the advantages of graphite, such as chemical stability and electric conductivity and active coals like high specific surface area and adsorption capacity). These composites were characterized by a (high mesopore volume and a controllable narrow pore size distribution) using five different fatty acids, C$_{17}$ to C$_{20}$ and C$_{22}$, as feed. The same decarboxylation rates were obtained for pure fatty acids, but they observed extensive catalyst poisoning and/or sintering and coking occurred with low purity fatty acids as reactants. One reason for catalyst poisoning using behenic acid (C$_{22}$) as feedstock was its high phosphorus content. Jozef Mikulec et al.[21] studied the direct transformation of triacylglycerols (TAG) to diesel fuels by using a commercially available NiMo and Ni-W hydrorefining catalysts. They showed that during hydrodesulfurization, hydrodeoxygenation also occurs and the TAG can be converted to fuel by using a feed consisting of 6.5 % vol. of TAG with gas oil. Thus, the prepared fuel, after hydroprocessing at 320–360 °C and at 3.5–5.5 MPa hydrogen pressure, was characterized by standard performance and emission parameters. They observed that the selectivity to hydrodeoxygenation/hydrodecarboxylation products had increased with temperature. Hydrodeoxygenation of oleic acid and canola oil over alumina-supported nitrides of molybdenum, tungsten and vanadium was tested at 380–410 °C and 7.15 MPa hydrogen pressure. The molybdenum nitride catalyst was found superior to the vanadium and tungsten nitrides for catalytic hydrotreating of oleic acid in terms of fatty acid conversion, oxygen removal and production of normal alkanes (diesel fuel cetane enhancers)[22]. Salmi et al.[23] demonstrated the catalytic deoxygenation of tall oil fatty acids (TOFA) over palladium catalysts supported on mesoporous carbon at 300 °C using dodecane as a solvent. A maximum of 95 % selectivity to linear C$_{17}$ hydrocarbons was achieved. They also checked the effect of reaction atmosphere and initial tall oil concentration on the reaction rate and yield of reaction products. Lestari et al.[24] obtained diesel-like hydrocarbons from catalytic deoxygenation of stearic acid using SBA-15 (type of mesoporous silica) supported Pd nanoparticles at 300 °C and 17 bar pressure in a semi-batch reactor. They also investigated the effect of different loading of palladium on SBA-15. They had characterized the catalyst with X-ray diffraction, micrograph images, and X-ray photoelectron spectroscopy. The deoxygenation of methyl octanoate and methyl stearate over alumina-supported Pt was studied in a flow reactor as well as in semi-batch reactor. The conversion of both methyl esters resulted in hydrocarbons with one carbon less than the fatty acid of the corresponding ester as the dominant products. In inert gas He, the condensation products (diphenylketone and octyloctanoate) were observed by esterification and ketonization. In contrast, when this reaction was carried out in H$_2$, mostly paraffins (mainly C$_7$ and C$_8$ hydrocarbons) were obtained[25]. Catalytic deoxygenation of palmitic and stearic acids mixture was studied over four synthesized Pd catalysts supported on synthetic carbon (Sibunit) in a semi-batch reactor at 260–300 °C using dodecane as a solvent. The effect of metal dispersion was found to have great effect on the catalysis and an optimum metal dispersion giving the highest reaction rate was reported. The main liquid phase products were n-heptadecane and n-pentadecane[26]. Murzin et al.[27] studied the kinetics of liquid phase ethyl stearate decarboxylation and stearic acid deoxygenation for production of diesel fuel hydrocarbons over a Pd/C catalyst in a semi-batch reactor. The kinetic behavior was tested in a wide temperature range of 300–360 °C. Furthermore, they performed a supplementary investigation of the reaction intermediates, and the main kinetic regularities were established in both cases. Snare et al.[28] discussed a novel method for production of diesel-like hydrocarbons via catalytic deoxygenation of fatty acids. They tested stearic acid as a model compound, which was deoxygenated to heptadecane formed from the stearic acid alkyl chain. The deoxygenation reaction was carried out in a semi-batch reactor under constant temperature (300 °C) and pressure (6 bar). A thorough catalyst screening was performed to obtain the most promising metal and the support used for the catalyst. The catalysts were characterized by N$_2$-physisorption, CO-chemisorption, and temperature-programmed desorption of hydrogen. Complete conversion of stearic acid is reported with >98 % selectivity toward deoxygenated C$_{17}$ products. Ten-

tative reaction route of stearic acid at 300 °C is also proposed. The deoxygenation of vegetable oils was studied over a Ni/Zr-laponite (a synthetic clay that swells to produce a clear, colorless thixotropic gel when dispersed in water and used as support in many reaction) catalyst in various nickel loading. Stearic acid has been used as a model compound and the liquid and gaseous products analyzed using gas chromatograph equipped with thermal conductivity detector and flame ionization detector. The authors concluded that the Ni/Zr-laponite catalyst had successfully converted stearic acid, a model compound of vegetable oil into smaller C-number of hydrocarbons representing direct decarboxylation of stearic acid, stating that zirconia-pillared laponite clays are promising catalyst supports for decarboxylation of vegetable oils due to their large pore size and surface area which is accessible for the large molecules of the reactants[29].

Very little literature information is available regarding the deoxygenation reaction in the absence of hydrogen. Decarboxylation of oleic acid without hydrogen was carried out by Chang Hyun Ko *et al.*[30] using hydrotalcites as support with three different MgO contents (30, 63 and 70 wt.%). The effect of MgO content on hydrotalcites and reaction temperatures on the decarboxylation performance in terms of oleic acid conversion and product distribution were investigated. In addition, the stability of hydrotalcites in the decarboxylation reaction was also examined by XRD analysis. It was found that MgO content in hydrotalcites and reaction temperature played key roles in the decarboxylation reaction. Pure hydrocarbons, such as octane, nonane and heptadecene were produced in the case of MG63 and MG70 at 673 K while decanoic acid formed as a side product in case of the blank test and MG30 catalyst at 673 K. Martin *et al.*[31] studied deoxygenation of saturated C_8, C_{12} and C_{18} carboxylic acids in a hydrogen-free atmosphere using supported Ni and Pd catalysts (1–10 wt.%) in autoclaves (25 mL). They reported diesel-like hydrocarbons as product and observed that the chain length of carboxylic acid has a strong impact on the conversion as well as alkane selectivity.

Lou *et al.*[32] studied carbohydrate-derived catalysts prepared from various carbohydrates such as D-glucose, sucrose, cellulose and starch. They reported that the starch-derived catalyst showed the best catalytic performance. The carbohydrate-derived catalysts exhibited substantially higher catalytic activities for both esterification and transesterification as compared to the two typical solid acid catalysts (sulfated zirconia and niobic acid), and gave markedly higher yield of methyl esters in converting waste cooking oils containing 27.8 wt.% high free fatty acids (FFAs) to biodiesel. They also

reported that these promising solid acid catalysts are highly suited for the production of biodiesel from waste oils containing high FFAs. Boro *et al.*[33] investigated biodiesel production via transesterification of mustard oil with methanol using solid oxide catalyst derived from waste shell of *Turbonilla striatula*. The shells were calcined at different temperatures for 4 h and catalyst characterizations were carried out by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), Fourier transform infrared spectrometer (FT-IR), thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) and Brunauer–Emmett–Teller (BET) surface area measurements etc. Formation of solid oxide i.e. CaO was confirmed at calcination temperature of 800 °C. The effect of the molar ratio of methanol to oil, the reaction temperature, catalyst calcination temperature and its amount used for transesterification were studied to optimize the reaction conditions. Biodiesel yield of 93.3 % was achieved when transesterification was carried out at 65±5 °C in the presence of 3.0 wt.% catalyst and at 9:1 methanol to oil molar ratio. BET surface area indicated that the shells calcined in the temperature range of 700–900 °C exhibited enhanced surface area and higher pore volume than the shells calcined at 600 °C. The authors also investigated the reusability of the catalysts prepared at different temperatures. Deng *et al.*[34] studied biodiesel production from Jatropha oil catalyzed by nanosized solid basic catalyst. They also described the synthesis procedure for hydrotalcite-derived particles with Mg/Al molar ratio of 3/1 by a co-precipitation method using urea as precipitating agent, subsequently with microwave-hydrothermal treatment (MHT) followed by calcination at 773 K for 6 h. Because of their strong basicity, the nanoparticles were used as catalyst for biodiesel production from Jatropha oil after pretreatment. Experiments were conducted with the solid base catalyst in an ultrasonic reactor under different conditions. In optimized conditions, the biodiesel yield of 95.2 % was achieved, and its properties were close to those of the German standard. Guo *et al.*[35] examined the use of calcined sodium silicate as a novel solid base catalyst in the transesterification of soybean oil with methanol for the production of biodiesel. It catalyzed the transesterification of soybean oil to biodiesel with ~100 % yield in the presence of 3.0 wt.% sodium silicate and at a methanol/oil molar ratio of 7.5:1. They observed that the oil containing 4.0 wt.% water or 2.5 wt.% free fatty acid (FFA) could also be transesterified using this catalyst.

Synthesis of biodiesel from soybean oil using transesterification over a lithium orthosilicate (Li_4SiO_4) catalyst was reported under the optimal

reaction conditions of a methanol/oil molar ratio of 18:1, in the presence of 6 % (wt/wt oil) catalyst, and at a reaction temperature of 65 °C for 2 h. They reported biodiesel yield of 98.1 % using Li_4SiO_4 catalyst directly without pretreatment. The effects of the methanol/oil ratio, catalyst amounts, reaction time and reaction temperature on the conversion were also tested. The solid base catalyst was highly active, air-insensitive and could be reused for at least ten cycles without loss of activity[36]. Meng *et al.*[37] studied the biodiesel production in the presence of a solid Ca/Al composite oxide-based alkaline catalyst containing $Ca_{12}Al_{14}O_{33}$ and CaO prepared by chemical synthesis and thermal activation from sodium aluminate solution and calcium hydroxide emulsion. They also studied the effect of calcination temperatures ranging from 120 °C to 1000 °C on activity of the catalyst. The catalyst calcined at 600 °C showed the highest activity with >94 % yield of fatty acid methyl esters (i.e. biodiesel) when applied to the transesterification of rapeseed oil at a methanol:oil molar ratio of 15:1 and at 65 °C for 3 h. Li *et al.*[38] studied the preparation, characterization and application of heterogeneous solid base catalysts prepared by neodymium oxide with potassium hydroxide for biodiesel production from soybean oil. The obtained catalyst was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), N_2 adsorption-desorption isotherm and the Hammett indicator method. The obtained catalyst showed longer lifetime and maintained activity after being used five times, and was noncorrosive and environmentally benign. The effects of the molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and reaction time were investigated. The experimental results showed that a 14:1 M ratio of methanol to oil, addition of 6.0 % catalyst, 60 °C reaction temperature and 1.5 h reaction time gave the best results and the biodiesel yield of 92.41 %. The properties of obtained biodiesel were close to commercial diesel fuel and is rated as a realistic fuel as an alternative to diesel. Gomes *et al.*[39] reported experimental work on the use of new heterogeneous solid base catalysts for biodiesel production: double oxides of Mg and Al lamellar hydrotalcites (HT). The most suitable catalyst system was Mg:Al(2:1) hydrotalcite calcined at 507 °C and 700 °C, respectively, which led to higher values of fatty acid methyl esters (FAME). The quality parameters of biodiesel obtained in the transesterification reaction were within the limits specified by the European Standard EN 14214. Production of fatty acid methyl esters (FAME) from soybean oil and rapeseed oil was reported using modified CaO as solid base catalyst by connecting bromo octane

to the surface of CaO chemically. Over modified CaO, 99.5 % yield of the FAME was obtained from soybean oil using 15:1 molar ratio of methanol to oil after 3 h of reaction at a reaction temperature of 65 °C, which is much higher than the yield (35.4 %) over commercial CaO in the same reaction conditions. The influence of the amount of modifier and various reaction conditions, such as mass ratio of catalyst to oil, reaction temperature and molar ratio of methanol to oil, were investigated in detail[40]. Wang *et al.*[41] prepared a new solid base catalyst containing $Ca_{12}Al_{14}O_{33}$ and CaO by chemical synthesis method and it was used in the transesterification of rapeseed oil with methanol to produce biodiesel. The physicochemical properties of the catalyst were analyzed by Hammett indicators, X-ray diffraction (XRD), infrared spectroscopy (IR), Brunauer–Emmett–Teller (BET) and scanning electron microscopy (SEM), respectively. The results showed that the methyl ester (ME) content reached 90 % after 3 h at 65 °C, with a methanol/oil molar ratio of 15:1, 6 wt.% catalyst amounts at a stirring rate of 270 rpm. Moreover, the catalyst could be used repeatedly for at least 7 cycles with ~87 % yield of ME, which indicated high stability. In order to utilize waste concrete as a catalyst for biodiesel production, thermally activated hydrated cement had been carefully used as a catalyst in the transesterification of soybean oil into FAME. More than 98 % FAME conversion was achieved under the optimal conditions, i.e., calcination temperature 650 °C for 3 h, reaction temperature 65 °C, catalyst amount 32.8 wt. % (cement and fine aggregate) and oil/methanol molar ratio 1/24. In this work, the authors also studied the recycling of cement as a catalyst[42]. Shu *et al.*[43] discussed a carbon-based solid acid catalyst prepared by the sulfonation of carbonized vegetable oil asphalt and used to catalyze the transesterification of methanol with cottonseed oil. Characterization techniques used to determine the physicochemical properties of the catalysts were scanning electron microscopy/energy dispersive spectroscopy, BET surface area and pore size measurement, thermogravimetry analysis and Fourier transform infrared spectroscopy. The sulfonated multi-walled carbon nanotubes (s-MWCNTs) were also prepared and used to catalyze the same transesterification as the asphalt catalyst. The authors compared both catalysts and found that the asphalt-based catalyst showed higher activity than the s-MWCNTs for the production of biodiesel, which may be correlated to its high acid site density, its loose irregular network and large pores can provide more acid sites for the reactants. The 89.9 % conversion of cottonseed oil was obtained in the presence of asphalt-based catalyst when the methanol/cottonseed oil molar ratio was 18.2, at 260 °C, after 3.0 h of

reaction. The catalyst/cottonseed oil mass ratio was 0.2 % and the catalyst was recyclable. The sulfonated polycyclic aromatic hydrocarbons provide an electron-withdrawing function to keep the acid site stable. The catalyst can substantially reduce energy consumption and waste generation in the production of biodiesel. Liang et al.[44] developed a highly efficient procedure for the synthesis of biodiesel from vegetable oil and methanol. The KF/MgO was selected as the most efficient catalyst for the reactions with the yield of 99.3 %. The key features of this methodology are operational simplicity, without purification of raw vegetable oil, low cost of the catalyst, high activity, no saponification and catalyst reusability.

Flyash loaded with KNO_3 base catalyst was used in the transesterification of sunflower oil with methanol to methyl esters in a heterogeneous manner. The catalyst, prepared by loading of 5 wt.% KNO_3 on fly ash followed by its calcination at 773 K, exhibited maximum oil conversion (87.5 wt.%). The influence of various reaction parameters, such as catalyst loading, methanol to oil molar ratio, reaction time, temperature, reusability of the catalyst on the catalytic activity was investigated[42]. It is reported that, with an increase in KNO_3 loading from 0 % to 5 % (wt/wt), the percentage of oil conversion was found to increase from 33 % to 87.5 %. Further increase in the KNO_3 loading amount resulted in the drop of oil conversion. The low surface area of fly ash might be responsible for the lower degree of dispersion and less number of active catalytic sites for the transesterification reaction. K_2O derived from KNO_3 might be an essential component in the catalyst for its efficiency[45]. Kim et al.[46] investigated the catalytic activity of a phosphazenium hydroxide (PzOH) catalyst incorporated onto silica (SiO_2) in the transesterification of vegetable oils with methanol. The PzOH stably incorporated onto silica (SiO_2) maintained its basicity and converted methanol molecules to methoxide ions. The $PzOH/SiO_2$ catalyst exhibited high activity in the transesterification of palm, corn, grape seed, and soybean oils (S-oil) with methanol, achieving ~90 % conversion at 75 °C with a catalyst loading of 0.2 g per 4.8 mL of S-oil. Although the accumulation of organic materials on $PzOH/SiO_2$ reduced its activity, this accumulation was effectively removed by washing with methanol. The high activity of $PzOH/SiO_2$ catalyst was responsible for its strong basicity and the free mobility of the PzOH moiety.

Sun et al.[47] examined ZrO_2 supported La_2O_3 catalyst prepared by impregnation method, in the transesterification reaction of sunflower oil with methanol to produce biodiesel. It was found that 21 wt.% La_2O_3, catalyst calcined at 600 °C, showed the optimum catalytic activity. The basic property of

the catalyst was determined by CO_2-TPD, and the results showed that the fatty acid methyl ester (FAME) yield was related to their basicity. It was found that the crystallite size of support ZrO_2 decreased by loading of La_2O_3, and the model of the solid-state reaction on the surface of La_2O_3/ZrO_2 catalyst was proposed. In another approach, controlled feeding of oil into a pool of alcohol allowed easy dispersion of oil creating large interfacial area for mass transfer in the transesterification process. As a result, product yield higher than 95 % could be achieved at lower energy input compared to the conventional method. Comparisons made with conventional batch and co-solvent enabled the method to show differences and highlight improvements. Reactions were conducted in a one-liter reactor. The effect of residence time, temperature and molar ratio of canola oil with methanol in the presence of potassium hydroxide as the catalyst were studied. Samples were collected at regular intervals and analyzed by gas chromatography (GC) to determine the reaction progress[48]. Kansedo et al.[49] presented the study of the transesterification of palm oil via heterogeneous process using montmorillonite KSF as heterogeneous catalyst. The study was carried out using a design of experiment (DOE), specifically, response surface methodology (RSM), based on four-variable central composite design (CCD) with α (alpha) = 2. The transesterification process variables were reaction temperature, x_1 (50–190 °C), reaction period, x_2 (60–300 min), methanol/oil ratio, x_3 (4–12 mol mol^{-1}) and amount of catalyst, x_4 (1–5 wt.%). It was found that the yield of palm oil fatty acid methyl esters (FAME) could reach up to 79.6 % using the following reaction conditions: reaction temperature of 190 °C, reaction period at 180 min, ratio of methanol/oil at 8:1 mol mol^{-1} and amount of catalyst at 3 %.

A fly ash supported heterogeneous CaO catalyst was developed by using waste eggshell for transesterification of soybean oil to yield fuel-grade biodiesel. The active metal precursor $Ca(OH)_2$ of the catalyst was economically derived from waste eggshell calcination and the mesoporous, high activity strong base catalyst was prepared using wet-impregnation method. X-ray diffraction (XRD), scanning electron microscope (SEM), low temperature N_2 adsorption–desorption (BET), and BJH method studies manifested the well-dispersed presence of CaO over the fly ash framework. The specific surface area of 0.701 m^2 g^{-1}, pore volume of 0.0044 cm^3 g^{-1}, 5.2 nm pore diameter and 1.6 mmol HCl g^{-1} catalyst basicity rendered high catalyst activity, which could be demonstrated through high biodiesel yield from refined soybean oil by transesterification with methanol. Optimal parametric values computed by using response surface methodol-

ogy (RSM) corresponding to maximum (i.e. 96.97 %) FAME yield were CaO loading of 30 wt.%, 1.0 wt.% catalyst concentration and 6.9:1 methanol/oil molar ratio. The developed catalyst exhibited higher reusability characteristics and superior catalytic activity as compared to unsupported CaO catalyst derived from eggshell. An effective waste valorization avenue was thus created through preparation of a novel low-cost heterogeneous catalyst from these industrial and municipal wastes for synthesis of fuel-grade biodiesel[50]. Arzamendi *et al.*[51] investigated the activity and selectivity of a series of NaOH catalysts supported on alumina for the transesterification with methanol of refined sunflower oil. The performance of the supported catalysts was also compared with that of homogeneous NaOH. The effect of variables such as molar methanol/oil and catalyst/methanol ratios and NaOH loading of the supported catalysts was checked. The results showed that the transesterification rate largely depends on the catalyst/methanol ratio, whereas the product selectivity seems to be governed by the methanol/oil molar ratio. Calcination of the NaOH/ γ-Al$_2$O$_3$ catalysts had a negative effect on their activity. On the other hand, the performance of the NaOH/alumina catalysts just dried at 393 K was not far from that of homogeneous NaOH. Measurements of sodium leached during the course of the transesterification reactions evidenced some lack of chemical stability of the supported NaOH catalysts under reaction conditions. Therefore, progress should be made to prepare more stable catalysts based on supported NaOH for this application.

The transesterification of soybean oil with methanol was studied in a heterogeneous system, using alumina loaded with potassium iodide as a solid base catalyst. After loading KI of 35 wt.% on alumina followed by calcination at 773K for 3 h, the catalyst showed the highest basicity and the best catalytic activity for this reaction. The catalysts were characterized by XRD, IR, SEM and the Hammett indicator method. Moreover, the dependence of the conversion of soybean oil on the reaction variables such as catalyst loading, molar ratio of methanol to oil, and reaction time, was also studied. The conversion of 96 % was achieved under the optimum reaction conditions (methanol to oil molar ratio of 15:1, 8 h, and 2.5 % catalyst loading)[52]. Canakci *et al.*[53] explored the potential of restaurant waste lipids as biodiesel feedstock. They conducted experiments to determine the level of free fatty acids and moisture in feedstock samples from a rendering plant. Levels of free fatty acids varied from 0.7 % to 41.8 %, and moisture from 0.01 % to 55.38 %. Biodiesel was also prepared from non-edible oil of *Pongamia pinnata* by transesterification of the crude oil with methanol in the presence of KOH as

catalyst. Maximum oil to ester conversion of 92 % was achieved using a 1:10 molar ratio of oil to methanol at 60 °C. Tetrahydrofuran (THF), used as a co-solvent, increased the conversion up to 95 %. Solid acid catalysts viz. Hb-Zeolite, Montmorillonite K-10 and ZnO were also used for this transesterification. Important fuel properties of methyl esters of pongamia oil (biodiesel) compared well (viscosity = 4.8 centipoise at 40 °C and flash point = 150 °C) with ASTM and German biodiesel standards[54]. Liu *et al.*[55] reported transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. Catalyst preparation was carried out by calcination SrCO$_3$ at 1200 °C for 5 h. SrO has strong basicity and BET surface area of 1.05 m^2 g^{-1}. The conversion obtained was 95 % at temperature of 65 °C, catalyst content of 3 wt.%, molar ratio of methanol to oil of 12:1 and reaction time of 30 min. Further, the biodiesel yield only slightly reduced when the SrO catalyst was subsequently reused for 10 cycles. The main step was the formation of ionic complex by SrO with methanol. Liu *et al.*[56] also studied transesterification of soybean oil to biodiesel using CaO as a solid catalyst. The BET surface area of the catalyst was 0.56 m^2 g^{-1}. The reaction was carried out in the presence of 12:1 M ratio of methanol to oil, 8 wt.% catalyst concentration at 65 °C. Biodiesel yield of 95 % was obtained after 3 h of reaction. The authors also reported comparative activity of CaO with K$_2$CO$_3$/γ-Al$_2$O$_3$ and KF/γ-Al$_2$O$_3$ catalysts, respectively. Preparation of these catalysts was carried out by an impregnation method with the help of aqueous solution of potassium carbonate/potassium fluoride and followed by calcination of impregnated catalysts at 550 °C for 5 h. It was observed that CaO maintained sustained activity for a longer time (20 cycles) after repeated use, and the biodiesel yield was also not affected, while K$_2$CO$_3$/γ-Al$_2$O$_3$ and KF/γ-Al$_2$O$_3$ catalysts were not able to maintain activity, and the biodiesel yield also got affected after every reuse. This was because the alkali metal compounds dissolved in methanol, which reduced the active ingredients and there by decreased biodiesel yield in the subsequent experiments. It was also observed that the presence of trace amounts of water (2.8 by wt.%) in soybean oil, acted as promoter. However, if the amount of water increased above 2.8 by wt.% of soybean oil, it hydrolyzed FAME under basic conditions and also induced soap formation. The catalytic activity of activated calcium oxide was also evaluated for the production of biodiesel by transesterification of sunflower oil in a batch reactor with 13:1 methanol to oil molar ratio, 3 wt.% catalyst content at 60 °C. Under these conditions, the reaction was completed in 100 min and showed 94 % conversion. The specific surface area of catalyst was 32 m^2 g^{-1} and mean pore size

diameter (MPS) was ~ 25–30 nm. The authors observed poisoning of active surface site of CaO by the atmospheric H_2O and CO_2. Therefore, to improve catalytic activity of CaO, it was subjected to an activation treatment at high temperature (P700 °C) before the reaction and as a result of this, the main poisoning species (the carbonate group) from the surface was removed. In the presence of the catalyst activated at high temperature, some leaching of the active species was observed. However, leaching did not affect the catalytic activity and the catalyst was reusable for 8 cycles. The obtained yield of FAME reduced from more than 90 % in the first cycle to 80 % in the second cycle, and there after the performance stabilized[57]. Kawashima et al.[58] described the research that was aimed at studying the acceleration of the catalytic activity of calcium oxide (CaO) for developing an effective heterogeneous catalyst for biodiesel production by the transesterification of plant oil with methanol. The activation of CaO by pretreatment with methanol and transesterification reaction conditions was examined. The obtained optimal reaction conditions were 0.1 g of CaO, 3.9 g of methanol, 15 g of rapeseed oil, and 1.5 h activation time at room temperature. Such optimum conditions provided a methyl ester yield of 90 % within a reaction time of 3 h at 60 °C. During the reaction, pretreatment with methanol, a small amount of CaO is converted into $Ca(OCH_3)_2$ which acts as an initiating reagent for the transesterification reaction and produces glycerin as a by-product. Subsequently, a calcium–glycerin complex is formed due to the reaction of CaO with glycerin. The complex formed acts as a main catalyst and accelerates the transesterification reaction. Kouzu et al.[59] studied CaO catalyst for transesterification of soybean oil using methanol to oil mole ratio of 12:1 M at reflux temperature for 2 h in a glass batch reactor. A maximum biodiesel yield of 93 % was achieved. CaO was obtained after calcination of pulverized limestone at 900 °C for 1.5 h. Calcium diglyceride and calcium methoxide were used as reference samples. The novel efficient procedure was developed for the synthesis of biodiesel from soybean oil and methanol. K_2CO_3 supported on MgO was selected as the most efficient catalyst for the reaction with the yield of 99 %. They provided a simple method for the preparation of the catalysts in which K_2CO_3 was supported on carriers by the solid-state method. The required amount of K_2CO_3 and carriers were mixed together in a mortar and skived for 30 minutes, followed by drying at 80 °C for 4 h. The obtained catalysts were calcined at 600 °C for 3 h at a heating rate of 1 °C min^{-1} in air. Operational simplicity, low cost of the catalyst used, high biodiesel yields, short reaction time and reusability of the catalysts were the key features of this

methodology[60]. Sree et al.[61] prepared a series of Mg-Zr catalysts with varying Mg to Zr ratio by co-precipitation method. The physicochemical properties of catalysts were examined by BET surface area, X-ray diffraction, X-ray photoelectron spectroscopy and temperature programmed desorption of CO_2. The catalytic activity of these catalysts was evaluated for transesterification of both edible and non-edible oils to their corresponding fatty acid methyl esters at room temperature. The Mg/Zr (2:1 wt./wt.%) catalyst exhibited exceptional activity towards transesterification reaction. The effects of different reaction parameters, such as catalyst to oil mass ratio, reaction temperature, reaction time and methanol to oil molar ratio, were studied to optimize the reaction conditions.

Samart et al.[62] utilized 15 wt.% KI loaded on mesoporous silica as a solid base catalyst for transesterification of soybean oil with optimum reaction conditions: 16:1 methanol to oil ratio, 5 wt.% catalyst, 70 °C and 8 h reaction time. Maximum of 90 % conversion was obtained. The maximum activity of catalyst was obtained when 15 wt.%. KI solution was impregnated on mesoporous silica by incipient wetness impregnation method. Shumaker et al.[63] synthesized biodiesel using calcined layered double hydroxide catalysts by soybean oil. The authors also examined the catalytic properties of calcined Li-Al, Mg-Al and Mg-Fe layered double hydroxides (LDHs) in two transesterification reactions, namely, the reaction of glyceryl tributyrate with methanol, and the reaction of soybean oil with methanol. Li-Al catalysts showed high activity (> 98 %) in these reactions at the reflux temperature of methanol, the Mg-Fe and Mg-Al catalysts exhibited much lower methyl ester yields (23.9 and 19.7 %, respectively). CO_2 TPD measurements revealed the presence of weak, medium and strong basic sites on both Mg-Al and Li-Al catalysts, respectively. Li-Al catalyst calcined at 450–500 °C possessed higher concentrations of medium and strong base sites responsible for higher transesterification activity. The layered double hydroxide of Li-Al catalysts decomposed to the mixed oxide when calcined at 450–500 °C without the formation of crystalline lithium aluminate phases. Li et al.[64] prepared mixed oxide catalysts from Mg-Co-Al-La layered double hydroxide (LDH) at various Mg:Co:Al:La ratios by co-precipitation followed by calcination. These catalysts were tested for the transesterification of canola oil with ethanol to produce biodiesel in a batch reactor at 473 K for 5 h. The catalytic activity of the Mq_2 CoAl catalyst was demonstrated and showed to be stable and reusable, maintaining its activity even after 7 cycles.

Karmakar et al.[65] proposed an Indian perspective for the production of biodiesel from various

feedstock. Extensive focus was given on the production of biodiesel from non-edible oil sources, specifically from Jatropha seeds. The authors suggested that scientific research should therefore be directed towards oil seeds, such as Karanja, Sal, Mahua, and Neem, etc., which are widely available and sustainable in the diverse socio-economic and environmental conditions of rural India. Among the various feedstock, the evergreen neem oil may be a potential feedstock for biodiesel production. Authors attempted to overview the morphology of the neem tree, various useful uses, physical and chemical characteristics of neem oil and optimized the biodiesel production process from neem oil. Thiruvengadaravi et al.[66] reported the production of a biodiesel by acid-catalyzed esterification of Karanja oil (KO), which contains higher amounts of free fatty acid (FFA) (> 2 %). Pretreated KO was converted to biodiesel by a process of alkaline-catalyzed transesterification. Optimum acid-catalyzed esterification was achieved using 1 % sulfated zirconia (SZ) as a solid acid catalyst with a methanol-to-oil ratio of 9:1, at 60 °C and reaction time of 2 h. During this process, FFA was converted into fatty acid methyl esters. The acid value of karanja oil was reduced to 1.3 mg KOH g^{-1} from 12.3 mg KOH g^{-1}, which confirmed the conversion of karanja oil to biodiesel. Consequently, this pretreatment reduces the overall complexity of the process and reduces the cost of producing biodiesel. Dhar et al.[67] produced biodiesel from high-FFA neem oil and its performance, emission and combustion characterization was verified in a single cylinder DICI engine. In this study, biodiesel was produced in two steps, i.e., esterification followed by transesterification. The physical, chemical and thermal properties of the biodiesel obtained were characterized. Performance, emission and combustion characteristics of this biodiesel and its various blends with mineral diesel were compared with baseline data in a direct injection (DI) diesel engine. Brake specific fuel consumption for biodiesel and its blends was higher than mineral diesel and brake thermal efficiency of all biodiesel blends was found to be higher than mineral diesel. Brake specific carbon mononxide (CO) and hydrocarbon (HC) emissions for the biodiesel fuelled engine were lower (0–50 % and 19–42 %, respectively) than mineral diesel; however, NO emissions were higher (52–66 %) for biodiesel blends. Detailed combustion characterization revealed that combustion starts earlier for higher biodiesel blends; however, combustion was slightly delayed for lower blends of biodiesel in comparison with mineral diesel. The rate of heat release (90–110 kJ deg^{-1} m^{-3}) for all biodiesel blends was almost identical to mineral diesel. Combustion duration for biodiesel blends was found to be shorter than min-

eral diesel. Biodiesel produced from high FFA neem oil was found to be marginally inferior compared to mineral diesel.

The free fatty acids present in *Azadirachta indica* (Neem) oil were esterified with phosphoric acid-modified catalyst. During the esterification, the acid value reduced from 24.4 to 1.8 mg KOH g^{-1} oil. The catalyst was characterized by NH$_3$ TPD, XRD, SEM, FTIR and TGA analysis. During phosphoric acid modification, the hydrophobic character and weak acid sites of the mordenite had increased, which led to better esterification as compared to H-mordenite. The authors reported the optimization parameters for transesterification as follows: methanol to oil ratio 6, catalyst loading 1 % and temperature 60 °C[68]. Ghadge et al.[69] reported biodiesel production from mahua (*Madhucaindica*) oil having high free fatty acids (19 %). The high FFA level of mahua oil was reduced to less than 1 % by a two-step pretreatment process. Each step was carried out at 60 °C in the presence of the methanol-to-oil ratio of 0.30–0.35 v/v, 1 % H$_2$SO$_4$ (v/v) as an acid catalyst, in 1h reaction time. After the reaction, the mixture was allowed to settle for an hour, and the methanol-water mixture separated at the top was removed. The bottom product was transesterified to produce biodiesel in the presence of methanol (0.25 v/v) and KOH (0.7 % w/v) as alkaline catalyst. The fuel properties of mahua biodiesel were found to be comparable to those of conventional diesel, and met both American and European standards. The transesterification reaction for the production of biodiesel from soybean frying oil with methanol was studied in the presence of different heterogeneous catalysts (Mg MCM-41, Mg-Al Hydrotalcite, and K$^+$ impregnated zirconia). The basis of selection of catalysts was a combination of porosity and surface basicity. Particularly, Mg-Al hydrotalcite showed the highest activity (conversion 97 %). It was observed that the catalyst activity of ZrO$_2$ in the transesterification reaction increased as the catalyst was enriched with potassium cations due to increasing basicity[70].

Methanolysis of soybean oil using Mg–Al hydrotalcites as heterogeneous catalyst was investigated. The authors evaluated the effect of Mg/Al ratio on the basicity and catalytic activity for biodiesel production. Oil conversion was 90 % over Mg/Al [Al/(Mg+Al) = 0.33]catalyst when the reaction was carried out at 230 °C with a methanol to soybean oil molar ratio of 13:1, after 1 h in presence of 5 wt.% catalyst loading. The reusability and stability of this catalyst was also investigated[71]. Barbosa et al.[72] performed the transesterification of mixtures of castor oil and soybean oil in the presence of ethanol via base-catalyzed (KOH). It was observed that, ethanolysis of vegetable oil mixtures, containing up to

25 wt.% of castor oil, yielded biodiesels that were more easily purified than those obtained from pure castor oil and, hence, relatively high process yields could be obtained. Viscosity and specific density of biodiesels produced by transesterification of oil mixtures were in between those of biodiesels derived from the individual pure oils. The results obtained indicated that the use of castor oil as a raw material for the production of biodiesel would be viable. The use of a mixed oil as a feedstock would also allow the possibility of producing biodiesel with custom-designed characteristics without post-production blending.

Conclusions

In view of the rising cost of petroleum products, there is an energy crunch along with the shortage of petrochemicals. The literature search revealed several alternate routes for the production of fuel and energy. However, this matter is complicated because of the greenhouse effect and global warming. In order to overcome these environmental issues, there is need to develop newer catalytic systems, which could give better yields of desired products in terms of fuel and energy.

In this review, we have discussed the importance of biofuel, the types and sources of biofuel. Biomass gasification, production of syngas and bio-oil is also presented. Furthermore, this review extensively examines the overall production processes of biofuels from triglycerides, vegetable oils and different fatty acids through various catalytic routes.

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