Heterogeneous Catalysis of Second Generation Oil for Biodiesel Production: A Review

Fatai A. Aderibigbe[1], Suleiman Shiru[1],*, H. B. Saka[1], M. K. Amosa[2,3], Sherif Ishola Mustapha[1], Mohammed I Alhassan[1], Ayoade L. Adejumo[4], Morufudeen Abdulraheem[1], R. U. Owolabi[5]

Abstract

The demand for cleaner fuels has been on the rise lately, prompting researchers to explore alternative cleaner technologies to meet the growing demand. This has led to the introduction of renewable fuels such as bioethanol and biodiesel. Depending on the feedstock employed for production, renewable fuels can be divided into first, second, and third generation. Reliance on first generation biofuel feedstocks has led to inherent competition between foods versus fuels in the society in the last decade. Further technological prospects in research and development have provided insight into the use of second generation biofuel feed-stocks from non-edible agricultural waste products, energy crops, and crop residues. Zeolites and modified zeolites as heterogeneous catalysts have been highly prospective for the transesterification process of these oils. Modified zeolite can act as a bi-functional catalyst because of its acidic and basic sites. Here, a review of transesterification reaction technology, zeolite and modified zeolite as a heterogeneous catalyst to generate biodiesel was discussed. Current status, challenges and future prospects are also discussed.

Keywords: Biodiesel, Heterogeneous catalyst, Homogeneous catalyst, Transesterification, Zeolite

Received: November 19, 2020; *revised:* January 16, 2021; *accepted:* February 22, 2021

DOI: 10.1002/cben.202000035

1 Introduction

The world's total energy consumption primarily is increasing annually due to growth in population and modernization. As at year 2015, the world's total primary energy consumption was over 150 000 000 GW and it has been predicted to attain up to about 57 % by the year 2050 [1]. The rise in energy depletion will ultimately cause more greenhouse gas emissions and environmental harms. Presently, close to 81 % of overall consumed energy globally is sourced from fossil fuels, prompting negative influence on ecological system and human health [1].

The transportation system is an important part of the development of the economy of any country worldwide. Recently, the worldwide transportation sector's main problem is the supply of energy, which is satisfied by crude oil such as diesel fuel and petrol [2]. The transport sector averagely consumes large amount of fuel, and this is actually caused by the expansion in the vehicle industry [3]. Rife predicts that the transportation sector alone will account for 63 % in global increase in total liquid fuel consumption between 2010 and 2040 [4]. Likewise, the boom in growth of the vehicle industry globally has elevated the release of injurious pollutant into the atmosphere. The transportation sector accounts for close to 23 % of global greenhouse gas emission [5]. The International Energy Agency (IEA) forecasts that the emissions of greenhouse gas emanating from the transport sector will jump to 93 % between the years 1990–2020 and also carbon dioxide (CO_2) of about 8.59 billion metric tons will be freed to the earth's atmosphere from now to

[1] Dr. Fatai A. Aderibigbe, Suleiman Shiru*, H. B. Saka, Sherif Ishola Mustapha, Mohammed I Alhassan, Morufudeen Abdulraheem
Department of Chemical Engineering, University of Ilorin, Ilorin, Nigeria.
E-Mail: shirusuleiman@gmail.com

[2] Dr. M. K. Amosa
Department for Management of Science and Technology Development, Ton Duc Thang University, Ho Chi Minh City, Vietnam.

[3] Dr. M. K. Amosa
Faculty of Environment and Labour Safety, Ton Duc Thang University, Ho Chi Minh City, Vietnam.

[4] Dr. Ayoade L. Adejumo
Department of Chemical Sciences, Osun State University, Osogbo, Nigeria.

[5] Dr. R. U. Owolabi
Department of Chemical Engineering, University of Lagos, Lagos, Nigeria.

© 2021 Wiley-VCH GmbH

2035 [6]. Furthermore, poor air quality comes mainly from mobile releases like particulate matter, nitrogen oxides (NOx), hydrocarbons, carbon dioxides (CO_2) and carbon monoxides (CO) [6]. To solve this challenges, the use of oil seed as feedstock is becoming reliable.

The oilseed sector is a dynamic and growing enterprise all around the world. The oilseed production and processing industry is led by the United States [7]. Some foremost oilseed crops cultivated in the North American region are peanuts, soybeans, cottonseed, and sunflower. The present vegetable oilseed proficiencies in the north-central regions of America have the ability to supply close to 59 % of the Navy's projected requirements in 2020 in that region [8]. Solvent extraction together with cold press technologies are normally used to process vegetable oilseeds to create vegetable oil, which is then further refined into liquid hydrocarbon biofuel. Palm oils together with soybean (sourced from food crops) are normally referenced as first generation oils. Jatropha, Camelina, algae oils (gotten from non-food crops) are referenced as second generation oils [9]. Vegetable oil that is not edible is in no way competing with food and its sources. Waste vegetable cooking oil, plant oil, and oil sourced from wastes gotten from processed oilseed foods are classified as non-food plant oil [10].

Some ways of transforming vegetable oil to biofuel are fermentation, transesterification, hydro-processing, catalytic cracking, and thermal cracking. There are merits and demerits associated with each method, but this study focuses on transesterification [11]. Transesterification is a simple technology with cost effective ability that produces hydrocarbon biofuel from vegetable oil [12].

Greenhouse gas emissions can be highly reduced by hydrocarbon biofuels. The technology of hydrocarbon biofuel really does not need several alterations to the current fuel vehicle engine or supply structure [13]. Biofuel are employed in many fields including hydraulic operating fluid, lubrication and heat absorption. Several factors like refinement, chemical processing, feedstock and distribution/transportation determines the budget of hydrocarbon biofuel production. The future prospect of hydrocarbon biofuel is dependent on appreciable cost lessening [13]. Even though the feedstock quantity is paramount to economic cost, catalysts relevance is also paramount during chemical processing. Catalytic agent to be used is expected to be highly effective and discerning. Zeolite based catalytic agents are well applied for vegetable oil chemical processes [13].

Biofuel feedstocks are classified from first to third generation. Second generation biodiesel mainly obtained from non-edible oils proves to be extra attractive and encouraging to ensure biodiesel production is continuous [14]. Even though, the nullification of competition with food or feed may not be totally assured by non-edible oils yet, it holds the potential to reducing this factor. Non-edible oil feedstocks are toxic and cannot be used as food sources [15]. Many factors are required in the planting of edible plant oils, which are lush land, water, and production yield. This poses less of a problem for non-edible plant oils as it easily can be grown in barren lands with low cost, minimal maintenance, minimal soil fertility, and minimal water requirement. In addition, planting of non-edible oils by the use of barren or unused lands proves to be an alternate tactics to replantation rather than forest clearing [15]. Another merit of non-edible or second generation feedstocks is its low cost, which is one of the focal arguments that ascertain the budget of overall biodiesel production derived from vegetable oil [16].

Micro-algae biomass is used to develop third generation biofuel that enjoy great productivity of lipids, that are trans esterified after extraction to achieve biodiesel, classifying it into one of the most promising feedstocks for biofuel production [17]. Algae were classed with second generation biofuel before. Conversely, algae provide much better yields with less resource efforts compared to other feedstocks, researchers proposed that they be classed in their own group [18]. Usage of various groups of carbon sources is one of the foremost advantages of algae. Algae have been mentioned to be tied directly to carbon producing sources like industries and power plants where it could directly transform emissions into usable fuel. This simply means that minimal release of carbon dioxide from these settings and that consequently, total emissions would be minimized significantly [19].

Unfortunately, algae have some setbacks. When cultured in wastewater, algae need large amounts of nitrogen, water, and phosphorus to mature [19]. Production of fertilizer to meet the requirements of algae employed to produce renewable fuel would create more greenhouse gas emissions than were salvaged by employing algae-based biofuel to start with. This also implies that higher cost is needed for algae base renewable fuel compared to other conventional fuel sources [20].

Accordingly, in this paper, biodiesel production from non-edible-based oils using various catalysts of heterogeneous form was discussed. It is targeted toward understanding background production of biodiesel as well as the rewards and drawbacks of both heterogeneous and homogeneous catalyst for biodiesel production. In allusion to many current review papers obtainable on biodiesel production form heterogeneous catalyst, the focus of this paper is on the state-of-the-art use of zeolite and modified zeolite for production of low cost non-edible based biodiesel.

2 Biodiesel

This is simply a mono-alkyl ester of long chain fatty acids gotten from non-edible oils, edible oils, waste cooking oil or animal fat. In the formation of biodiesel different feed stocks are used, which are normally classified as either first or second generation [21].

A reduction of 77, 45.7, 65.7, and 44.2 % for carbon dioxide, carbon monoxide, particulate matter, and unburned hydrocarbons respectively have been observed by the use of biodiesel fuel [22]. In effect, global warming will be highly reduced by application of biodiesel. With direct application or little modification, biodiesel can be used in diesel engines. It can be blended with conventional diesel at any ratio devoid of hindrance to the engine performance [22].

Greater lubricity is observed compared to conventional known diesel fuel because of little or no sulfur content in biodiesel, thereby improving the engine durability. Biodiesel has shown good oil qualities, like higher combustion efficiency,

© 2021 Wiley-VCH GmbH

higher cetane number, and less emission [23]. Numerous factors summing up the biodiesel cost are raw materials, other reactants, its storage and nature of purification. It has been established that the major determining factor for biodiesel production cost is feedstock, summing up close to 80 % of the overall operating budget [24]. More economical feedstock may be applied like waste fats and oils, which can save a lot of capital. Higher cost of biodiesel has been a major setback for its commercialization than conventional based petroleum diesel. The application of technologies and diverse approaches to evaluate optimum conditions of production of biodiesel economically and theoretically have been conducted [25].

Currently various methods are available and have been applied for reducing the viscosity of vegetable oil [26]. The easiest method applied for viscosity of oil reduction in biodiesel is transesterification [27]. Biodiesel feed stocks are distributed all around the world as can be viewed in Tab. 1. They are sourced from edible materials, non-edible materials and neutral sources.

2.1 Biodiesel Production

Some advantages and disadvantages of biodiesel to conventional diesel are mentioned in Tab. 2. The most popular methods in use today for biodiesel production are blending of oils or direct use, transesterification, pyrolysis, and micro-emulsion. Amidst all these methods, transesterification is presently proposed by several scientists as the most desirable because the fuel produced is of better quality [28].

2.1.1 Micro-Emulsification

Viscosity is one of the major physical properties of raw vegetable oil, which hinders its direct application as fuel [29]. Researchers have revealed that, micro-emulsion development is among some of the prospective way out for this viscosity hindrance [30]. It can be explained as a dispersion of colloidal equilibrium of optically isotropic fluid microstructures with 1–150 nm size range, molded from two liquids that are not miscible and one or more ionic or non-ionic amphiphiles [31].

Micro-emulsions are made up of three constituents which are in oil phase, an aqueous phase and a surfactant. They are clear and stable isotropic fluids [32]. Micro-emulsions having solvents such as ethanol, methanol, 1-butanol, and ethanol have been studied for this particular aim. Butanol, hexanol and octanol are all micro-emulsions that can meet diesel engines maximum viscosity limitations [33]. As reported by [34], a micro-emulsion prepared by blending methanol, soybean oil, cetane improver and 2-octanol in the ratio has satisfied the Engine Manufacturers Association (EMA) test [35].

2.1.2 Pyrolysis

Pyrolysis is the chemical change that occurs during the use of energy of thermal form without oxygen, to form bond cleavages and a range of small molecules formation. The major pyrolysis methods with varying properties such as temperature, heating rate and residence time are mentioned in Tab. 3. Pyrolysis mostly is carried out at a range of temperature between 400–600 °C [36]. Depending on the rate of pyrolysis, the process yields bio-oil, biogas, and bio-char. From these conditions of operations stated, pyrolysis process can be categorized into flash pyrolysis, fast pyrolysis and conventional pyrolysis. The process chosen for bio-oil production is the fast pyrolysis method [37].

One of the demerits of pyrolysis is introduction of distillation equipment to perform separation of the many segments. In addition, the product gotten shares related properties with gasoline which contains sulfur making it a less ecofriendly method [38].

The apparatus for carrying out pyrolysis and thermal cracking are costly for moderate outputs. Similarly, with chemical similarity to diesel fuel and petroleum-derived gasoline, oxygen removal in thermal processing in turn removes any environmental advantage of using an oxygenated fuel [39]. The process gives an end product with poor material value and on certain occasions, more gasoline than diesel fuel [40].

Table 1. Biodiesel feedstock distribution around the world.

Region	Edible oils	Non-edible oils	Other sources	Ref.
Africa	Palm oil, Coconut oil and Soya beans oil	Jatropha curcas, Jatropha and castor oil	Microalgae, Animal fats and waste cooking oil	[6]
Asia	Soybeans oil, Rapeseed oil, Sunflower oil, Palm oil and Coconut oil	Jatropha oil, Karanja (pongomia oil), Rubber seed and Castor oil	Microalgae and Waste cooking oil	[6]
Europe	Rapeseed oil, Sunflower oil and Cottonseed oil	Rubber seed and Linseed	Animal fats and Waste cooking oil	[6]
North America	Soybeans oil, Peanut oil and Rapeseed oil	Jatropha and Neem	Waste cooking oil, Animal fats and Beef tallow	[6]
South America	Cotton seed oil, Soybean oil and Palm oil	Jatropha and Castor oil		[6]
Australia and Oceania		Jatropha curcas and Pongamia	Waste cooking oil, Animal fats and Beef tallow	[6]

© 2021 Wiley-VCH GmbH

Table 2. Some merits and demerits of biodiesel.

S/NO	Merits	Demerits	Ref.
1	Biodiesel does not require drilling, transportation, or refinement like conventional diesel.	Biodiesel possesses a corrosive nature against copper and brass.	[29, 31]
2	Production of biodiesel is easier than conventional diesel and is less time consuming.	Biodiesel facilitates excessive engine wear.	[29, 33, 84]
3	Biodiesel is more cost efficient than conventional diesel because it is produced locally.	Carbon deposits can be observed on piston and head of the engine. Prolonged storage period brings about Biodiesel degradation.	[31]
4	Biodiesel possesses the potential for stimulating sustainable rural development and a solution for energy security issue.	Coking of injectors on the piston and head of the engine occurs after a while.	[33]
5	It can be put into use without adding additional lubricant, unlike diesel engine.	Biodiesel lower engine speed and power.	[6, 29]
6	Biodiesel can make the vehicle perform better as it possesses higher cetane number.	The biodiesels on the average decrease power by 5 % compared to that of conventional diesel at rated load.	[6, 31, 33]
7	Biodiesel releases fewer emissions such as PM, CO_2, CO, SO_2, and HC compared to conventional diesel.	The higher viscosity due to the large molecular mass and chemical structure of vegetable oils leads to a problem in pumping, combustion, and atomization in the injector system of a diesel engine.	[33]
8	Biodiesel has higher combustion efficiency, portability, availability, and renewability.	The high viscosity, in long-term operation, introduces the formation of injector deposits, plugging of filters, lines and injectors, ring sticking and incompatibility with conventional lubricating oils.	[31]
9	Requirement of engine modification up to B20 not necessary. Biodiesel is Non-flammable, non-toxic, reduces tailpipe emissions, visible smoke and noxious fumes		[31]

Table 3. Pyrolysis methods with differences in residence time, heating rate, temperature, and major product obtained.

Pyrolysis methods	Residence time	Heating rate [°C s^{-1}]	Temperature [°C]	Major products	Ref.
Conventional/slow pyrolysis	Long 5–30 min	Low 10	Med-high (400–500)	Gases char, bio-oil (tar)	[33]
Fast pyrolysis	Short 0.5–2 s	High 100	Med-high (400–650)	Bio-oil (thinner), gases char	[6]
Ultra-fast/flash pyrolysis	Very short < 0.5 s	Low 10	High (700–1000)	Gases bio-oil	[6]

2.1.3 Blending

Vegetable oils direct blending has been considered not suitable and unfeasible for both indirect and direct diesel engines using diesel. Some known disadvantages of this process are free fatty acid content, acid composition, high viscosity, polymerization, and gum formation caused by oxidation during combustion and storage, thickening of lubricating oil and carbon deposits [41]. In another view, incomplete combustion and deterioration of oil are the pronounced problems known with the practice of direct vegetable oils as fuels. With this situation it is advised to dilute vegetable oils with materials like solvent/ethanol and diesel fuels [42].

Dilution achieves viscosity reduction and density of vegetable oils [43]. Noted that adding of diesel fuel to 4 % ethanol improves the thermal power of the brake, its torque and its thermal efficiency, while reducing the specific fuel consumption of the brake. It was further stated that since the boiling point of ethanol is lower than that of diesel fuels, it could assist the invention of the combustion process through an unburned blend spray [43].

2.1.4 Transesterification Reaction

Transesterification or alcoholysis can be defined as a chemical reaction whereby alcohol and triglycerides react with the aid of a catalyst to form glycerol and esters as can be seen in Fig. 1 [44]. The chemistry of transesterification reaction is shown in Fig. 1 from the reactants, catalyst to the product obtained. Thus, transesterification involves three continuous reversible reactions, which are alteration of triglycerides to diglycerides, then alteration of diglycerides to monoglycerides. Glycerides are then lastly altered into glycerol, producing a single ester in

© 2021 Wiley-VCH GmbH

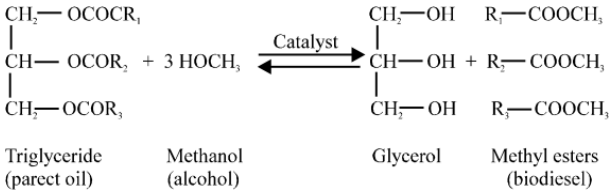


Figure 1. Chemistry of transesterification reactions [27].

every step. When introduced into a reaction, a catalyst enhances and improves the rate of reaction so that the product can be enhanced [28].

Transesterification reaction could involve a catalyst or not. A transesterification reaction involving a catalyst is often performed either chemically like acidic or basic catalyzed transesterification or application of catalysts in enzymatic forms such as lipase-catalyzed transesterification [45]. Since introduction of a catalyst is crucial for reaction to take place various catalytic method were considered [46].

2.1.4.1 Homogeneous Base Catalysts

Homogeneous catalysis entails the application of the liquid form catalyst, mostly acidic and basic catalysts. Emphasis on catalysis of acidic form is centered on the carbonyl group protonation in triglycerides and the alcohol confronting the protonated carbon to form a tetrahedral in-between [47]. Homogenous base transesterification process type requires the raw materials to be of high purity and post separation reaction of catalyst, by-product, and product at the end of the reaction. This method makes biodiesel production cost higher [27].

Biodiesel is often made by basic homogeneous catalyst, which are hydroxides, an alkaline metal alkoxides and sodium or potassium carbonates [48]. Homogeneous base catalysts are often employed in the industries because of several reasons, namely, cost and readily available, mild operation condition, reasonable conversion can be attained in a minimal time, high catalytic activity, etc. [49]. In general, alkali catalytic transesterification methods are done at minimal pressures and temperatures [1.4–4.2 bar and 333–338 K] with minimal concentration of catalyst [0.5–2 wt %]. Atmospheric pressure or small overpressure, reaction at alcohol reflux temperature, moderate stoichiometric alcohol/oil molar ratio, reaction times (typically 1 h) and catalyst concentration are the established process conditions for basic homogeneous catalyst [50]. The setbacks of this process are due to the free fatty acid content, sensitivity to purity of reactants, water concentration of the sample. Possession of a significant amounts of free fatty acids and water content by the oils causes soap formation which hinders conversion to biodiesel [48].

Oils with high free fatty acids forms soap when they react with basic catalyst, which is difficult to separate from biodiesel, glycerin and wash water. The alkali catalyst is expended in soap formation and its efficiency reduces due to the fact that water makes the reaction partially change to saponification [51]. When performing the process, minimization of side reactions like hydrolysis and saponification must be ensured. Saponification yields soap and water from excess free fatty acid in the feedstock [27].

2.1.4.2 Homogeneous Acid Catalysts

In history, the first ever process taken to produce biodiesel (ethyl ester) from palm oil by means of sulfuric acid and ethanol is the catalyzed acidic transesterification process [52]. The acid catalyzed process occurs because of triglyceride reaction with an alcohol and an acid catalyst to produce glycerol and biodiesel. Acid catalyzed process is economically viable and easier with oil having considerable free fatty acid content. A higher temperature and longer reaction time is needed for reaction catalyzed by acid unlike the reaction catalyzed by base [52].

Acid catalyzed transesterification is performed by mixing directly, the acidified alcohol with the oil. This allows transesterification and separation to take place in one step, with both solvent and esterification reagent duties assumed by the alcohol [27]. Acid catalyzed transesterification reaction should be performed where there is no water. This is to prevent competition of carboxylic acids formation which lowers the turn-out of alkyl esters [53].

Often hydrochloric, sulfuric and sulfonic acids are the most employed acidic catalysts used but of the three, sulfuric acid is the most common. The use of alternative acids has also witnessed various researches performed to verify its yield effect [54]. Co-solvents are applied to bridge the resistance of mass transfer caused by alcohol immiscibility with oil. Applying different acids often assists in getting different alternatives for production of efficient biodiesel feedstock of low value [55].

2.1.4.3 Heterogeneous Base Catalysts

The use of a heterogeneous form of alkali catalyst is to break the restrictions barrier peculiar with homogeneous base catalyst usage, amongst is saponification that impede the separation of glycerol from methyl ester layer. In addition, under mild conditions during transesterification process shows better catalytic activity [56].

Due to the high presence of free fatty acid content in low-cost feed stocks, low output is always observed in the alkali catalyzed transesterification reaction to produce biodiesel. This is because free fatty acid reacts with alkali resulting to form soap, which further cause serious separation and emulsification problem [57]. To address this issue, a recently developed solution is the two-step catalytic process for biodiesel production. In step one, a pretreatment of feedstock is done to lower the free fatty acid content by the introduction of an acidic catalyst like ferric sulfate or sulfuric acid. In the second step, an alkali (base) catalyst is introduced to produce biodiesel [58]. Nonetheless, the issue of catalyst removal is also encountered in both steps. Neutralization of the acid catalyst can be used to address the issue in step one, by introducing in the second step, an extra basic catalyst. However, this extra introduction to the reaction will be an added cost to biodiesel production [59].

© 2021 Wiley-VCH GmbH

Modified basic zeolite catalyst can fill this loophole with its acidic and strong basic properties. Modified zeolite can serve as a better catalyst for this purpose because it can simultaneously carry out both esterification and transesterification reaction as a bi-functional synthesized catalyst [60].

Basically, acidic or basic catalyst residue in the biodiesel can cause engine issues. Engine metallic parts can be affected because alkali catalyst can produce higher levels of incombustible ash. Consequently, the acid and alkali catalysts should at all times be removed when completion of biodiesel production is finished [51]. Bi-functional solid catalyst which performs as an alkali and acid at the same time can circumvent these issues because solid acid catalysts have a strong esterification capacity for high for free fatty acids oils and similarly basic catalysts can carry out strongly the triglycerides transesterification [61]. The two-functional solid catalysts have been proposed as a choice for simultaneous esterification and transesterification reaction for biodiesel production [62].

2.1.4.4 Heterogeneous Acid Catalysts

Solid acid-base catalyst has shown that it can act as catalyst for esterification and transesterification reactions simultaneously when feedstock of low quality is involved. These catalysts develop fewer environmental problems, less toxic and less corrosive [63].

Heterogeneous catalyst growth is a vital entity to be blended into a continuous flow reactor. Such a process that is continuous can reduce purification costs as well as product separation, ensuring it is relevant economically and can contend with conventional diesel fuel of commercial form [64]. For transesterification reaction, an acid catalyst should possess features like a large pores system that are interconnected, a hydrophobic surface and a moderate to high strong acid sites concentration [65].

Technologically, acid heterogeneous catalysts have proven to be beneficial due to the possession of an array of acid sites with strengths varying for Lewis or Bronsted acidity when equated to homogeneous acid catalysts [66]. Acid heterogeneous catalysts like tungstated zirconia and sulphated zirconia were applied to catalyze transesterification reaction because it contains reasonable acid strength site [59]. Between the solid catalysts, zirconia showed reasonable selectivity towards methyl ester and glycerol production because of acid strength [67]. In-turn, zirconia has demerits of lower activity and high cost as opposed to liquid acids [68].

2.1.5 Merits and Demerits of Heterogeneous and Homogeneous Catalysts

The main concentration of modern studies is in the rational advancement of solid catalysts that are recyclable. The major advantages and disadvantages of each class of catalyst used to perform transesterification are mentioned in Tab. 4. Heterogeneous catalysts have been established as favorable alternatives to the difficulty experienced during the recycling of homogeneous acid and base catalysts [69].

3 Zeolites

The technological advancement in zeolites and its use has not slowed down for years. Apparently, the exceptional versatility of zeolite allows its various uses almost infinitely. With 35 natural zeolite minerals of different species available, structures running into hundreds can be made artificially which in other words, broadens the scope of use of zeolite materials [46]. Zeolite materials in the form of crystalline aluminosilicates connected by atoms of oxygen are formed naturally. With channels of equal sizes and molecular pores, their framework structure is three in dimension [70]. This pore possesses the capability to grip particles that are suitable to their sizes and favorably dismisses bigger ones as can be seen in Fig. 2.

Zeolites are often used widely as industrial heterogeneous catalysts because of its un-harmful and inexpensive nature to the environment. Zeolites express generous surface area and high porosity. If molecular size of free fatty acid is comparably lower than that of triglyceride, zeolites are usually more effective for esterification than transesterification reactions [71]. The synthetization of mesoporous zeolites would provide great opportunity to avoid the limitation of diffusion and improvement of transesterification of vegetable oils [72]. For the past two decades, concentrated attention and research activities have been diverted to the enhancement and accessibility of active sites in micro-porous zeolite frameworks. Some array of different synthetic methods has been proposed to obtain hierarchical structures, they can all be put into two major types, which are "top-down" and "bottom-up" methods [73]. The former starts with micro-porous zeolites that are then post synthetically modified to produce hierarchical zeolite structures.

3.1 Applications of Zeolites

Zeolites are good adsorbents because of their micro-porous structures possess ultra-porosity properties. In the natural gas

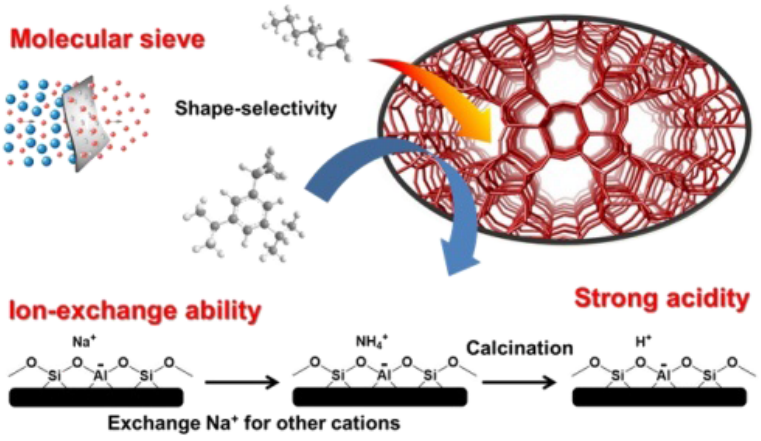


Figure 2. Diagrammatic representation of zeolite molecular sieves [28].

© 2021 Wiley-VCH GmbH

Table 4. Benefits and limitations peculiar to the classes of catalysts.

Class of Catalyst	Merits	Demerits	Ref.
Heterogeneous acid catalyst	Esterification and transesterification takes place simultaneously	Often attracts higher costs	[84–88]
	Ease of separation between the product and catalyst	High reaction conditions and longer reaction times	
	Insensitive to water content and free fatty Acid in the oil	Low reaction rates	
	Favored method if low-grade oil is used	Unsuitable side reaction	
	Re-usable and can be regenerated	Requires more energy input	
	Recyclable	End product maybe contaminated because of leaching of active sites	
Heterogeneous alkali catalyst	Reaction can take place at mild temperature and relatively lower energy	Due to its basicity, it is sensitive to Free Fatty Acid in the oil	[85, 87–89]
	Reaction rate is relatively faster than acid catalyzed transesterification	Saponification can happen if the Free Fatty Acid content in the oil is higher than 2 wt %	
	Ease of separation between the product and catalyst	When exposed to ambient air poisoning of the catalyst can occur	
	Re-usable and recyclable	Requires higher molar ratio of alcohol to oil	
	Possesses long life times	More waste water is produced from purification	
		Diffusion limitation	
Homogeneous acid Catalyst	Esterification and transesterification takes place simultaneously	Can bring about equipment corrosion	[84, 86, 89]
	Insensitive to water content and free fatty Acid in the oil	Low reaction rate is experienced	
	High yield of biodiesel is produced	Difficulty in separating the product and catalyst	
	Avoidance of saponification can be achieved		
Homogeneous alkali Catalyst	Cheap, economically feasible and readily available (NaOH and KOH)	More wastewater is produced from purification	[84, 85, 87, 88]
	Requires less energy because reaction can occur at mild reaction condition	Saponification will reduce the biodiesel yield and cause problem during product purification	
	Reaction occurs 4000 times faster than Acid catalyzed reaction	If the free fatty acid content in the oil is more than 2 wt % saponification can occur	
	Water is not formed during transesterification reaction	Sensitive to Free Fatty Acid content in the oil	

industry, zeolites great adsorption selectivity of CO_2, this makes particularly, the use of zeolite an excellent material in gas-gas separation process. Zeolite has shown that modifying its degree of hydration has an influence that is strong on the water vapor permeability and gases of all forms. Zeolite allows passage of only molecules that fits it pores thereby making it applicable as molecular sieves [74]. This was demonstrated in an attempt made in the nineties on the Chernobyl catastrophe site and Fukushima coast, in Japan 2011, where scientists used quantities of zeolites to absorb the radioactive pollution as much as possible by cesium 137 [75]. Zeolite as an ion-exchange material allows the possibility of removal of cations from a solution. The exchange of ion occurs between a solution and zeolite containing cations showing a higher attraction towards the zeolite than the positive counter-ion already in the structure [76].

Bearing in mind the high concentration of active acid (Brønsted and Lewis) sites it possesses, zeolites are also applied as catalytic agents. Furthermore, their specificity to some selected molecules makes them a catalyst of choice for many. Zeolite are specific catalyst because their activity only supports certain chemical reactions due to the restriction in the size limit of the penetration of reactant species which relies on their size in contrast to the pore sizes [46].

3.2 Zeolite as a Catalyst

Zeolite as a catalyst possesses the features of shape selectivity and acidic sites. They differ from crystal in inner electric fields, pore structures and properties of the surface ascribed to its

© 2021 Wiley-VCH GmbH

changing catalytic properties. Accommodation of cations of diverse varieties like Mg^{2+}, K^{+}, Ca^{2+}, Na^{+}, and several others, due to its alkali nature is also a known characteristic of zeolite [77].

Marchetti et al. [78] applied zeolite as catalysts for converting high free fatty acid oils to FAME [78]. VOx over Ultra Stable Y zeolite (USY) (Acid) and NaY zeolites (Alkali) calcined at 300 °C for 3 h yielded oil to biodiesel conversion in just 10 and 50 min, respectively [78]. Presence of water had a helpful effect at the beginning of the reaction and undesirable effect towards the end of the reaction and thereby reducing the conversion of final product [78].

Chung et al. [79] achieved free fatty acid removal from waste cooking oil by esterification with methanol by applying numerous zeolite catalysts. The mordenite (MOR) , silicalite, fauja site (FAU), ZSM-5 (MFI), and beta (BEA) zeolites were applied with varying molar ratio of Si/Al in the reaction [79]. Pore structure and acidic properties of the zeolite catalysts were described in reference to the free fatty acid conversion. The MFI zeolite brought about an advancement of the exclusion effectiveness of free fatty acid through cracking free fatty acid in its pore structure because of its pore mouth narrowness [79]. Weakening of acid strength of the zeolites reduced the catalytic activity of free fatty acid removal. Acid sites of zeolites that are strong brought about the surplus alteration of free fatty acid. The catalytic activity of acidic zeolite was hindered by pore structure and acid strength in free fatty acid removal [79].

3.3 Modified Zeolite as a Catalyst

Natural zeolite has shown some restrictions during catalysis, such as small pores and cavities leading to severe diffusion shortcomings of reactant molecules and low adsorption capacity compared to metal oxides [80]. To overcome the diffusion setbacks, numerous methods have been introduced like acidic or basic treatment solutions, thickness or size decrease of crystals of zeolite and zeolite pores expansion with steam [81]. Numerous studies have been made using modified Zeolite as heterogeneous catalyst for transesterification process for biodiesel production.

Wang et al. [82] used low-Al zeolite beta as a heterogeneous catalyst in biodiesel production from microwave-assisted transesterification of triglycerides. Alkali-treated zeolite beta in the result shows that it can catalyze transesterification reaction effectively. Experimental settings applied in the reaction are 1:1 (wt/wt) catalyst to oil and 15:1 (wt/wt) alcohol to oil. Na/catalyst (a loading at 1.93 wt %) at 100 °C was used to conduct transesterification reaction. Through the condenser into the flask - triolein, methanol and catalyst were added then irradiated at 100 °C at 800 W for diverse reaction times [82].

Gangil et al. [83] worked on synthesis of biodiesel from karanja oil using modified mordenite (Zeolite) as a heterogeneous catalyst and concluded that transesterification of karanja oil with methanol was efficiently catalyzed by 20 % NaOH/mordenite, yielding methyl ester of 95.14 wt % amidst the tested catalysts. Un-calcined catalyst activity exceeds calcined catalyst. Dealumination and pore structure of mordenite collapsed at high calcination temperature. Furthermore, increase in calcination temperature decreased the alkali sites in the zeolite. During the reaction, the leaching Na type was little from the solid support [83].

4 Knowledge Gap and Future Perspectives

A major knowledge gap identified based on this review is the use of bi-functional solid catalysts in hierarchical nano-porous form. Catalysts with hierarchically nano-porous form have properties which are structurally versatile like surface area which is high and large pore volume which lessen diffusional limitations of conventional solid catalysts with only framework of micro-porous form. Most studies on heterogeneous catalysis of second generation oils have identified the issues of saponification and high water content of these oils. Many have proposed the application of bi-functional solid catalysts which performs as an alkali and acid at the same time can circumvent this issue because solid acid catalysts have a strong esterification capacity for high for free fatty acids oils and similarly basic catalysts can carry out strongly the triglycerides transesterification. It is proposed that bi-functional catalysts will perform better in hierarchical nano-porous forms.

Reactants like triglycerides are often at times restricted from fully utilizing catalytic sites of some zeolites thereby decreasing the catalytic activity within the pores. Transesterification reaction catalysed by zeolite led to the formation of unwanted by-product like dimethyl ether from methanol dehydration. Best performance of these catalysts is determined by the interchange between the zeolite hydrophobicity and acid strength. This is because of high SiO_2/Al_2O_3 ratios which increases the catalysts hydrophobicity. Better performance of these catalysts can be achieved by introducing the design of larger channels and pores.

Hierarchically nano-porous modified zeolite is highly recommended for chemical industries with various catalytic reactions in the industry. When compared to zeolite or other heterogeneous catalysts of conventional form with only micro-pores, the major aim for the development of the hierarchical nano-porous modified zeolite synthesis strategy is to improve the catalytic performance of zeolites or other heterogeneous catalysts of conventional form by reducing or simplifying quick catalytic deactivation limitation, weak activity to bulky molecules limitation and low molecular diffusion efficiency limitation.

5 Conclusion

Biodiesel is an eco-friendly biofuel which influences social and economic developments. This paper review gives broad details on biodiesel development, its feed-stocks distribution globally, merits and demerits of biodiesel and transesterification technology.

Furthermore, the concentration of catalyst and the type of catalyst used are two major factors that transesterification reaction strongly relies on. The often applied catalytic concentration is around 1–12 %. A comprehensive review of the relevance of zeolites as a heterogeneous catalyst in biodiesel

© 2021 Wiley-VCH GmbH

production was established. An effort has also been made to comprise all the important contributions and highlighting the most pertinent available literature for investigating the prospects of hierarchical nano-porous modified zeolite as the best alternative in the biofuel industry.

Conflict of interests

The authors acknowledge no conflict of interest



Fatai A. Aderibigbe was formerly the head of Department of Chemical Engineering, University of Ilorin, Ilorin, Nigeria. He attended Obafemi Awolowo University, Ile-Ife for his B.Sc., M. Sc., and Ph.D. degrees in Chemical Engineering. He is a COREN (Nig.) registered Engineer and member of both Nigerian Societies of Engineers and Chemical Engineers. His area of specialization is Biochemical/Biotechnology, Adsorption processes and Reaction Engineering.



Suleiman Shiru has a Bachelor's Degree in Chemical Engineering from Federal University of Technology, Minna, Nigeria. He is currently pursuing his Master's Degree in Chemical Engineering, University of Ilorin, Nigeria. His research interests include Environmental engineering, Petroleum engineering and Renewable energy.



H. B. Saka obtained his first degree in the field of chemical Engineering (B.Tech.) in 2015 at Ladoke Akintola University of Technology, Ogbomosho Oyo state, Nigeria. In 2019 he got his Masters of Engineering in Chemical Engineering (M.Eng.) from the University of Ilorin, Ilorin, Kwara State. His research interest includes but not limited to Biofuel technology, Adsorption process and Catalyst development. He is currently working in one of the reputable oil and gas Industries in Nigeria as the Quality control and Assurance Manager.



Sherif Ishola Mustapha is a lecturer in the Department of Chemical Engineering, University of Ilorin. His research interest includes nanotechnology for water treatment application, catalysis for energy application, conversion of biomass to biofuels and other high-value products.



Abdulraheem Morufudeen holds a B.Eng. (Chemical Engineering) from Ahmadu Bello University Zaria, Nigeria and is currently studying for his Master's degree (Chemical Engineering) at University of Ilorin, Nigeria. His area of specialization is renewable energy (Biochemical and Biotechnology).

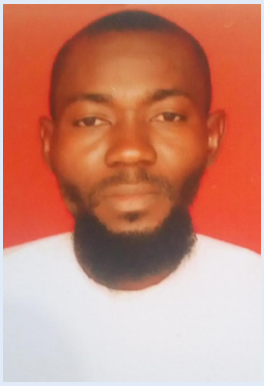


Ayoade L. Adejumo was Head of the Chemical Sciences Department, Osun State University, Osogbo, Nigeria and is presently at the Department of Mechanical Engineering, Faculty of Engineering and Environmental Sciences, Osun State University. He graduated from Ladoke Akintola University of Technology, Ogbomoso, Nigeria for his B.Eng. and Obafemi Awolowo University, Ile-Ife, Nigeria for his Master's and Ph.D. degrees, all in Chemical Engineering. He is a member of the Nigerian Society of Engineers (NSE), a Registered Engineer with the Council of the Regulation of Engineering in Nigeria (COREN). He has demonstrated deep teaching and research in industrial enzymes application, biomass conversion into biofuel and chemical kinetics.

© 2021 Wiley-VCH GmbH



R. U. Owolabi graduated from Ladoke Akintola University of Technology and University of Lagos for his Bachelor's degree and Master's degree respectively, both in chemical engineering. He also obtained his Ph.D. in chemical engineering at the University of Lagos. He has demonstrated deep teaching and research in green and sustainable chemistry, biomass conversion into biofuel, biodiesel or bio energy, polymerization processes, polymer chemistry and synthesis, chemical kinetics and reaction engineering, chemicals and fuels derived from biomass building block. He is a member of the Nigerian society of engineers and council of the regulation of engineering.



Mohammed I Alhassan holds B.Eng. and M.Eng. in Chemical engineering. He joined the service of University of Ilorin in November 2017 as an academic staff in Department of Chemical engineering.



M. K. Amosa is currently a Senior Chemical Engineer with the Department of Petroleum Resources, Nigeria. He is a trained Chemical Engineer with bachelor's and master's Degrees in Chemical Engineering. He obtained a Ph.D. Degree in Environmental Process Engineering from the International Islamic University Malaysia and won the best doctoral degree award. He was a NRF/DST SARChl Research Fellow in Sustainable Process Systems Engineering at the School of Chemical & Metallurgical Engineering, University of the Witwatersrand (Wits), Johannesburg from 2015 to 2018. While at Wits, he won the most highly cited researcher award of the University in 2017. His research interests include process systems engineering and separation processes.

Abbreviations

IEA	International Energy Agency
EMA	Engine Manufacturers Association
FAME	fatty acid methyl esters
MOR	mordenite
FAU	faujasite
ZSM-5	Zeolite Socony Mobil 5

References

[1] M. Hajjari et al., A review on the prospects of sustainable biodiesel production: a global scenario with an emphasis on waste-oil biodiesel utilization, *Renewable Sustainable Energy Rev.* **2017**, *72*, 445–464.

[2] A. Demirbas, Importance of biodiesel as transportation fuel, *Energy Policy* **2007**, *35 (9)*, 4661–4670.

[3] C. Azar, K. Lindgren, B. A. Andersson, Global energy scenarios meeting stringent CO2 constraints – cost-effective fuel choices in the transportation sector, *Energy Policy* **2003**, *31 (10)*, 961–976.

[4] A. Liaquat et al., Potential emissions reduction in road transport sector using biofuel in developing countries, *Atmospheric Environ.* **2010**, *44 (32)*, 3869–3877.

[5] K. W. Steininger et al., Austria's consumption-based greenhouse gas emissions: Identifying sectoral sources and destinations, *Global Environ. Change* **2018**, *48*, 226–242.

[6] H. Mahmudul et al., Production, characterization and performance of biodiesel as an alternative fuel in diesel engines – A review, *Renewable Sustainable Energy Rev.* **2017**, *72*, 497–509.

[7] E. Aragie, K. Pauw, V. Pernechele, Achieving food security and industrial development in Malawi: Are export restrictions the solution?, *World development* **2018**, *108*, 1–15.

[8] R. J. Nelson, K. D. Kephart, *Feedstock Development in the North Central Region for Green Diesel and Jet Fuels*, White Paper, Sun Grant Initiative-North Central Center South Dakota State University **2011**.

[9] G. Liu, B. Yan, G. Chen, Technical review on jet fuel production, *Renewable Sustainable Energy Rev.* **2013**, *25*, 59–70.

[10] X. Zhao, L. Wei, J. Julson, First stage of bio-jet fuel production: non-food sunflower oil extraction using cold press method, *AIMS Energy* **2014**, *2 (2)*, 193–209.

[11] X. Zhao et al., Catalytic cracking of inedible camelina oils to hydrocarbon fuels over bifunctional Zn/ZSM-5 catalysts, *Korean J. Chem. Eng.* **2015**, *32 (8)*, 1528–1541.

[12] R. Zarchin et al., Hydroprocessing of soybean oil on nickel-phosphide supported catalysts, *Fuel* **2015**, *139*, 684–691.

[13] H. SaraJliJa, N. ČukelJ, D. NoVotNi et al., Preparation of Flaxseed for Lignan Determination by Gas Chromatography-Mass Spectrometry Method, *Czech j. Food Sci.* **2012**, *30 (1)*, 45–52.

[14] A. K. Azad et al., Prospect of biofuels as an alternative transport fuel in Australia, *Renewable Sustainable Energy Rev.* **2015**, *43*, 331–351.

© 2021 Wiley-VCH GmbH

[15] A. Silitonga et al., Overview properties of biodiesel diesel blends from edible and non-edible feedstock, *Renewable Sustainable Energy Rev.* **2013**, *22*, 346–360.
[16] M. M. K. Bhuiya et al., Prospects of 2nd generation biodiesel as a sustainable fuel – Part: 1 selection of feedstocks, oil extraction techniques and conversion technologies, *Renewable Sustainable Energy Rev.* **2016**, *55*, 1109–1128.
[17] B. Ravindran et al., Recent advances and future prospects of microalgal lipid biotechnology, in *Algal Biofuels* (Eds: S. Kumar Gupta, A. Malik, F. Bux), Springer, Berlin 2017, 1–37.
[18] V. Akubude, K. Nwaigwe, E. Dintwa, Production of bodiesel from microalgae via nanocatalyzed transesterification process: A review. *Mat. Sci. Technol.* **2018**, *2*, 216–225.
[19] V. Akubude, K. Nwaigwe, E. Dintwa, *Mat. Sci. Energy Technol.* **2019**, *2 (2)*, 216–225.
[20] G. Dragone, B. D. Fernandes, A. A. Vicente et al., Third generation biofuels from microalgae, in *Current Research, Technology and Education Topics in Applied Microbiology and Microbial Biotechnology* (Ed. A. Méndez-Vilas), Formatex Research Center, Norristown, PA **2010**.
[21] S. Cesarini et al., Moving towards a competitive fully enzymatic biodiesel process, *Sustainability* **2015**, *7 (6)*, 7884–7903.
[22] S. H. Y. S. Abdullah et al., A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production, *Renewable Sustainable Energy Rev.* **2017**, *70*, 1040–1051.
[23] O. Özener et al., Effects of soybean biodiesel on a DI diesel engine performance, emission and combustion characteristics, *Fuel* **2014**, *115*, 875–883.
[24] L. Meher, D. V. Sagar, S. Naik, Technical aspects of biodiesel production by transesterification – a review, *Renewable Sustainable Energy Rev.* **2006**, *10 (3)*, 248–268.
[25] J. Singh, S. Gu, Commercialization potential of microalgae for biofuels production, *Renewable Sustainable Energy Rev.* **2010**, *14 (9)*, 2596–2610.
[26] Y. Sharma, B. Singh, S. Upadhyay, Advancements in development and characterization of biodiesel: a review, *Fuel* **2008**, *87 (12)*, 2355–2373.
[27] A. Abbaszaadeh et al., Current biodiesel production technologies: a comparative review, *Energy Convers. Manag.* **2012**, *63*, 138–148.
[28] M. Y. Koh, T. I. M. Ghazi, A review of biodiesel production from Jatropha curcas L. oil, *Renewable Sustainable Energy Rev.* **2011**, *15 (5)*, 2240–2251.
[29] S. Slomkowski et al., Terminology of polymers and polymerization processes in dispersed systems (IUPAC Recommendations 2011), *Pure Appl. Chem.* **2011**, *83 (12)*, 2229–2259.
[30] A. Tafere, Production and Characterization of Biodiesel from Avocado Peel Oil (APO), *M.Sc. Thesis*, Addis Ababa University 2018.
[31] A. Schwab, M. Bagby, B. Freedman, Preparation and properties of diesel fuels from vegetable oils, *Fuel* **1987**, *66 (10)*, 1372–1378.
[32] P. Kumar, R. Mazumder, Comparative Study on Formulation and Evaluation of Microemulsion Based Gel of Curcumin with Different Combinations of Polymers, *World J. Pharm. Res.* **2018**, *7 (15)*, 447–448.
[33] S. Jain, M. Sharma, Prospects of biodiesel from Jatropha in India: a review, *Renewable Sustainable Energy Rev.* **2010**, *14 (2)*, 763–771.
[34] F. Ma, M. A. Hanna, Biodiesel production: a review, *Bioresour. Technol.* **1999**, *70 (1)*, 1–15.
[35] H. Fukuda, A. Kondo, H. Noda, Biodiesel fuel production by transesterification of oils, *J. Biosci. Bioeng.* **2001**, *92 (5)*, 405–416.
[36] P. Basu, *Biomass Gasification and Pyrolysis: Practical Design and Theory*, Academic Press, Cambridge, MA 2010.
[37] D. Carpenter et al., Biomass feedstocks for renewable fuel production: a review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors, *Green Chem.* **2014**, *16 (2)*, 384–406.
[38] S. K. Narwal, R. Gupta, Biodiesel production by transesterification using immobilized lipase, *Biotechnol. Lett.* **2013**, *35 (4)*, 479–490.
[39] T. J. Morgan, R. Kandiyoti, Pyrolysis of coals and biomass: analysis of thermal breakdown and its products, *Chem. Rev.* **2013**, *114 (3)*, 1547–1607.
[40] S. F. Sing et al., Production of biofuels from microalgae, *Mitigation Adapt. Strategies Global Change* **2013**, *18 (1)*, 47–72.
[41] P. S. Bisen et al., Biodiesel production with special emphasis on lipase-catalyzed transesterification, *Biotechnol. Lett.* **2010**, *32 (8)*, 1019–030.
[42] S. Czernik, A. Bridgwater, Overview of applications of biomass fast pyrolysis oil, *Energy Fuels* **2004**, *18 (2)*, 590–598.
[43] A. Bilgin, O. Durgun, Z. Sahin, The effects of diesel-ethanol blends on diesel engine performance, *Energy Sources* **2002**, *24 (5)*, 431–440.
[44] A. P. Vyas, J. L. Verma, N. Subrahmanyam, A review on FAME production processes, *Fuel* **2010**, *89 (1)*, 1–9.
[45] S. Grebemariam, J. M. Marchetti, Biodiesel production technologies: A review, *AIMS Energy* **2017**, *5 (3)*, 425–457.
[46] G. Lemoine, Comparison of different types of Zeolites used as Solid Acid Catalysts in the Transesterification reaction of Jatropha-type oil for Biodiesel production, *M.Sc. Thesis*, Worcester Polytechnic Institute **2013**.
[47] E. Aransiola et al., A review of current technology for biodiesel production: State of the art, *Biomass Bioenergy* **2014**, *61*, 276–297.
[48] L. C. Meher et al., Transesterification of karanja (Pongamia pinnata) oil by solid basic catalysts, *Eur. J. Lipid Sci. Technol.* **2006**, *108 (5)*, 389–397.
[49] A. Kawashima, K. Matsubara, K. Honda, Acceleration of catalytic activity of calcium oxide for biodiesel production, *Bioresour. Technol.* **2009**, *100 (2)*, 696–700.
[50] M. Bhuiya et al., Prospects of 2nd generation biodiesel as a sustainable fuel – Part: 1 selection of feedstocks, oil extraction techniques and conversion technologies, *Renewable Sustainable Energy Rev.* **2016**, *55*, 1109–1128.
[51] C. Enweremadu, M. Mbarawa, Technical aspects of production and analysis of biodiesel from used cooking oil – A review, *Renewable Sustainable Energy Rev.* **2009**, *13 (9)*, 2205–2224.
[52] Y. Zhang et al., Biodiesel production from waste cooking oil: 1. Process design and technological assessment, *Bioresour. Technol.* **2003**, *89 (1)*, 1–16.

 © 2021 Wiley-VCH GmbH

[53] P. Mahanta, A. Shrivastava, Technology development of biodiesel as an energy alternative, in *Challenges and Strategies for Sustainable Energy Deficiency and Environment* (Eds: O. Singh, J. P. Pandey, D. S. Chauhan), New Age International, New Delhi **2006**.

[54] J. Y. Park et al., Effects of water on the esterification of free fatty acids by acid catalysts, *Renewable Energy* **2010**, *35 (3)*, 614–618.

[55] A. Hajinezhad et al., Biodiesel production from Norouzak (Salvia lerifolia) seeds as an indigenous source of bio fuel in Iran using ultrasound, *Energy convers. Manag.* **2015**, *99*, 132–140.

[56] J. Calero et al., Development of a new biodiesel that integrates glycerol, by using CaO as heterogeneous catalyst, in the partial methanolysis of sunflower oil, *Fuel* **2014**, *122*, 94–102.

[57] A. Murugesan et al., Production and analysis of bio-diesel from non-edible oils – a review, *Renewable Sustainable Energy Rev.* **2009**, *13 (4)*, 825–834.

[58] M. Charoenchaitrakool, J. Thienmethangkoon, Statistical optimization for biodiesel production from waste frying oil through two-step catalyzed process, *Fuel Process. Technol.* **2011**, *92 (1)*, 112–118.

[59] Z. Helwani et al., Technologies for production of biodiesel focusing on green catalytic techniques: a review, *Fuel Process. Technol.* **2009**, *90 (12)*, 1502–1514.

[60] T. Saba et al., Biodiesel production from refined sunflower vegetable oil over KOH/ZSM5 catalysts, *Renewable Energy* **2016**, *90*, 301–306.

[61] C. R. Venkat Reddy, R. Oshel, J. G. Verkade, Room-temperature conversion of soybean oil and poultry fat to biodiesel catalyzed by nanocrystalline calcium oxides, *Energy Fuels* **2006**, *20 (3)*, 1310–1314.

[62] M. E. Borges, L. Díaz, Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review, *Renewable Sustainable Energy Rev.* **2012**, *16 (5)*, 2839–2849.

[63] S. Zhang et al., Rapid microwave-assisted transesterification of yellow horn oil to biodiesel using a heteropolyacid solid catalyst, *Bioresour. Technol.* **2010**, *101 (3)*, 931–936.

[64] R. M. de Almeida et al., Transesterification reaction of vegetable oils, using superacid sulfated TiO2–base catalysts, *Appl. Catal. A* **2008**, *347 (1)*, 100–105.

[65] A. Dalai, M. Kulkarni, L. Meher. Biodiesel productions from vegetable oils using heterogeneous catalysts and their applications as lubricity additives in *Proc of the EIC Climate Change Technology Conf. 2006*, IEEE, New Jersey **2006**.

[66] E. Lotero et al., Synthesis of biodiesel via acid catalysis, *Ind. Eng. Chem. Res.* **2005**, *44 (14)*, 5353–5363.

[67] M. Mazou et al., Plant latex lipase as biocatalysts for biodiesel production, *Afri. J. Biotechnol.* **2016**, *15 (28)*, 1487–1502.

[68] S. Al-Zuhair, F. W. Ling, L. S. Jun, Proposed kinetic mechanism of the production of biodiesel from palm oil using lipase, *Process. Biochem.* **2007**, *42 (6)*, 951–960.

[69] Y. M. Sani, W. M. A. W. Daud, A. A. Aziz, Activity of solid acid catalysts for biodiesel production: a critical review, *Appl. Catal. A* **2014**, *470*, 140–161.

[70] D. Bradshaw et al., Design, chirality, and flexibility in nanoporous molecule-based materials, *Acc. Chem. Res.* **2005**, *38 (4)*, 273–282.

[71] S. Z. Abidin, K. F. Haigh, B. Saha, Esterification of free fatty acids in used cooking oil using ion-exchange resins as catalysts: An efficient pretreatment method for biodiesel feedstock, *Ind. Eng. Chem. Res.* **2012**, *51 (45)*, 14653–14664.

[72] M. Hassani et al., Preparation, characterization and application of zeolite-based catalyst for production of biodiesel from waste cooking oil, *J. Sci. Ind. Res* **2014**, *73*, 129–133.

[73] K. Ariga, A. Vinu, Y. Yamauchi et al., Nanoarchitectonics for mesoporous materials, *Bull. Chem. Soc. Jpn.* **2011**, *85 (1)*, 1–32.

[74] M. L. Lind et al., Influence of zeolite crystal size on zeolite-polyamide thin film nanocomposite membranes, *Langmuir* **2009**, *25 (17)*, 10139–10145.

[75] K. Roberson, *Silence Deafening – Fukushima Fallout... A Mother's Response*, VisionTalk, Playa Del Rey, CA **2012**.

[76] N. I. Sternsdorff Cisterna, Food after Fukushima: Scientific Citizenship and Risk in Japan, *Ph.D. Thesis*, Harvard Universeity, Cambridge, MA **2014**.

[77] A. S. Chouhan, A. Sarma, Modern heterogeneous catalysts for biodiesel production: A comprehensive review, *Renewable Sustainable Energy Rev.* **2011**, *15 (9)*, 4378–4399.

[78] J. Marchetti, A. Errazu, Comparison of different heterogeneous catalysts and different alcohols for the esterification reaction of oleic acid, *Fuel* **2008**, *87 (15–16)*, 3477–3480.

[79] K. H. Chung, D. R. Chang, B. G. Park, Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts, *Bioresour. Technol.* **2008**, *99 (16)*, 7438–7443.

[80] A. Ates, Role of modification of natural zeolite in removal of manganese from aqueous solutions, *Powder Technol.* **2014**, *264*, 86–95.

[81] Y. Wu et al., Enhanced catalytic isomerization of α-pinene over mesoporous zeolite beta of low Si/Al ratio by NaOH treatment, *Microporous and Mesoporous Mater.* **2012**, *162*, 168–174.

[82] Y. Y. Wang, D. J. Lee, B. H. Chen, Low-Al zeolite beta as a heterogeneous catalyst in biodiesel production from microwave-assisted transesterification of triglycerides, *Energy Procedia* **2014**, *61*, 918–921.

[83] S. Gangil et al., Synthesis of Biodiesel from Karanja Oil Using Modified Mordenite as a Heterogeneous Catalyst, in *Biofuels and Bioenergy (BICE2016)*, Springer, Berlin **2017**, 15–24.

[84] M. Balat, H. Balat, Progress in biodiesel processing, *Appl. Energy* **2010**, *87 (6)*, 1815–1835.

[85] M. K. Lam, K. T. Lee, A. R. Mohamed, Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review, *Biotechnol. Adv.* **2010**, *28 (4)*, 500–518.

[86] K. Narasimharao, A. Lee, K. Wilson, Catalysts in production of biodiesel: a review, *J. Biobased Mater. Bioenergy* **2007**, *1 (1)*, 19–30.

[87] I. Atadashi et al., The effects of catalysts in biodiesel production: A review, *J. Ind. Eng. Chem.* **2013**, *19 (1)*, 14–26.

[88] D. Y. Leung, X. Wu, M. Leung, A review on biodiesel production using catalyzed transesterification, *Appl. Energy* **2010**, *87 (4)*, 1083–1095.

[89] A. Sagiroglu et al., Comparison of biodiesel productivities of different vegetable oils by acidic catalysis, *Chem. Ind. Chem. Eng. Q.* **2011**, *17 (1)*, 53–58.

© 2021 Wiley-VCH GmbH

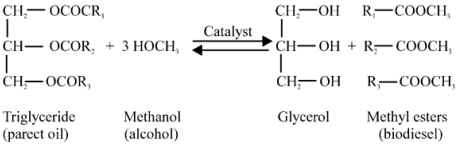
The demand for cleaner fuels has been on the rise lately. This has led to the introduction of biofuels such as biodiesel and bioethanol. The potential for renewable energy sources is widely broadened because it can exponentially surpass the energy demand of the world. The major factor that defines cost of biodiesel production resulting from vegetable oil is the cost of feedstock.

Heterogeneous Catalysis of Second Generation Oil for Biodiesel Production: A Review

F. A. Aderibigbe, S. Shiru*, H. B. Saka, M. K. Amosa, S. I. Mustapha, M. I Alhassan, A. L. Adejumo, M. Abdulraheem, R. U. Owolabi

ChemBioEng Rev. **2021**, *8 (2)*, **XXX** ··· **XXX**

DOI: 10.1002/cben.202000035



© 2021 Wiley-VCH GmbH