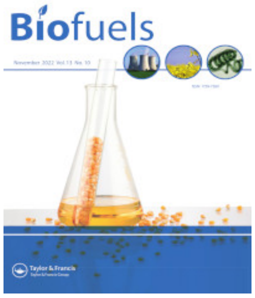


Biofuels

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/tbfu20

A retrospect on recent research works in the preparation of zeolites catalyst from kaolin for biodiesel production

Jane Mngohol Gadin, Eyitayo Amos Afolabi, Abdulsalami Sanni Kovo, Ambali Saka Abdulkareem & Moritiwon Oloruntoba James

To cite this article: Jane Mngohol Gadin, Eyitayo Amos Afolabi, Abdulsalami Sanni Kovo, Ambali Saka Abdulkareem & Moritiwon Oloruntoba James (2022): A retrospect on recent research works in the preparation of zeolites catalyst from kaolin for biodiesel production, Biofuels, DOI: 10.1080/17597269.2022.2132723

To link to this article: https://doi.org/10.1080/17597269.2022.2132723

BIOFUELS
https://doi.org/10.1080/17597269.2022.2132723

Taylor & Francis
Taylor & Francis Group

REVIEW

A retrospect on recent research works in the preparation of zeolites catalyst from kaolin for biodiesel production

Jane Mngohol Gadin[a], Eyitayo Amos Afolabi[a], Abdulsalami Sanni Kovo[a,b], Ambali Saka Abdulkareem[a,b] and Moritiwon Oloruntoba James

[a]Department of Chemical Engineering, Federal University of Technology, Minna, Niger State, Nigeria; [b]African Centre of Excellence for Mycotoxin and food safety, Federal University of Technology, Minna, Nigeria

ABSTRACT

Biodiesel production has been commercialized nevertheless, persistent efforts for better product characteristics and quantity are common place. Advancement of catalysts for improved biodiesel yield and quality has also been attempted through scientific experimentations. The heterogenous, alkaline nature and the ability to leverage active sites, pores and selectivity for biodiesel betterment have spurred the researching of zeolites. They are also flexible to adjustments, which makes it easier to remediate shortcomings like mass transfer limitations and to form numerous composites, even at nanoscale. Universal details on zeolite and its niche among catalysts in relation to feedstock processing are presented in this review. This article also discussed how the abundance and suitability of kaolin, a start material, contributed to creative researching of zeolite and its composites. Also, process routes and methods for biodiesel conversion were explained too. Of these methods, transesterification is widely deployed. Merits and demerits of alkaline, acidic and enzymatic catalysis for transesterification were featured and the concept of supported catalyst was briefly explained. This article has made efforts to review recent developments in zeolite synthesis from kaolin, specifically the hierarchical type. This ready appraisal would serve as a robust tool for choosing a desirable catalyst for biodiesel production on a commercial scale.

ARTICLE HISTORY
Received 25 July 2022
Accepted 1 October 2022

KEYWORDS
Catalyst; zeolite; biodiesel; kaolin; transesterification

Introduction

Energy consumption is on the steady increase worldwide occasioned by speedy advancement in global peopling as well as urbanization to outpace supply [1]. By the end of 2021, world oil production is expected to rise by 3.8 million barrel/day starting from April [2]. One of the severities associated with fossil fuel usage that has led to the search for alternatives was stated by Olivier et al. [3] who reviewed emissions of all greenhouse gases globally with premium placed on CO_2. In their reports citing the year 2018, increased emissions of these gases (disregarding emissions from land-use change) recommenced at the rate of 2.0% (±1%) and reached an equivalent 51.8 gigatons of CO_2 ($GtCO_2$ eq) in six years counting from 2012. However, a comparatively reduced annual change of 1.3% on the average instead of a 2.5% predicted surge was attributed to the usage of biofuels beyond that timeframe. Therefore, adopting bio-derived fuel is crucial to cutting down of the carbon footprint [4] as it will help the earth replenish itself through unburdened natural cycles.

Some of the alternatives to fossil fuels widely researched are biomass, solar, offshore wind and hydropower. Recently, biomass became the center of attraction as a suitable means to meet future demand for energy [5]. Biomass originated directly and indirectly from photosynthetic activities [6]. Hence, the photosynthetic turnover estimated to be 720 billion tons per year, indicates the abundance of cellulose compared to all other organic raw materials on a global scale [7].

More so, vegetable oil is an edible type of biomass. Although, non-edible oils, animal fats and microalgae oil can also be used for biodiesel production [8], repeated frying in cooking operations rendered used edible vegetable oil unsuitable for further consumption. This conclusion was backed up with evidence of increased free fatty acid (FFA) constituents of used oil after the process of frying [9].

Biomass can be transformed into biofuel through biochemical and the more significant thermochemical conversion routes. Transesterification is the favored conversion process for biodiesel generation. It involves an ester compound exchange by an alcohol in the alkyl group of the glyceride present [10]. Thus, the reacting of triglycerides molecules with alcohol to produce methyl ester and a less desired glycerol is resultant. Also, methanol is the preferred diluent compared to other alcohol types due to its low price and suitability to most vegetable oil variants [11]. Generally, transesterification can be promoted by acidic, alkaline and enzymatic catalysts in a homogenous or heterogenous typed reaction [12]. Nevertheless, zeolites are preferred for catalyzed transesterification reactions because of their crystalline and molecular sieve attributes. Zeolites are widely adopted industrially because they are inexpensive and environmentally benign. Also, they offer generously larger surface area and are highly porous [13]. Notwithstanding, the major limitation of zeolites are their micro-pore sizes ranging between ∼0.5 and 1.5 nm which

CONTACT Abdulsalami Sanni Kovo ✉ kovo@futminna.edu.ng Department of Chemical Engineering, Federal University of Technology, P.M.B 65, Main Campus, GidanKwano, Minna, Niger State, Nigeria.

Table 1. Availability and biodiesel performance of some virgin feedstocks.

Feedstock	Oil content (wt %)	Crop yield (kg/ha/year)	Conversion type/methanol: oil	Temperature (°C)	Time (min)	Catalyst	Biodiesel yield (%)	References
Tobacco seed	35–49	1170	Mild pyrolysis	350	NA	NA	67	[21,22]
Mahua seed	35–50	20–200	Transesterification 5:1	65	60	KOH	91	[23,24]
Tung seed	30–40	450–600	Transesterification 5:1	55	60	KOH	93	[25,26]
Yellow oleander	60–65	52,000	Transesterification 4.5:1	60	30	KOH	93	[27]
Candlenut	60–65	16,000	Transesterification 5:1	40	45	–	99.3	[28]
Cotton seed	17–23	649	Transesterification 6:1	55	60	KOH	96	[29,30]

prevents large molecules from reacting effectively in their pore cavities [14]. Furthermore, Kaolin can be economically viable start materials for synthesizing micro-spherical Y and X zeolite types and other zeolitic molecular sieves. An example of such is Maciver et al. [15] who produced zeolite X from kaolin clay sourced from Kono-Boue and Chokocho, Rivers State, Nigeria.

To give a good description of efforts to get efficient zeolites from kaolin for biodiesel production, recent literatures were critically evaluated to identify state-of-the-art approaches and to spot varieties of feedstocks and promoting agents deployed to maximize biodiesel synthesis. This is aimed at opening up new frontiers in biocatalyst synthesis for biodiesel production, which would in turn boost the current bioenergy mix. Also, waste and inedible oil conversion to biodiesel over catalyst as discussed would add economic value and solve their disposal problems concurrently. In like manner, innovative methods discussed and use cases outlined (especially for zeolite and its composites) would enlighten and serve as a guide for research and industrial manufacture of products. This article promotes catalysts (specifically zeolite) for lawful and environmentally benign synthesis of biodiesel.

Biodiesel

Biodiesel is considered eco-friendly and is derived from oil-based renewable sources [16]. Its chemical contents are high fatty acids of alkyl esters such as; fatty acid methyl and ethyl esters. Although, majority of modern diesel engines are fashioned to run on fossil-derived oil, the physicochemical attributes of biodiesel can attain that standard too [17]. The amount of sulphur in the fossil variant is required to be beneath 15 ppm onwards from the year 2017 [18]. However, traces of sulphur are found in biodiesel made from waste cooking oil [19]. Hence, analysis to ascertain its sulphur regulatory compliance should be done. Product quality is dependent on the raw material to be converted and the extent of refinement after conversion [20]. Table 1 shows the oil content and the biodiesel yield from some selected virgin feedstocks. Also, acidity can occur during the production process and by the degree to which ageing occurs during storage. A gradual increase of acidity implies further degradation of biodiesel [31,32].

Feedstock for biodiesel production

A number of bio-lipids can be precursor for biodiesel synthesis. Sourcing for lipid-containing stocks is highly reliant on local soil conditions, climate and geographical availability. As a result, there are no universal pursuits in regularization of feed-oil properties. Common materials from which oils for conversion are derived are soybean, groundnut, sunflower, cottonseed, coconut, rapeseed, canola, palm and palm-kernel [33]. Also, animal sources like beef, sheep tallow and poultry oil can be starting materials as well [34]. Other sources include jatropha, Camelina sativa, almond, neem seed, fish oil and barley [35]. Sesame, oat, sorghum, karanja, laurel, okra seed, rice bran, poppy seed and wheat are also sources of lipids.

Biodiesel is expensive compared to fossil-based diesel, and this can be blamed chiefly on the expensive vegetable oil [36,37]. This has triggered much research interest for cost-effective measures for biodiesel production, opening new frontiers. A lion share (more than 80%) of biodiesel production expenses goes into feed-oil purchase which is significant to the economics of scale [38]. Biodiesel may become less competitive due to high prices, threat to food security, agricultural value chain disruption and land use charge.

To overcome these stumbling blocks, a new iteration of feedstocks with reasonable cost and quality is put forward forthwith to keep biodiesel competitive. These alternatives may include waste restaurant greases, cooking oils, soap stocks, animal fats, acid oils, tall oil, oils from inedible seeds, trees and aquatic plants like algae. Also, genetic alteration can be a tool to promote desired qualities in crops grown for biodiesel production [39]. Traits such as high recoverable oil, shorter growth cycle and compatibility with hydroponic farming are worthy research interests.

Virgin oils as feedstock

Maiden oils are usually the first point of call for biodiesel synthesis. By geography, pure oil used in the European Union is mostly from the abundant rapeseed while Argentina and the USA get oil from their massive yield of soybean. However, palm and sunflower are commonplace to Asian and Central American countries. Less popular options are oils from safflower, peanuts, linseed and animal fats. Virgin edible oils are peculiar raw material for producing biodiesel because they contain low FFA [40]. Thus, they do not need pretreatment, do not deactivate catalyst nor do they yield secondary products like soap. However, majority of oil crops are already in high demand for food. Hence, there is a great concern already because of the food versus fuel dispute to which the public is extremely sensitive [41]. Typical fatty acid constituents of selected edible oils are shown in Table 2 [42].

Table 2. Percentage fatty acid constituents of different but common oil sources [41].

Fatty acid composition (%)	Cottonseed oil	Lard oil	Soybean oil	Tallow oil	Coconut oil	Palm oil
Lauric (C12:0)	0.1	0.1	0.1	0.1	46.5	0.1
Myristic (C14:0)	0.2	1.4	0.1	0.8	19.2	1.0
Palmitic (C16:0)	20.7	23.6	0.2	23.3	9.8	42.8
Stearic (C18:1)	2.6	14.2	3.7	19.4	3.0	4.5
Oleic (C18:2)	19.2	44.2	22.8	42.4	6.9	40.5
Linoleic (C18:2)	55.2	10.7	53.7	10.7	2.2	10.1
Linolenic (C18:3)	0.6	0.4	8.6	0.4	0.0	0.1

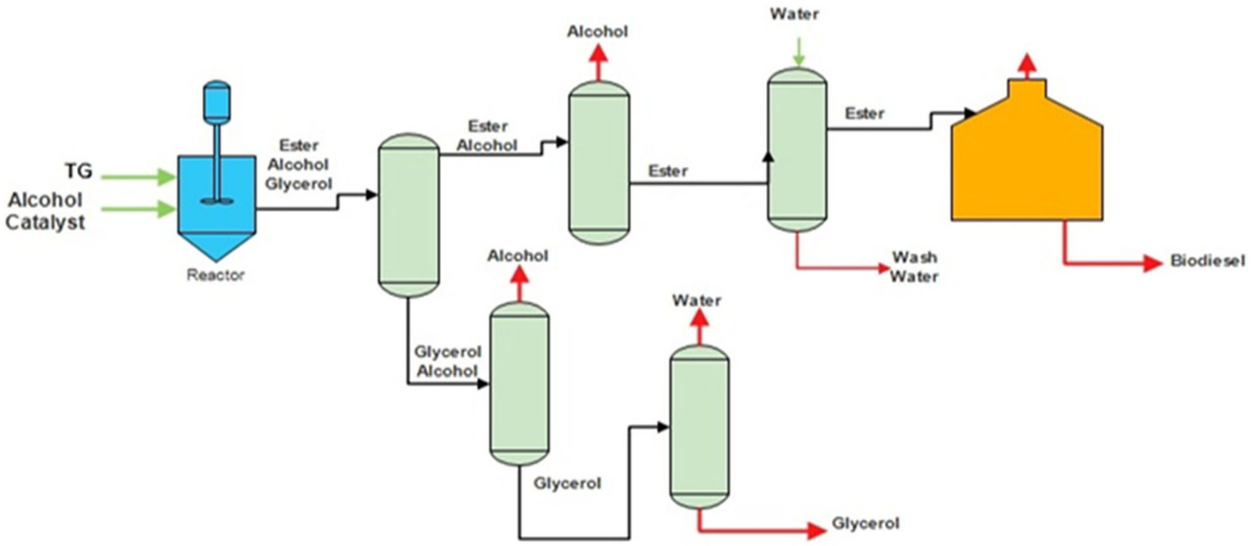


Figure 1. Batch reaction process for biodiesel production.

In addition to the issue of land availability for farming, the fuel versus food contest also gets a number of governments infuriated. The populace harsh reception or outright rejection of such an arrangement is a major setback to the use of virgin oil as a raw material. Therefore, instead of fielding pure vegetable oil, waste cooking oil can be adopted in its stead as feed oil for commercial production of biodiesel.

Waste cooking oil as raw material

The expression 'waste cooking oil' (WCO) was coined to refer to edible oil utilized for food making once and no longer viable for such purpose anymore. WCO can be difficult to manage in waste streams due to waxing at ambient temperatures and other complications. Considering the food safety and standards authority of India-FSSAI's directive for edible purposes, used cooking oil is dimmed unfit for reuse if its polar content exceeds 25% [43]. In that light, competition with food is eliminated making WCO adoption for producing biodiesel a welcome idea.

Awogbemi et al. [44] who compared properties of maiden and waste cooking oil gave a record of WCO generated in selected regions. Canada was reported to churn out about 120,000–135,000 tonnes/year, while the United States generate 0.6 million tons of yellow grease. For South Africa, 200,000 tonnes of WCO were estimated annually in the absence of actual data. On the other hand, Mannu et al. [45] who studied innovative ways in which WCO can be applied as raw material estimated that less than 60% of WCO generated worldwide is disposed inappropriately. Unfortunately, published data covering Sub-Sahara Africa is not available. All the same, Nigeria's current population size of over 170 million and the majority of start-ups outside the tech space are invested in fast food conglomerates, motels and restaurants. Therefore, feasible volumes of WCO accumulated by these establishments from their daily manufacturing can be expected to price cheaply.

Process routes for biodiesel production

There are majorly two ways of processing of feedstock into final product. They include batch and continuous processing methods.

Batch process system

The simplest equipment for alcohol esters synthesis is a batch, stirred tank reactor. Displayed by Figure 1 is a process flow diagram depicting a typical batch system. Alcohol is usually mixed with triglyceride in mole ratios ranging between 4:1 and 20:1. However, ratio 6:1 is commonly used [18, 46]. The reactor may be outrightly covered or fitted with a reflux type condenser. Usually, it is operated at about 65 °C although, the temperatures range of 25–85 °C have been reported too [47]. Frequently used as accelerators are sodium hydroxide and potassium hydroxide at loadings ranging from 0.3 to 1.5% [48]. At the onset of reaction, thorough mixing is needed to homogenize the alcohol, oil and catalyst. However, less mixing is required towards the reaction ending to accelerate the extent of reaction and facilitate inhibitory product-glycerol separation from the ester–oil in another phase. A conversion rate within the 85–94% bracket can be obtained [47]. Another approach is the two-step reaction involving glycerol sequestration after each step, thereby increasing the extent of total reaction to 95% and above [49,50]. Higher temperatures and alcohol-oil ratios can as well, raise final

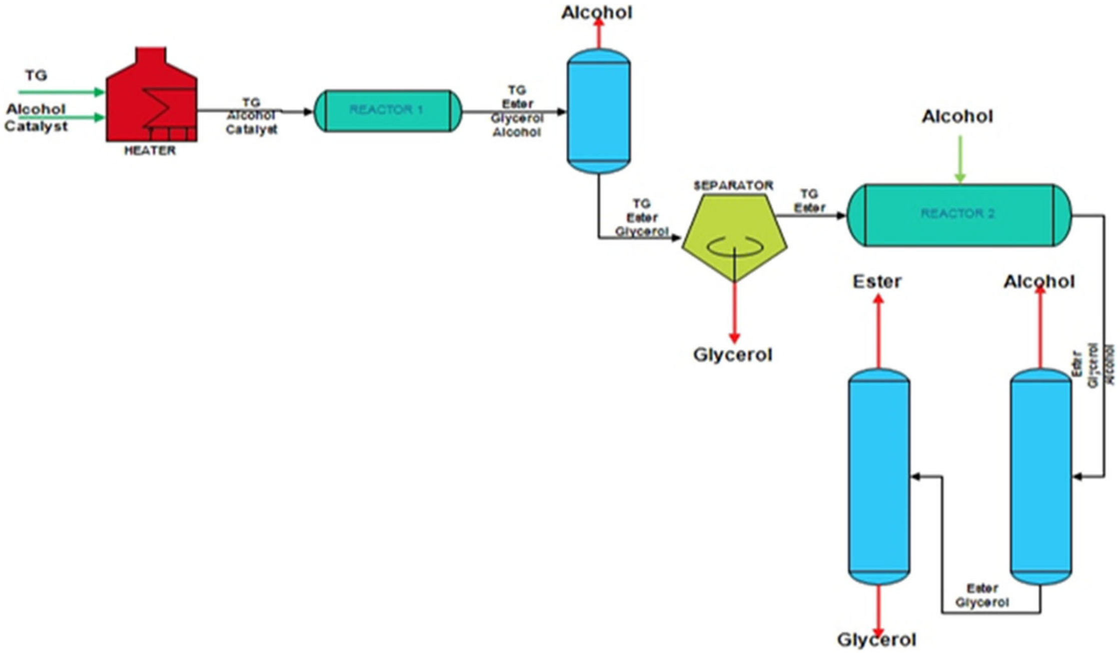


Figure 2. Plug flow reaction system for biodiesel production.

percentages to reasonable values. Reaction times are expected to bottom at 20 min and peak at times beyond an hour.

Continuous production systems

A popular variant of the continuous process features a serial set up of continuous stirred tank reactors (CSTRs). These CSTRs can have different volumes to allow for a longer residence time, thereby completing reactions to reasonable extents. During reaction, decanting of incipient product-glycerol is carried out in the first CSTR. Whereas in the second CSTR, higher probability of reaction ramp for a 98% and above conversion exists [51]. A critical factor in designing CSTRs for this purpose is adequate mixing to guarantee uniformity of content throughout the reactor volume. This would promote fair distribution of glycerol product in the ester phase.

For this process route, a lot of activities demand extreme mixing. These may necessitate that motionless mixers or pump be deployed to trigger reaction. But in some cases, the reacting mixture continuously moves in a plug manner, with marginal mixing axially. Referred to as the plug-flow reacting setup (PFR), it simulates a number of small CSTRs as if they were connected together in series [52]. It is characterized by relatively brief residence times, taking about 6–10 min to achieve a nearly completed reaction.

In contrast, oscillating flow reactor (OFR) permits longer residence times since mixing is unconnected to the net flow. However, it allows for reduced reactor's length-to-diameter ratio. Polymer-supported catalysts and suspended solid catalysts are compatible with OFRs for transesterification reactions [53]. This is an advantage to scale-up of this method for commercialization since it reduces the overall capital and pumping cost. A suitable arrangement of PFRs is portrayed by Figure 2 for easier removal of glycerol by decanting. Mostly, this method of production requires elevated temperatures and pressures to enhance the rate of reaction.

Standards and techniques for biodiesel characterization

Due to regulations biding in several continents of the world, biodiesel is required to meet with certain standards before usage. For instance, fossil diesel was mandated to contain below 15 ppm Sulphur starting 2017 [17]. Biodiesel-the alternative might contain traces of sulphur [18] and would have to be tested to ascertain its regulatory compliance. Such testing can be done with the wavelength dispersive X-ray fluorescence technique based on the ASTM D 2622 standard. Further, the ASTM D 6751 slates 0.5 mg KOH/g acid value for biodiesel but allows for a maximum of 0.8. This value can be determined by titrimetric means availed by the ASTM D 664 method. Notably, biodiesel behaves differently at ambient temperatures below 50 °C. Hence, its cold-filter plugging point (CFPP) is to be determined to verify operability limits in cold regions. Standardized filters are employed within the timing of 60 s to record the lowest temperature of flowthrough as CFPP in tandem with the ASTM D 6371 procedure. Similar but different to this is the cloud point which is frequently used as a measure of much a lower-than-ambient temperature usability of biodiesel. It is required that cloud point of biodiesel be within the range −3 to 15 according to ASTM D 6571. As for the cetane number value, the EN and ASTM standards are 51 and 47 respectively [54]. This is to make sure that commercial biodiesel retains good ignition quality for combustion. Cetane number can be determined using the widely acclaimed ISO 5165:2017 which require a special indirect-injected diesel engine equipment. In addition, biodiesel should have a pour point value between −5 and 10 as stated by ASTM 6571 [55]. Therefore, techniques that measure its pumpability at lower temperatures are commonly used to ascertain such.

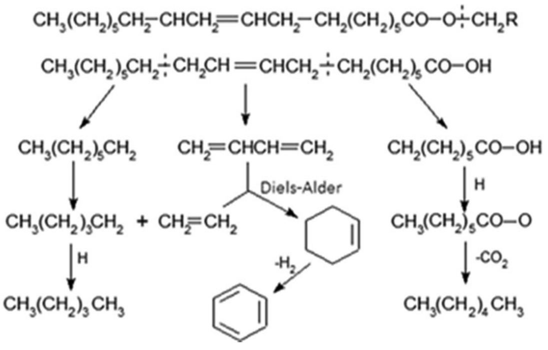
Methods for biodiesel production

There are several methods of getting biodiesel from feedstock. These methods differ from each other in efficiency, public reception and manufacturer preference. They include pyrolysis, supercritical process, mechanical stirring, microwave method, esterification and transesterification.

Pyrolysis (thermal cracking)

The transformation of organic substances into their energy-dense versions by means of heat with or without the help of a catalyst excluding air is termed pyrolysis [56]. Conversion of fats by pyrolysis has been studied for several years, particularly in regions of the earth which lacked potentials for petroleum discovery. Earliest attempts to convert vegetable oil using this method were triggered by the rush for synthetic petroleum [57]. This dated as far back as the First World War, when researchers started to try out pyrolysis of vegetable oils to obtain products suitable for fuel purposes [58].

The numerous reaction paths and products that can be arrived at the finish of a pyrolytic reaction make its kinetics difficult. Also, equipment for conversion is expensive for moderate throughputs. All the same, processing of materials including animal fats, natural fatty acids and artificial prototypes has been studied under pyrolytic conditions. Such was the case with Omidghane et al. [59] studies which centered on pyrolysis of fatty acid from brown grease. Their report found out that although the pyrolysate is similar to petroleum-derived liquid, it was rich in sulphur due to the usage of bio-solids as substitute for water. Cracking of triglycerides thermally produces a class of compounds that includes alkanes, alkenes, alkadienes, aromatics and carboxylic acids. Constituents of the thermally decomposed outcome significantly vary with feedstock selection. The pyrolysate may contain traces of water and sediment too. Although, product may have a low copper corrosion value, amount of ash, carbon residue and pour point value are usually absurd [20]. Carboxylic acids content of product implies that enough oxygen is available to corrode metal. Hence, catalytic cracking or hydrocracking of pyrolysate is required to increase the saturated alkanes in the product fuel. Often than not, catalytic hydrocracking is more suitable for fuel upgrade because it favors higher alkane and aromatics fractions [60]. A reaction showing decomposition of triglycerides thermally is presented in Equation 1. It is of importance to know that the removal of oxygen during heat conversion eliminates the environmental benefits of harnessing oxygenated fuels. Also, this approach produces fuel of lower grade and sometimes a lot of gasoline compared to biodiesel in the product stream.



(1)

Supercritical conversion method

The quest for reduced catalyst usage for biodiesel production has prompted the development of water-added supercritical solutions. The ease for product separation is a perk to production with this method. This is because glycerol would dissolve in water easily compared to methanol [10]. Supercritical fluid (SCF) requires the provision of a single-phase environment which is unique and advantageous. Such advantages include quick mixing of species, increased heat and/or mass exchange as well as accelerated reactions. SCFs are environmentally friendly, highly scalable and easy to adopt for commercialization. SCFs are recommended for separating, extracting and oxidizing of organic materials of value [61]. Majority of supercritical reactions are carried out at temperatures ranging from 340 to 400 °C and pressures of 20–70 MPa [62]. Regardless of moisture content, supercritical method involves the use of methanol but excludes catalysis. Yet, the FFA constituents of feedstock are totally esterified by this method [63].

Microwave method

Microwave irradiation is a trusted technique for improved extraction, accelerated esterification, and hydrolytic types of chemical reactions [64]. This can be attributed to the ease, rapidity, evolution of equipment technology, innovations to cheapen electrical energy and targeting of optimal food compatibility. These advantages are the drivers for progressive modelling of microwave patterns for heating. These models are intended to support re-invention of new and improved commercial foods.

In microwave assisted transesterification reactions, energy is conveyed in heat form to the raw material chiefly by radiating the exposed surfaces. Conduction and convection facilitate heating on the sidelines too. Appreciable transesterification can take place quickly (say 30 s) with alcohol to oil molar ratio of about 12:1, converting waste cooking oil to ethyl ester continuously at a 97% yield [65]. Albeit, the kinetics of microwave impact in a chemical reaction especially the non-thermal effects are under contention [64]. Nevertheless, the outcomes of transesterification show a clear and considerable enhancement of reaction rates. This, in turn, saves a considerable amount of time and cost [66].

Ultrasonic reaction method

Special chemical and physical effects can be induced by an ultrasonic field when cavitation bubbles collapse. This has been found useful in sonodynamic therapy, sonofusion, conversion of biomass, manufacture of nanostructured materials and sonochemical degradation of toxic chemicals and pollutants [67]. Ultrasonic irradiation at reduced frequencies can facilitate the formation of emulsions from immiscible liquids creating small droplets [68]. A larger interfacial area can also be generated if the ultra-sonication apparatus is positioned closer to the immiscible fluid interface of a two-phase reaction system.

Ramírez-Sanabria et al. [69] used ultrasonic-based technique for the optimization of palm oil transesterification. With radiation frequency between 20 and 47 KHz and

Table 3. Catalysts under various transesterification conditions for biodiesel production.

Feedstock	Catalyst/active phase	Catalyst type/in phase with reactant	Catalyst loading (wt %)	Alcohol to oil ratio (molar)	Temperature (°C)	Reaction Time (h)	Biodiesel yield (wt %)	Ref.
Waste cooking oil	S-TiO$_2$/SBA-15	Acidic/heterogenous	1	15:1 (methanol: oil)	200	30 min	94.96	[82]
Waste cooking oil	Mashed eggshells/ Eggshell-calcium diglyceroxide	Alkaline/heterogenous	1.5–3	10:1–12:1 (methanol: oil)	60–65	50–90 min	93.10–96.07	[83]
Waste cooking oil	(BaAl$_2$O$_4$)	Alkaline/heterogenous	12	21:1 (methanol: oil)	65	2.5	93.28	[84]
Soybean oil	rGO-SO3H	Acidic/heterogenous	3	20:1 (methanol: oil)	80	2.0	99	[85]
Canola oil	(f-MgO)	Alkaline/Heterogenous	NA	16:1 (methanol: oil)	190	2.5	93.4	[86]
Jatropha oil	*Musa paradisiaca* trunk/ Carbonates and oxides of alkali and alkaline earth metals	Alkaline/Heterogenous	5	9:1 (Methanol: oil)	65	9 min	97.65	[87]
Spirulina Microalgae oil	MgO/ ZSM-5	Alkaline/Heterogenous	3	15:1 (Methanol: oil)	75	1.0	92.1	[88]
Waste cooking oil	Magnetized sulfonated Palm kernel shell	Acidic/Heterogenous	3.66	13:1 (methanol: oil)	65	1 h 25 min	90.2	[89]
Leather tanning waste	Crab shell/CaO	Alkaline/heterogenous	3.87	12:1 (Ethanol: oil)	60	3h 35 min	98.7	[90]
Tung seed oil	(KOH)	Alkaline/homogenous	NA	5:1 (methanol: oil)	55	1.0	93.0	[24]
Yellow oleander	(KOH)	Alkaline/homogenous	NA	4.5:1 (methanol: oil)	60	30 min	93.0	[27]
Waste cooking oil	Polyhydroxybutyrate /*Candida rugosa and Rhizomucormeihei*	Enzymatic	1 (5 % water)	6:1 (methanol: oil)	45	24.0	96.5	[91]
Waste cooking oil	CO$_2$$^+$ chelated magnetic particle/*Psedomonasflourescens* lipase	Enzymatic	7.5 (5 % water)	4:1 (methanol: oil)	50	12.0	95	[90]

Table 4. Summary appraisal of transesterification types.

S/N	Transesterification type	Merits	Demerits
1	Uncatalyzed reactions	1. Environmentally benign due to smaller amount of chemicals involved. 2. Glycerin of high quality is produced. 3. Presence of water sometimes accelerates reaction. 4. Reactants are not required at high purity due to absence of a catalyst that can be affected.	1. The process is energy intensive. 2. High alcohol to oil ratio is prerequisite. 3. Reactions require very high temperatures and pressures to initiate. 4. Desired product conversion rate is poor.
2	Liquid catalyzed reactions	1. High efficiency and conversion rate. 2. Cost of production can be affordable if chemical is cheap. 3. Quick scale-up as well as large-scale operation is possible. 4. Produced methanol can be re-channelled back into the process. 5. Reactant and catalyst are both in a single phase hence, diffusion is limitless.	1. It is difficult to separate product from catalyst, extra wash step needed. 2. Methanol recycle is complex. 3. Clean water consumption/ wastewater disposal is high 4. Reaction proceeds at relatively high temperatures and consume enormous energy. 5. The risk of environmental pollution is high due to high wastewater generation and untreated disposal.
3	Solid catalyzed reactions	1. Catalysts can be easily separated from products and recovered in a simple manner. 2. Catalysts are reusable times over thereby, eliminating the need for frequent repurchases. 3. Flexible to accommodate bio-based and environmentally friendly solids conversion for use as catalyst. 4. Proceeds at normal temperatures and consumes less energy. 5. Sustainable and economical to scale-up compared to liquid catalyzed reactions.	1. Diffusion limitation is pronounced because reactants and catalysts are in different phases. 2. Catalyst may be too expensive to use without the help of a support. 3. Catalyst may require lots of costly processing and expertise to be on par with liquid catalyst on performance basis. 4. Catalysts may deactivate quickly in the presence of impurity.
4	Enzyme catalyzed reactions	1. Moderate reaction condition. 2. The small amount of methanol required in the reaction. 3. Have no pollution to natural environment.	1. Limitation of enzyme in the conversion of short chain of fatty acids. 2. Chemicals exist in the process of production are poisonous to enzyme.
5	Supercritical fluid techniques	1. Easy to be controlled. 2. It is safe and fast. 3. Friendly to environment.	1. High temperature and high pressure in the reaction. 2. High cost of production. 3. Energy wastage is typical to the process.

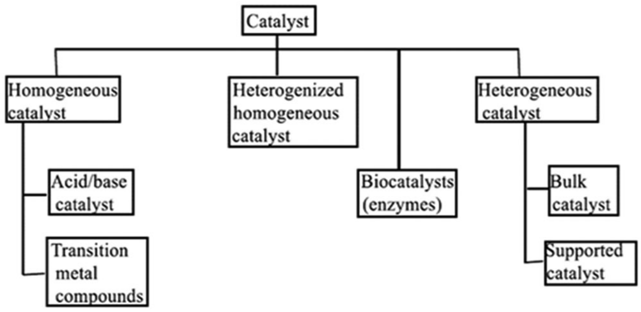


Figure 3. General classification of catalysts.

reduced reaction times, increased production of alkyl ester was obtained in the absence of a catalyst. This can be credited to the variation in intensity of micro-turbulence created by cavitation bubbles dispersed in the reacting mixture. Further, the device for identifying physical and/or chemical effects of ultrasound under several conditions can be attached to a bubble dynamics mode [70]. This method is effective for fabrication, analysis and process intensification of biodiesel synthesis. The development of cavitation reactors would proffer a realistic competition to conventional transesterification [71].

Mechanical stirring method

Most operational biodiesel industrial plants apply the mechanical stirring method. Feed is converted batchwise or continuously using the homogeneous catalyst type, preferably sodium methylate or sodium hydroxide. After reaction, catalyst recovery in form of sodium soap in the glycerol phase, sodium glycerate and sodium methylate is possible.

For this method, a temperature range of 60–70 °C is commonly used and reaction concludes in about 120 min [61]. Mixing of sodium hydroxide catalyst and methanol is carried out in a separate unit to form metal alkoxide prior to reacting. Afterwards, the mixture is transferred into a reactor containing the feed-oil and then stirred. A batch reactor equipped with stirring mechanisms, a semi-continuous or CSTR can be used. To ensure continuous liquefaction of alcohol, a condenser can be attached to the reactor. Also, the alcohol boiling point is kept within the temperature range of the reaction. Finally, constant stirring to facilitate reaction at the interfacial film is carried out because of immiscibility of oil in alcohol [72].

Esterification reaction method

Within the context of biodiesel synthesis, the direct chemical reaction of fatty acid (and to a minimal extent, free fatty acids) with alcohol to produce alkyl ester and water is referred to as esterification. The reaction that takes place between the alcohol and the fatty acid molecule directly makes this phenomenon dissimilar to transesterification. Therefore, the intermediate steps involving the severance of the glycerin backbone from fatty acid chains are eliminated. As a consequence, esterification reactions for biodiesel do yield glycerin as a by-product.

Figure 4. Dual template mechanism shape selective zeolites synthesis [137].

If methanol is adopted as the alcohol type for all industrial esterification, a fundamental picture of such reaction is painted by Equation 2. It is noteworthy that esterification performs optimally with pure oils and thoroughly refined animal fats. This is so because of the near-absence of impurities like sulfated proteins, which have the ability to interfere with biodiesel synthesis and quality. Roughly 84% of virgin oil fed into biodiesel esterification is gotten exclusively from rapeseed—an oil plant largely grown in the EU [73].

Lipids always contain free fatty acid regardless of purity or reusage. However, oils with values of FFA above 4% would produce unusual amount of soap during esterification than expected in a regular base-catalyzed reaction. In almost all cases, such high concentration would hinder the realization of reaction.

$$\begin{array}{l} R_1\text{—COOH} + CH_3OH \rightleftharpoons R_1\text{—COO—}CH_3 + H_2O \\ \text{Free fatty acid (FFA) Methanol Methyl ester Water} \end{array} \tag{2}$$

Transesterification reaction method

The largest portions of biodiesel synthesized all time were gotten through transesterification. This involves the chemical reaction of low carbon chain alcohol with triglyceride to create fatty acid alkyl ester. Notably, transesterification would proceed quicker if short-chain alcohols like methanol or ethanol is used. This reaction is altogether sluggish under usual circumstances if a promoter catalyst is not introduced. Catalyzing the reaction has its complementary complications nevertheless, the relative insolubility of oil in alcohol is a valid reason for introducing a catalyst. This would initiate a phase-exchange and an ion exchange drive, thereby reducing the time of reaction in multipliers [36]. Typically, accelerating this type of reaction is carried out with a base catalyst like potassium or sodium hydroxide at standard conditions.

Transesterification is made up of a series of successive but reversible reactions [46]. Conversion of triglycerides is stepwise, progressing to diglyceride, monoglyceride and finally, to glycerol. In addition, a small amount of water formed during conversion may encourage soap formation as a transesterification product. Parameters affecting transesterification reaction include mole ratio of methanol to oil [19, 39], moisture content [46], free fatty acid constituents [74], reaction time [75,76] and temperature [77]. Monitoring and controlling these parameters are critical to the quality and yield of biodiesel from transesterification reactions. A summary of insights into transesterification types is presented in Table 4.

Catalyst for transesterification reactions

Catalysis is an indispensable technology employed to accelerate and redirect chemical modifications. It is about triggering a boost in the rate of chemical change thanks to the involvement of a material referred to as a catalyst [78]. Harnessing of catalysts at low volumes for top-notch biodiesel quality and yield is puzzling to biodiesel researchers [79]. It is required that a good catalyst possess a controlled surface, protracted stability, good porosity, primed activity and chiefly, selectivity. Others are high rebuff to poisoning and deactivation, enough tolerance for temperature fluctuations, extreme forbearance to heating and finally, a display of mechanical strength by resistance to crushing [80]. A comparison with transesterification types that do not incorporate catalysts is presented in Table 4.

A catalyst's activeness is proportional to its base site concentration, specific surface area and base strength [81]. Considering a reaction proceeding at a very slow rate, the volume of the vessel required for that reaction would be unreasonably large and high-priced [10]. Also, if product selectivity is weak, reacting species would not be used up efficiently, resulting into an unnecessary separation step to recover desired products. Figure 3 classified catalysts for transesterification by the state of aggregation in which they act. The merits and demerits to these catalysts determine their adoption for transesterification reactions. This is because the purity, recovery and yield of product are dependent on them. Table 3 shows selected catalysts used under varying transesterification conditions for biodiesel production.

Alkaline catalysts

Base catalysts are the most popular for accelerating biodiesel conversion processes. The major privilege associated with using them is that they induce much yield of esters quickly under clement conditions of reaction [46]. Nevertheless, base catalysts display acute sensitivity in the presence of free fatty acids. To this end, only virgin oils with minimal acid values can generate higher yields with base catalyst assistance. Therefore, vegetable oils are always de-acidified before reaction to eliminate this sensitivity. Common catalysts that are alkaline in nature include alkali metals, alkali metal carbonates, potassium hydroxide and sodium hydroxide.

Acidic catalysts

Acid catalysts require a fairly elevated temperature (~100 °C) and pressure (~5 bars) to function [92]. They are sluggish in action compared to their alkaline counterparts and are corrosive to equipment. Nevertheless, these types of catalysts can effectively esterify FFAs found in either pure or used oils. Hence, they are highly favored for processing free fatty acid–containing feedstock [93]. An example of such feedstock is waste edible oil. Some homogeneous catalysts which display acidic properties include phosphoric acid (H_3PO_4), hydrochloric acid (HCL), sulphuric acid (H_2SO_4), aryl sulphurnic acid and a combination of any of these.

Enzymes as catalysts

Microorganisms are sources from which enzymes or lipases are extracted or deliberately cultured for biocatalytic purposes. Some of the merits of adopting biocatalysts include the ability to operate at ambient conditions of pressure, temperature, pH and capacity to yield glycerol of superb qualities [12]. However, disadvantages like extended reaction times and unreasonable catalyst concentrations requirements are turn-offs [10]. Also, they are too expensive for industry-scale usage and are difficult to separate from the biodiesel and glycerol at reaction completion. Other drawbacks are escalated deactivation, little conversion efficiency, and thermal instability during usage. This can be seen in Table 3, where enzymatic transesterification of waste edible oil requires 12 and 24 h in Wang et al. [90] attempt to enhanced the attributes of enzyme immobilized onto CO^{2+}-chelated magnetic nanoparticles for biodiesel production. From the same table, Binhayeeding et al. [91] findings in waste cooking oil conversion with the aid of single and mixed immobilized lipases on polyhydroxyalkanoate reflect this also.

Supported catalysts

A supported catalyst is usually an active material fixated on a solid with surface area suitable and large enough to accommodate it. A supported catalyst can be created if a promoter, an active phase and support is available. The promoter provides stability while the active phase takes part in the chemical reaction. The support is a receptive material to holds deposits of the active phase, giving it a form. Materials used as supports can either take part or be inactive in reactions. Regardless of this, reactants should be accessible to the active phase on the support to increase the chances for satisfactory catalytic activity [94]. The ability to expose active agents to reactants is crucial to precious metal catalysts usage. This is because it validates whether the presence of the metal actually improved catalysis compared to when the bulk support systems is used undoped [95]. Materials used as supports should have a porous structure that can smoothly facilitate inward and outward diffusion of reactants and products [36]. This would ensure maximization of the catalyst's activeness to near capacity. Although, the promoter is meant to improve stabilization, the support is expected to be capable of forming a solid interaction with the dopant by itself. This would be beneficial should the active phase possess particles of unusual structure. An active phase can be too reactive in some cases therefore, a support material with the opposite of the aforementioned characteristics would be needed to limit contact time between the catalyst and the reactants [96]. Usage of substrates for support of active metal phases is cost-effective for catalyst synthesis and a good method for the extension of its operational lifespan. Surprisingly, the performance of catalyst may also be influenced by the support through synergistic electronic interactions [46]. This requires that the active agent be graciously concentrated on the external surface of the supporting substrate. Incorrect positioning and dispersion of dopants can affect the stability, activity and selectivity of the catalyst adversely. Therefore, the dispersion of active components should be guided by their interaction with the surface of the support as stated by the X-ray dispersion analysis (XRD) [97].

Bulk catalysts and dopants

A potent catalyst can have some smaller amount of another active substance introduced into it, making it the bulk material. The minority component can be an additive to or a replacement within the bulk material and is referred to as the dopant. Doping of a catalyst tends to improve its performance compared to it in its pure form, or rather, improve its preference for selected product formation. This was confirmed by Sumari et al. [98], who impregnated zeolite with silver to catalyze glycerol conversion to ethanol using ultrasonic method. Although, catalyst surface area was reported to slightly decrease from 1339 to 1279 m^2/g, acidity value heightened to 3.6253 from 0.0774 mmol/g. Also, a higher product yield of 13.6% was reported, thanks to the composite catalyst. In like manner, Fattahi et al. [99] investigated ester bond formation in zeolite-based catalysts by loading HUSY zeolite with cerium. The resultant Ce/HUSY and the original HUSY zeolites were used to trans-esterify soybean oil. Notably, the former was adjudged to be more active and productive. Therefore, composite catalysts are research-worthy especially in pursuit of new zeolite forms, novel dopants, as well as for conversion of newer generation feedstock.

Nanoparticulate dopants

Majority of nanosized dopants are transition metals with nano-silver gaining initial dominance in zeolite/nanocomposite catalyst development [100]. More so, the nanosized dopants tend to dwell as nanoparticles or nanoclusters on/in the bulk catalyst [101].

An example is the work documented by Alaya-Ibrahim et al. [102] who developed nano-silver doped zeolite from Nigerian Ahoko kaolin. Their findings confirmed increased treatment of wastewater in connection with nano-dopant in composite compared to virgin catalyst. Nonetheless, gold nanoparticle from laser ablation/crystallization inclusion on zeolite and cobalt-doped ZnO nanoparticles obtained from imidazole frameworks of zeolite are examples of novel means of sourcing nano-dopants [103,104].

Some other reports of the use of this technique are cerium loading on HUSY zeolite by Fattahi*et al.*, [99] and Cu/Cu based nanoparticles synthesis for catalytic processes by Gawande et al. [105]. From their work, copper nanoparticles were produced using laser ablation systems leveraged on the abundance of the earth metals studied to open new frontiers for catalytic applications.

Table 5. Biodiesel production with selected zeolite-based catalysts.

Feedstock	Catalyst/active phase	Conversion method/process route	catalyst Loading (wt %)	Methanol to oil ratio (molar)	Temperature (°C)	Reaction time (h)	Biodiesel yield (wt%)	Ref.
Beech Wood (Lignocel-HBS 150-500)	H-ZSM 5: Al-MCM-41 (3:1)	Pyrolysis/fixed bed reactor	50	NA	500	15 min	95.89	[149]
Waste Frying Oils	HZSM-5 zeolite nanosheets	Transesterification/ batch mixing	5–10	6:1–25:1	60–180	0–24	0–48.29	[150]
Methyl Butanoate (biodiesel surrogate)	HZSM-5 zeolite	Pyrolysis/ Plug flow reactor	200 mg packed in 0.03 mL/min of feed	NA	150	10 min	–	[151]
Waste fried oil	Na+/Zeolite–Chitosan	Electrolytic transesterification/ Batch	1 (2% water)	8:1	25	30 min	96.5	[152]
Jatropha seed oil	K/Hierarchical NaY		6–12	16:1	60	3	53.7–97.3	[89]
Commercial waste cooking oil	K/clinoptilolite Zeolite nanocomposite	Transesterification/ batch	4	16:1	70	2	93.6	[153]
Commercial waste cooking oil	Na/clinoptilolite Zeolite nanocomposite	Transesterification/ batch	4	16:1	70	2	95.2	[89]
Commercial waste cooking oil	Ca/clinoptilolite Zeolite nanocomposite	Transesterification/ batch	4	16:1	70	3	96.4	[89]
Commercial waste cooking oil	Mg/clinoptilolite Zeolite nanocomposite	Transesterification/batch	4	16:1	70	2.5	98.7	[89]

Kaolinite clay

Kaolin or China clay is the term used to describe rocks that are rich in kaolinite. It is produced by chemical weathering of potassium feldspar to be soft, earthy and white (di-octahedralphyllosilicate clay). Aluminosilicate minerals like feldspar can be weathered by reaction with water and carbon dioxide [106]. Except in few regions of the world, its deposits are pink-orange-red in color with a distinctive rust hue thanks to iron oxide. Milder concentrations of zeolite in dwarfs may change its color to white, yellow or light orange.

Availability of kaolinite clay in Nigeria

The largest chunks of Kaolinite clay precipitate available are usually found with granitic rocks and are either sedimentary or residual in nature [107]. Deposits of kaolin have been discovered in Africa and in abundance at specific places in Nigeria. Nigerian states like Anambra, Ondo, Kogi, Plateau, Enugu, Borno Kaduna, Bauchi, Katsina, Ogun, Sokoto and Oyo hold deposits in commercial quantities. Proven reserves of kaolin in Nigeria are quantified to be approximately 800 million tonnes [108]. Ahoko village in Kogi State is notably for kaolin sampling for research purposes. The preference for Ahoko kaolin was greatly influenced by the push for local resources to boycott costs associated with zeolite imports. Other influencing factors include the ease of processing into diverse forms of zeolite and the addition of value to an undervalued but abundant commodity.

Solid catalyst from kaolin

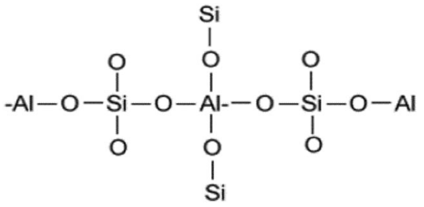
Kaolin clay is made up of about 10–95% kaolinite, which is a 1:1 layered phyllosilicate clay mineral. Kaolinite consist of two layers, one of SiO_4 tetrahedral and the other of gibbsite-like $Al(OH)_4$ octahedral amalgamated through longitudinal sideline chains to form a di-octahedral structure [109]. The chemical formula for kaolinite is $S_{i2}Al_2O_5(OH)_4$ ($Al_2O_5Si_2{\cdot}2H_2O$ or $Al_2O_{3.2}SiO_5{\cdot}2H_2O$) theoretically. Present as impurities in kaolin are oxide of metals (such as Fe_2O_3, CaO, P_2O_5, MnO, Na_2O, MgO, K_2O and TiO_2), quartz and mica [110]. Kaolin has found usefulness in several industrial processes such as adsorption, ion exchange, de-colorization, catalysis, catalyst supports and modification of catalysts [111].

Attributes of kaolin are chemical stability, extensive surface area, mechanical consistency, sufficient Lewis and Brönsted acid sites [112]. It is also environmentally benign yet, possesses cation-exchange ability (CEC). Kaolinite usage in the chemical industry is dependent on surface modification for enhancement of its reactivity and surface properties. To carry out these enhancements, mechano-chemical approaches, thermal exposures and chemical activation methods like intercalation, alkali, organic and inorganic acid treatments are used. The crystalline structure and pore size of kaolinite ready after modification for converting feed with bulky molecules [113].

Zeolites

Zeolite is the general name for a group of minerals known as tectosilicates [114]. They are framed as molecules of tetrahedral AlO_4^{-5} and SiO_4^{-4} held together by atoms of oxygen as shown by Equation 3. Zeolite is characterized by a high surface area and minimal pores. More so, they can be customized by tinkering with ratio of silica-alumina, structure, density and pore volume [115]. Also, zeolite can act as a bulk catalyst due to the ability to support many active phases (metals and non-metals) indicating flexibility for specific purposes and targeting. Zeolite in large, uniform and crystalline shapes is greatly patronized for purposes ranging from crystal structure evaluation, diffusion studies, functional materials experimentation and adsorption. This can be attributed to their peculiar crystal structure, microporous potential, and their impressive thermochemical stability.

Possibilities that the active sites of zeolite are unapproachable for reactants exist because of the rigid structure of its microporous parts. This event is certain if a zeolite catalyst is required for reactions involving molecules bulkier than its pores [116]. Hence, inward/outward diffusion limitation can increase the possibility of coking, thereby deactivating the catalyst and shortening its catalytic lifespan. In response to this setback, a new group of zeolites was devised to be hierarchical-an idea of appending secondary porosity to traditional zeolites. A zeolite whose mesopore size range has at least one supplemental pore system added to its intrinsic microporosity is regarded as a hierarchical type zeolite [117]. These types of zeolites are specialized for reactions involving bulky molecules as they possess reaction sites that are adequate. Also, they do not diminish in their attributes compared to original mesoporous zeolites especially in crystallinity and acidity.



$$\text{-Al}-\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}-\text{O}-\underset{\underset{\text{Si}}{\text{O}}}{\overset{\overset{\text{Si}}{\text{O}}}{\text{Al}}}-\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}-\text{O}-\text{Al} \quad (3)$$

Synthesis of zeolite

Zeolite is a crystalline molecular sieve and is indispensable to advanced industrial processes like catalysis, adsorption, petrochemical and bioprocesses. Its resizable pores among other attributes ensured its continued relevance despite the dynamism of these processes. In most cases, zeolite in its original form is limited by its micropore nature in the size range of ~0.5 to 1.5 nm [118]. Thus, screening out larger molecules from sites during reactions creating efficiencies and underutilization [119].

Some of the solutions proffered to the diffusion problem in zeolite matrices are discussed by Pal et al. [120]. Their work reviewed recent trends in morphology-controlled synthesis and application identifying MCM-41 (Mobil Composition of Matter-41) as a high surface area porous silica material. MCM-41 was reported to be based on a self-assembled supramolecular template mechanism. A flexible mesopore-sized material such as Santa Barbara amorphous-15 (SBA-15) and 16 was developed as a contribution to solving the zeolite diffusion problem [121].

Surprisingly, zeolites that are mesoporous in nature would permit porous ingress/egress of big molecules due to larger pore size compared to their microporous versions. Nevertheless, they are less stable hydrothermally and contain fewer acid sites in contrast to the original zeolites. This puts an embargo on their use for diverse industrial processes. Therefore, attempts to remediate mesoporous zeolite catalysts through their crystallinity framework are welcome for better industrial integration [119, 122]. Some of these efforts are centered on incorporating peculiar mesoporous and microporous qualities to obtain zeolite catalysts with superior crystalline structures [123]. One of these efforts was reported by Bandura et al. [124] who produced composites of zeolite-carbon from gismondite (NaX-C) and faujasite (NaP1-C) structures of high-carbon fly ash (HCFA). Specific surface areas of NaX-C, HCFA and NaP1-C were reported to be 67, 46 and 249 m^2/g, respectively. In addition, increased sorption of petroleum substances was reported to improve with these composites, which confirms the remediation of zeolite limitations through compositing techniques.

Other efforts at improving mesoporous zeolite usability include assembling of zeolite seeds to an arraigned mesoporous phase or by hydrolyzing zeolite products [125]. Acid and alkaline leaching are also methods of remediation [126]. Recent developments of this inclination include enlargement of micropores directly during zeolite synthesis [127,128]. Another is the nanosizing of zeolite for rapid diffusion into nanoparticulate forms during synthesis [129]. Also, using a structural directing agent or hydrothermal conditioning for crystallization is productive for creating mesopores during zeolite synthesis [129,130].

Hydrothermal treatment is plagued with challenges such as crystallization time lag, surface area, tampered purity, and yield [129]. These problems can be avoided by adding a smaller amount of zeolite seed (such as silicalite-1 or ZSM-5) in place of a templating agent during synthesis. This would strengthen the structural framework of the material synthesized by this means. In a template type synthesis, zeolite can possess perfectly arraigned mesopores while retaining the microporous structure after calcination. The outcome of this approach is hierarchical mesoporous zeolites, which offer the dual merit of having micro and meso-type pores in their structure. The micropores would respond to shape or size selectivity while the mesopores would provide facile diffusion pathways within the pore wall. Table 4 shows biodiesel yield under various conversion conditions with selected zeolite-based catalysts in use.

For zeolites, a micropore is said to be large enough if it has an aperture with more than 12-membered ring (12MR) [116]. Hydrothermal treatment using bulky organic amine as a pore generator can give rise to this type of aperture [129, 131]. The synthesis conditions can be optimized using high-throughput methods. Also, modification can be done with germanium to improve the produced mesoporous aluminosilicate.

Hierarchical (H-ZSM 5) mesoporous zeolites

Zeolites is said to be hierarchical and mesoporous if it possesses more than one level of porosity in composite with another. There are no severe penalties to their microporosity blamable on the presence of mesopores [132] Therefore, they are applicable to diverse industrial operations like catalytic cracking, Friedel-Crafts alkylation, phenol tert-butylation and esterification requiring specific attributes. Others are transesterification and benzene upgrade to phenol by oxidation. Li et al. [133] synthesized hierarchical mesoporous zeolite through one-step hydrothermal methodology and used it to convert methanol into aromatics. The yield of aromatic compounds was reported to increase by about 10% after the introduction of the mesoporous structure. Also, the extended lifespan of the catalyst was linked to shorter distance for reactant travel and mesopore facile diffusion of coke antecedents.

Methods of synthesis for HZSM-5 zeolite

Some of the ways of producing H-ZSM 5 zeolite include desilication and re-assembly strategy, dual template mechanism and direct manufacture using dual-functional surfactants. Others are hydrothermal synthesis, post-synthesis template removal, combined hydrothermal and alkaline leaching synthesis strategy.

Desilication and re-assembly strategy

The simplicity of this strategy has continually earned it a booming attention. This method can be adopted for producing varieties of zeolites. Considering a desilication process in an aqueous alkali solution, aluminol sites are less reactive but cater to sustaining of zeolite structure during silica extraction. This would in turn, increase the number of porous structures created. Therefore, desilication/re-assembly supports rapid formation of resizable pores through an external pore-directing agent chosen for the process while conserving Brønsted acid sites [134]. Desilication can afford a well-tailored mesoporosity by varying the concentration of alkali, tilting of the Si/AL balance of original zeolite, reaction timing and temperature [132]. However, it is notorious for tampering with the crystallinity of material to extents, which can be monitored through X-ray diffraction (XRD) spectroscopy [135]. This issue of decline in crystallinity can be remediated by strategic re-assembly after desilication based on the concept of pseudo-morphic transformation [129]. This is done by reuniting the silicates, aluminol, and ZSM-5 zeolite crystals fragments with the parent zeolite structure after extraction. This is can be expedited with hydrothermal treatment in the presence of a surfactant.

Typically, zeolite from alkaline treatment is expected to feature dual-mesopore size distribution and appreciable increase in external surface area compared to the original zeolite matrix [123]. Hence, micropore volumes can be calculated from nitrogen sorption measurements. In a study done by Silva et al. [136], alkaline desilication to tune hierarchical ZSM-5 zeolite containing Brønsted and Lewis acid sites at a specific ratio was carried out. It was in turn, used for the Friedel–Crafts acylation of anisole with acetic anhydride. Their findings established that tuned zeolite retained most of the initial microstructure while desired activities remarkably progressed with increasing mesoporosity. Also, improved internal diffusion of reactants was reported therefore, it is recommended for organic reactions.

Dual-template mechanism

This templating route uses a technique that combines two distinct templates to create mesopores and micropores in zeolite catalysts [14]. Each template is responsible for the generation of a type of pore and they do so simultaneously. Dual-template method was adopted by Wang et al. [137] who produced shape-selective zeolites with a one-step technique using TPAOH as y and $MeEt_3N^+ I^-$ as x templates shown by Figure 4. Their findings indicated improved para-selectivity linked to disappearing acid sites from the topmost surface of the material. Also, outstanding catalytic activity with respect to toluene alkylation with CH3Br was actualized. This implies that specific zeolites' functions can be targeted excellently through dual template manufacturing.

Dual-functional surfactant for direct synthesis

A surfactant is said to be dual-functional if it is capable of generating micro and mesopores simultaneously all by itself. Gemini surfactant is an example of a dual-functional surfactant and can act as both a microporous structural directing agent and a mesopore template in the same reaction [137].

Gemini surfactants are also referred to as dimeric surfactants and are known to contain double hydrophobic and hydrophilic units in their molecules [138]. Compared to regular surfactants, which contain half the number of hydrophilic tails and hydrophilic heads, dimeric surfactants are several times more active. They are designed to cater for the growth of liquid crystal-like meso-structural order and the nanocrystalline framework of zeolite at the same time [139]. With the help of the head units found in dimeric surfactants, structural topology and wall dimensions are adjustable during synthesis.

Also, pore sizes can be manipulated by adding hydrophobic enhancing agents. This would improve pore structure and strengthen zeolite framework providing significant enhancements for performance. Their benefits are more pronounced in organic reactions involving gigantic molecules, which render amorphous catalysts and regular zeolites ineffective.

Hydrothermal synthesis

Hydrothermal method is a mesoscale template-free and convenient technique for HZSM-5 zeolite manufacture. Although, steaming is pivotal, silicalite1 or zeolite seeding is optional to its execution. Hydrothermal treatment combined with seed crystal addition eliminates setbacks associated with crystallization time. Consistency and yield are also catered for while obtaining highly crystalline zeolite with sufficient surface area and pores [140].

If steaming and seeding are used in synthesis, triggering of a perfect ordering of zeolite structure is resultant. Seeds would initialize crystal cores to facilitate secondary generation and nucleation of nano-sized ZSM-5 zeolite crystals along suitable planes [141]. Incomplete intergrowth of ZSM-5 nano-stems in the same direction would lead to the formation of a novel variant of highly arranged porous zeolite. This type of ordering has been verified as a tool for crystal formation and enhancing monocrystalline structures. This tool was deployed by Zhang *et al.* [142] who used temperature-staged treatments to successfully decouple kinetics of nucleation from the formation stages of zeolites in an extremely concentrated gel. This resulted into a yield greater than 95% for beta-zeolite (Si/Al = 25–100, 21–66 nm) and more than 85% of nano-sized and distinct ZSM-5 zeolite (Si/Al = 100–∞, 36–88 nm). Thus, tremendous catalytic activity, remarkable lifespan and selectivity towards product despite zero template and additives are obtainable with this technique.

Also, the improvement in catalytic properties of zeolite produced can be attributed to easier avenue to active sites occasioned by the reduction in microporous channels [132]. Further, exposure of the intra-crystal mesopore of zeolites produced through this method makes them remarkably relevant to several industrial processes.

Alkaline leaching and hydrothermal combined strategy

Hierarchically structured zeolite can also be synthesized template-free using alkaline leaching and hydrothermal combined strategy. It leverages on the joint effect that hydrothermal treatment and alkaline can have on zeolite when applied. This requires that steaming be done initially and afterwards, alkaline leaching of the zeolite material be carried out before re-steaming once more. This was adopted by Fang *et al.* [143] who prepared hierarchical HZSM-5 by dealumination and desilication of commercial Al-rich HZSM-5 zeolite. The product was adjudged to be bettered after using a combination of steaming and alkaline leaching rather than using the latter alone. Also, aromatization of methanol which is an evaluation strategy for catalytic performance was carried out. It affirmed that combine treatment is the top performer compared to standalone leaching as it regards acidity and mesopore formation. Also, catalyst gotten through steam modification and alkali exposure exhibits enhanced isomerization activity and better aromatization activity.

Thermal and hydrothermal stability of HZSM-5 zeolite

Stability of a catalyst on exposure to heat in the presence or absence of water is prerequisite to its functionality and applicability. Majority of reactions undertaken in laboratory or industrially highly depends on prolonged catalyst stability. It is one of the measures of quantifying the lifespan of a catalyst and also a criterion for selecting the type catalytic process to be undertaken.

Specifically, to remediate hydrothermal stability of zeolites, modification like heteroatoms incorporation is proven to be effective [144]. Another modification strategy is silicate coating as used by Miyake et al. [145] who attempted to improve hydrothermal stability of acid sites in MFI type aluminosilicate zeolite (ZSM-5). This was done by coating with silicalite-1 shell layer and steaming coupled with NH_3 temperature programed desorption (NH_3-TPD). Afterwards, it was found that the extreme Si/Al ratio of the shell coating resulted in hydrothermal stability and that hydrophobicity of the shell prevented steam from Al sites of the ZSM-5 zeolite. Their result qualified silicate-1 shell coat as multifunctional rather than for shape selectivity only. More so, zeolite catalyst could withstand steam and extreme-temperature regeneration due to silicate coating.

In another study, Auepattana-aumrung et al. [146] investigated the relationship between catalyst stability and Al found in Na-ZSM-5 zeolite framework by reproducing it through rapid crystallization. After testing the product in a butane cracking reaction, the Si–ONa–Al in zeolite structure was found to sustain catalyst stability during reaction. This infers that Al composition of zeolite should be monitored because it is critical to stability especially when heat is unavoidable in the process to be catalyzed. Examples of processes that require hydrothermal and thermal stability include all petrochemical reactions and several other liquid refining processes. Therefore. This property should not be sacrificed for affinity, activity and performance improvements during catalyst synthesis.

Zeolite-composite synthesis

Composites of zeolites are often made after the zeolite and dopant are synthesized separately. Afterwards, they are brought together either by electrochemical, microemulsion, hydrothermal, co-precipitation or sol-gel techniques. Of these methods, hydrothermal is adjudged to be the best due to shorter synthesis time and ability to control crystal growth, nucleation, particle size and morphology of nanocomposite [147].

Tran et al. [148] adopted a facile hydrothermal synthesis method to synthesize magnetite Fe_3O_4/zeolite NaA nanocomposite as an adsorbent. Their work confirmed that hydrothermal method produces an effective nano-sized material in a shorter time compared to other approaches.

Biodiesel production with zeolite and its composites as catalyst

Zeolites are advantageous to biodiesel production because of their unique crystal structure, high stability, easier product purification and economic viability for large scale fuel production. Also, their high selectivity for product and the combination of self-potency as a catalyst and the ability to support dopants are highly coveted. Nevertheless, zeolite is seldomly used for biodiesel production in its original form due to limitations such as diffusion restraints, coking, quick deactivation and present but inaccessible active sites. Since the microporous region of zeolites are framed to be rigid, reactants with bigger molecules compared to pore dimensions would inevitably trigger these limitations [116]. Table 5 shows comparison of several attempts to produce biodiesel using HZSM-5 Zeolite standalone and in composites with dopants. It was observed that Fawaz et al. [150] could not achieve a 50% biodiesel yield using HZSM-5 zeolite nanosheets in batch transesterification of waste frying oils despite a top range temperature and time of 180 °C and 24 h. However, AbuKhadra et al. [153] produced biodiesel from commercial waste cooking oil-a similar feedstock but with a Ca/clinoptilotite zeolite nanocomposite achieving more than 95% yield before 3 h at comparably lower temperature of 70 °C. Also, Ratnasari et al. [149] who experimented the pyrolysis of Lignocel-HBS 150-500 from beechwood for biodiesel with a 3:1 HZSM-5/Al-MCM-41 also reported more than 95% product yield. Therefore, it is noteworthy that doping and compositing of zeolite catalysts is a formidable method for circumventing limitations associated with their conversion performance.

Recommendations

Zeolite has found its niche in several industries like manufacturing, midstream oil and gas and bioenergy. Advancing the development of zeolite and its composites is therefore, highly beneficial to energy, manufacturing and sustainable goals of nations. It is recommended that novel methods of producing zeolite catalyst be explored to make the overall cost of producing biodiesel feasible at industrially. This is crucial to the economy of scale and the competitiveness of biodiesel and other biofuels produced over zeolite as compared to fossil fuels. Also, regardless of the abundance and availability of kaolin, other viable raw materials for zeolite production should be experimented. This is paramount because kaolin has got other use cases (e.g. ornamental, art and construction) that compete with its use as a raw material for catalyst production. In addition, WCO generation and disposal in Nigeria and Sub-Saharan Africa should be tracked, manifested and agglomerated for sustainable environmental and energy benefits.

Summary and conclusion

The sustainability of biodiesel supply to an ever-increasing population and energy market requires a dramatic shift to waste and non-edible oils as feedstocks. This would ensure that production of biodiesel gain industrial relevance while adding to the value chain through energy plant farming and waste oil agglomeration. The ease for making this shift is leveraged on standards and requirements in place for biodiesel usage and not for raw materials to synthesizing it. Nevertheless, the product quality and amount of refining required are dependent on the physical and chemical properties of the starting materials. To convert starting materials of oil origins to biodiesel, transesterification is highly favored, with the esterification method regarded as alternative. Considering that the transesterification process is slow, it is often catalyzed using alkaline, acidic and enzymatic catalysts. Although the choice of catalyst is greatly influenced by economic factors like cost and reusability, greater decisions are made to resonate with free fatty acid and water content of starting oils. The Alkaline catalysts are known to speed up transesterification reactions better in terms of yield and time required than others, with the homogenous types topping the charts. But their acidic counterparts are slower yet, free fatty acid and water loving. These attributes make them versatile for wider range of reactions including esterification reactions. The enzymatic ones were reported to be the slowest; however, research into their usage for transesterification is burgeoning. Zeolites are heterogeneous and alkaline in nature with potency in their active sites, pores and selectivity for biodiesel production. Adjustments are mostly made to minimize the mass transfer limitation associate with it to improve biodiesel yield. The versatility and availability of kaolin in various locations of the world has aided research into and manufacture of various zeolite-based catalysts for biodiesel production.

Efforts to develop heterogeneous catalysts for biodiesel production especially zeolite-based ones, are presented in a surge of recent publications. These researches are extensive and continuously seeking to improve thermal stability, surface/pore activity, mechanical strength and active species retention. To achieve these, attempts to modify textural morphology, specific surface area and pore systems to berth new zeolite variants are made. One of such variants is the HZSM-5 zeolite which could gain future ascendance thanks to the abundance of kaolin, its readiness to form composites, ease of synthesis and uncomplicated equipment requirement for manufacture. The use of metal-HZSM-5 zeolite composites for transesterification has yielded biodiesel in percentages greater than 95% compared to its use as a standalone catalyst. This is so for other types of hierarchical zeolites in comparison to their composites. This has opened another frontier for research into materials especially nanoparticulate dopants for compositing HZSM-5 and other types of hierarchical zeolites. Excellent catalytic activity of dopants such as copper (Cu), nickel (Ni), calcium (Ca), potassium (K) for compositing and nano-compositing has been widely reported. It is noteworthy that the cost of bulk purchase of commercial zeolite for composite production makes it unattractive. Therefore, methods for the production of zeolite sustainably from kaolin should be prioritized as it is crucial to commercialization of its composites. The hydrothermal treatment and alkaline leaching combined strategy is commonly adopted for HZSM-5 zeolite synthesis. This is due to its capability of producing catalysts of higher isomerization and better aromatization activities.

Acknowledgment

Special thanks are given to the Department of Chemical Engineering, FUT Minna for their assistance.

Disclosure statement

No potential conflict of interest was reported by the author(s).

References

[1] Ghasemian S, Faridzad A, Abbaszadeh P, et al. An overview of global energy scenarios by 2040: identifying the driving forces using cross-impact analysis method. Int J Environ Sci Technol. 2020.

[2] IEA. Oil Market Report - May 2021, International Energy Agency, Paris; 2021. https://www.iea.org/reports/oil-market-report-may-2021.

[3] Olivier JGJ, Peters J. Trends in global and total greenhouse gas emissions- 2019 report, PBL Netherlands Environmental Assessment Agency, 1–70. 2020. https://www.pbl.nl/sites/default/files/downloads/pbl-2020-trends-in-global-co2-and-total-greenhouse-gas-emissions-2019-report_4068.pdf.

[4] Ogunkunle O, Ahmed NA. Overview of biodiesel combustion in mitigating the adverse impacts of engine emissions on the sustainable human–environment scenario. Sustainability. 2021; 13(10):5465–5495.

[5] Kumar J CR, Majid MA. Renewable energy for sustainable development in India: current status, future prospects, challenges, employment, and investment opportunities. Energ Sustain Soc. 2020;10(1):1–20.

[6] Garba MU, Oloruntoba MJ, Isah AG, et al. Production of solid fuel from rice straw through torrefaction process. Int J Sci Eng Investig. 2015;4(37):1–6.

[7] Tong C. Introduction to materials for advanced energy systems. Berlin: Springer, 2018. 1–911.

[8] Ayoub M, Yusoff MHM, Nazir MH, et al. A comprehensive review on oil extraction and biodiesel production technologies. Sustainability. 2021;13(2):788–806.

[9] Esfarjani F, Khoshtinat K, Zargaraan A, et al. Evaluating the rancidity and quality of discarded oils in fast food restaurants. Food Sci Nutr. 2019;7(7):2302–2311.

[10] Thangaraj B, Solomon PR, Muniyandi B, et al. Catalysis in biodiesel production–a review. Clean Energy. 2019;3(1):2–23.

[11] Narowska BE, Kułażyński M, Łukaszewicz M. Application of activated carbon to obtain biodiesel from vegetable oils. Catalysts. 2020;10(9):1049–1079.

[12] Lv L, Dai L, Du W, et al. Progress in enzymatic biodiesel production and commercialization. Processes. 2021;9(2):355–310.

[13] Mierczynski P, Szkudlarek L, Chalupka K, et al. The effect of the activation process and metal oxide addition (cao, mgo, sro) on the catalytic and physicochemical properties of natural zeolite in transesterification reaction. Materials. 2021;14(9): 2415–2417.

[14] Babic V. Increasing the porosity of zeolites Catalysis. Ph.D thesis Normandie Université; 2021 https://tel.archives-ouvertes.fr/tel-03167919.

[15] Maciver V, Dagde K, Konne J. Synthesis of zeolite X from locally sourced kaolin clay from Kono-Boue and Chokocho, Rivers state, Nigeria. ACES. 2020;10(04):399–407.

[16] Brett W. An overview of alternative fuels for commercial transportation. Breakthrough- Sustainability and Tech. 2021, April 20;13: 12. [cited 2022 February 3]. Available from: https://www.breakthroughfuel.com/blog/overview-alternative-transportation-fuels

[17] Wu G, Ge JC, Choi NJ. A comprehensive review of the application characteristics of biodiesel blends in diesel engines. Appl Sci. 2020;10(22):8015–8095.

[18] FutureBridge. Renewable diesel: an alternative fuel. 16:43. [cited 2022 February 23, 2022]. Available from: https://www.futurebridge.com/industry/perspectives-energy/renewable-diesel-the-fuel-of-the-future/.

[19] Elgharbawy AS, Sadik WA, Sadek OM, et al. A review on biodiesel feed-stocks and production technologies. J Chil Chem Soc. 2021;66(1):5098–5109.

[20] Chozhavendhan S, Vijay Pradhap Singh M, Fransila B, et al. A review on influencing parameters of biodiesel production and purification. Curr Res Green Sustain Chem. 2020;1–2(2):1–6.

[21] Gravalos I, Ziakas N, Loutridis S, et al. A mechatronic system for automated topping and suckering of tobacco plants. Comput Electron Agric. 2019;166:104986.

[22] Acharya N, Nanda P, Panda S, et al. Analysis of properties and estimation of optimum blending ratio of blended mahua biodiesel. Eng Sci Technol. 2017;20(2):511–517.

[23] Yan B, Zhang S, Chen W, et al. Pyrolysis of tobacco wastes for bio-oil with aroma compounds. J Anal Appl Pyrolysis. 2018; 136:248–254.

[24] Devarajan Y, Munuswamy DB, Nagappan B. Emissions analysis on diesel engine fueled with cashew nut shell biodiesel and pentanol blends. Environ Sci Pollut Res Int. 2017;24(14): 13136–13141.

[25] Demirbas A, Bafail A, Ahmad W, et al. Biodiesel production from non-edible plant oils. Energy Explor Exploit. 2016;34(2): 290–318.

[26] Gadhave SL, Ragit SS. Process optimization of Tung oil methyl ester (Verniciafordii) using the Taguchi approach, and its fuel characterization. Biofuels. 2020;11(1):49–55.

[27] Yadav AK, Pal A, Ghosh U, et al. Comparative study of biodiesel production methods from yellow oleander oil and its performance analysis on an agricultural diesel engine. Int J Ambient Energy. 2019;40(2):152–157.

[28] Pham LN, Van Luu B, Phuoc HD, et al. Production of biodiesel from candlenut oil using a two-step Co-solvent method and evaluation of its gaseous emissions. J Oleo Sci. 2018;67(5): 617–626.

[29] Durairaj RB, Anderson A, Mageshwaran G, et al. Performance and emission characteristics of cotton seed and neem oil biodiesel with CeO_2 additives in a single-cylinder diesel engine. Int J Ambient Energy. 2019;40(4):396–400.

[30] Onukwuli DO, Emembolu LN, Ude CN, et al. Optimization of biodiesel production from refined cotton seed oil and its characterization. Egypt J Pet. 2017;26(1):103–110.

[31] Thangaraj B, Solomon PR. Scope of biodiesel from oils of woody plants: a review. Clean Energy. 2020;4(2):89–106.

[32] Baena LM, Calderón JA. Effects of palm biodiesel and blends of biodiesel with organic acids on metals. Heliyon. 2020;6(5): e03735–3760.

[33] Ngoie IW. Biodiesel production from edible oil wastewater sludge with bioethanol using heterogeneous nano-magnetic catalysis. Electronic Theses and Dissertation, Cape Peninsula University of Technology; 2019. http://etd.cput.ac.za/bitstream/20.500.11838/2933/1/Ngoie__Ilunga_Wighens__211280224.pdf.

[34] Rosson E, Sgarbossa P, Pedrielli F. Bioliquids from raw waste animal fats: an alternative renewable energy source. Biomass Convers Biorefin. 2020;1–16.

[35] Madai IJ, Jande YAC, Kivevele T. Fast rate production of biodiesel from neem seed oil using a catalyst made from banana peel ash loaded with metal oxide (Li-Cao/$Fe_2(SO_4)_3$). Adv Mater Sci Eng. 2020;2020:1–11.

[36] Changmai B, Vanlalveni B, Ingle AP, et al. Widely used catalysts in biodiesel production: a review. RSC Adv. 2020;10(68): 41625–41679.

[37] Mizik T, Gyarmati G. Economic and sustainability of biodiesel production—a systematic literature review. Clean Technol. 2021;3(1):19–36.

[38] Achinas S, Horjus J, Achinas V, et al. A pestle analysis of biofuels energy industry in Europe. Sustainability. 2019;11(21): 5981–5981.

[39] Culaba AB, Ubando AT, Ching PML, et al. Biofuel from microalgae: sustainable pathways. Sustainability. 2020;12(19): 8009–8109.

[40] Erchamo YS, Mamo TT, Workneh GA, et al. Improved biodiesel production from waste cooking oil with mixed methanol–ethanol using enhanced eggshell-derived CaO nano-catalyst. Sci Rep. 2021;11(1):6708–6722.

[41] Yusoff MNAM, Zulkifli NWM, Sukiman NL, et al. Sustainability of palm biodiesel in transportation: a review on biofuel standard, policy and international collaboration between Malaysia and Colombia. Bioenergy Res. 2021;14(1):43–60.

[42] Sousa AM, Andrade TA, Errico M, et al. Fatty acid content in biomasses: State of the art and novel physical property estimation methods. Int J Chem Eng. 2019;2019:1–25.

[43] FSSAI. FSSAI issues directions regarding disposal and collection of used cooking oil, *foodsafetyhelpline*. 08:15; 2019. [cited 2021 11 June]. February 12. http://dx.doi.org/10.4067/S0717-97072021000105098.

[44] Awogbemi O, Onuh EI, Inambao FL. Comparative study of properties and fatty acid composition of some neat vegetable oils and waste cooking oils. Int J Low-Carbon Technol. 2019; 14(3):417–425. September

[45] Mannu A, Ferro M, Pietro D, et al. Innovative applications of waste cooking oil as raw material. Sci Prog. 2019;40:153–160.

[46] Rizwanul Fattah IM, Ong HC, Mahlia TMI, et al. 2020. State of the art of catalysts for biodiesel production, Front Energy Res, 8, 101–117. https://doi.org/10.3389/fenrg.2020.00101.

[47] Widayat Fernanda AAA, Silvie ES. Palm kernel shell bio-char catalyst for biodiesel production from waste cooking oil. IOP Conf Ser: Mater Sci Eng. 2021;1053–1070.

[48] Pruszko R. Chapter 23 - Biodiesel production. In Dahiya A, editor. Bioenergy. 2nd ed. Academic press; Elsevier; 2020. p. 491–514. https://doi.org/10.1016/B978-0-12-815497-7.00023-3

[49] Abdul Raman AA, Tan HW, Buthiyappan A. Two-step purification of glycerol as a value added by product from the biodiesel production process. Front Chem. 2019;7:774–790.

[50] Pitt FD, Domingos AM, Chivanga Barros AA, et al. Purification of residual glycerol recovered from biodiesel production. S Afr J Chem Eng. 2019;29:42–51.

[51] Castillo Gónzalez JP, Álvarez Gutiérrez PE, Medina MA, et al. Effects on biodiesel production caused by feed oil changes in a continuous stirred-tank reactor. Appl Sci. 2020;10(3): 992–1112.

[52] Toson P, Doshi P, Jajcevic D. Explicit residence time distribution of a generalised Cascade of continuous stirred tank reactors for a description of short recirculation time (bypassing). Processes. 2019;7(9):615–633.

[53] Bianchi P, Williams J, Kapp CO. Oscillatory flow reactors for synthetic chemistry applications. J Flow Chem. 2020;10(3): 475–490.

[54] Kamzolova SV, Morgunov IG. Physiological, biochemical and energetic characteristics of torulasporaglobosa, a potential producer of biofuel. Energies. 2021;14(11):3198–3221.

[55] Ibrahim MH, Dasin DY, Yahuza I. The physicochemical analysis of biodiesel produced from african sweet orange (citrus sinensis) seeds oil. Int J Eng Technol Manag Res. 2020;6:82–91.

[56] Moritiwon OJ, Afolabi EA, Garba MU, et al. Experimental investigation of fast pyrolysis of isoberlinadoka-derived sawdust for bio-oil production. Arab J Sci Eng. 2021;46(7):6303–6313.

[57] Gandidi IM, Wiyono A, Berman EG, et al. Experimental upgrading of liquid crude oil obtained from calophylluminophyllum by two-stage pyrolysis. Case Stud Therm Eng. 2019;16: 100544–101049.

[58] Channapattana SV, Kulkarni KK. Bio-diesel as a fuel in I.C. engines – a review. Int J Comput Sci Appl. 2009;2(1):22–26.

[59] Omidghane M, Bartoli M, Asomaning J, et al. Pyrolysis of fatty acids derived from hydrolysis of brown grease with biosolids. Environ Sci Pollut Res Int. 2020;27(21):26395–26405.

[60] Attia M, Farag S, Chaouki J. Upgrading of oils from biomass and waste: catalytic hydro-deoxygenation. Catalysts. 2020; 10(12):1381–1400.

[61] Zahan KA, Kano M. Biodiesel production from palm oil, its by-products, and mill effluent: a review. Energies. 2018;11(8): 2132–2160.

[62] Makareviciene V, Sendzikiene E. Noncatalytic biodiesel synthesis under supercritical conditions. Processes. 2021;9(1): 138–166.

[63] Hassan AA, Smith JD. Laboratory-scale research of non-catalyzed supercritical alcohol process for continuous biodiesel production. Catalysts. 2021;11(4):435–460.

[64] Jha A. Microwave assisted synthesis of organic compounds and nanomaterials. In Kumar B, editor, Nanofibers. Interchopen; 2021. p. 456–789. https://doi.org/10.5772/intechopen.98224

[65] Díaz-Ortiz A, Prieto P, de la Hoz A. A critical overview on the effect of microwave irradiation in organic synthesis. Chem Rec. 2019;19(1):85–97.

[66] Mohamad Aziz NA, Yunus R, Kania D, et al. Prospects and challenges of microwave-combined technology for biodiesel and bio-lubricant production through a transesterification: a review. Molecules. 2021;26(4):788–800.

[67] Saani SM, Abdolalizadeh J, Heris SZ. Ultrasonic/sonochemical synthesis and evaluation of nanostructured oil in water emulsions for topical delivery of protein drugs. Ultrason Sonochem. 2019;55:86–95.

[68] Sadatshojaie A, Wood DA, Jokar SM, et al. Applying ultrasonic fields to separate water contained in medium-gravity crude oil emulsions and determining crude oil adhesion coefficient. Ultrason Sonochem. 2021;70:105303–101073.

[69] Ramírez-Sanabria AE, López LL, Orozco MI. Optimization of the transesterification process of palm oil using ultrasound-based technique. Cienc Desarro. 2020;11(2):145–151. [Mismatch

[70] Barney CW, Dougan CE, McLeod KR, et al. Cavitation in soft matter. Proc Natl Acad Sci USA. 2020;117(17):9157–9165.

[71] Bucciol F, Colia M, Calci- Gaudino E, et al. Enabling technologies and sustainable catalysis in biodiesel preparation. Catalysts. 2020;10(9):988–1007.

[72] Shinde K, Kaliaguine S. A comparative study of ultrasound biodiesel production using different homogeneous catalysts. ChemEngineering. 2019;3(1):18.

[73] Strapasson A, Falcão J, Rossberg T, et al. Land use change and the European biofuels policy: the expansion of oilseed feedstock on lands with high carbon stock. Oil Seeds Fat Crops Lipids. 2019;26(39):39–12.

[74] Hsiao M-C, Liao P-H, Lan NV, et al. Enhancement of biodiesel production from high-acid-value waste cooking oil via a microwave reactor using a homogeneous alkaline catalyst. Energies. 2021;14(2):437–450.

[75] Coniwanti P, Surliadji L, Triandini D. The effects of catalysts type, molar ratio, and transesterification time in producing biodiesel from beef tallow. IOP Conf Ser: Mater Sci Eng. 2019; 620(1):012019–012633.

[76] Okwundu OS, El-Shazly AH, Elkady M. Comparative effect of reaction time on biodiesel production from low free fatty acid beef tallow: a definition of product yield. SN Appl Sci. 2019; 1(2):345–361.

[77] Vitidsant R, Kodama S, Sekiguchi H. Transesterification using ultrasonic spray of triolein containing CaO particles into methanol vapor in a 3-phase reactor. Processes. 2021;9(1): 181–195.

[78] Catalysis. Chemistry libreText, 15:48; 2021, March 20 [cited 2022 February 27]. Available from: https://chem.libretexts.org/@go/page/25181.

[79] Adewuyi A. Challenges and prospects of renewable energy in Nigeria: a case of bioethanol and biodiesel production. Energy Rep. 2020;6(4):77–88.

[80] Shinde P, S, Suryawanshi P, S, Patil, et al. A brief overview of recent progress in porous silica as catalyst supports. J Compos Sci. 2021;5(3):75–17.

[81] Refaat A, Attia NK, Sibak HA, et al. Production optimisation and quality assessment of biodiesel from waste vegetable oil. Int J Environ Sci Technol. 2010;5(1):183–213.

[82] Hossain MN, Bhuyan M, Alam A, et al. Optimization of biodiesel production from waste cooking oil using S-TiO2/SBA-15 heterogeneous acid catalyst. Catalysts. 2019;9(1):67–15.

[83] Gupta AR, Rathod VK. Waste cooking oil and waste chicken eggshells derived solid base catalyst for the biodiesel production, optimization and kinetics. Waste Manag. 2018;79: 169–178.

[84] Yadav M, Sharma YC. Transesterification of used vegetable oil using $BaAl_2O_4$ spinel as heterogeneous base catalyst. Energy Convers Manage. 2019;198:111795.

[85] Dos Santos TC, Santos ECS, Dias JP, et al. Reduced graphene oxide as an excellent platform to produce a stable bronsted acid catalyst for biodiesel production. Fuel. 2019;256:115793.

[86] Lee JH, Jeon H, Park JT, et al. Synthesis of hierarchical flower-shaped hollow MgO microspheres via ethylene-glycol mediated process as a base heterogeneous catalyst for transesterification for biodiesel production. Biomass Bioenergy. 2020; 142:105788.

[87] Basumatary B, Basumatary S, Das B, et al. Waste Musa paradisiaca plant: an efficient heterogeneous base catalyst for fast production of biodiesel. J Cleaner Prod. 2021;305:127089.

[88] Qu S, Chen C, Guo M, et al. Synthesis of MgO/ZSM-5 catalyst and optimization of process parameters for clean production of biodiesel from Spirulina platensis. J Cleaner Prod. 2020;276: 123382.

[89] Maneechot P, Sriprapakhan P, Manadee S, et al. Improvement of potassium species dispersed on hierarchical zeolite NaY by using combined methods between ultrasound and microwave-assisted impregnation as catalysts for transesterification of refined Jatropha seed oil. Biomass Bioenergy. 2021;153: 106202.

[90] Wang J, Li K, He Y, et al. Enhanced performance of lipase immobilized onto CO_2^+-chelated magnetic nanoparticles and its application in biodiesel production. Fuel. 2019;255:115794.

[91] Binhayeeding N, Klomklao S, Prasertsan P, et al. Improvement of biodiesel production using waste cooking oil and applying single and mixed immobilized lipases on polyhydroxyalkanoate. Renewable Energy. 2020;162:1819–1827.

[92] Mićić R, Tomić M, Martinović F, et al. Reduction of free fatty acids in waste oil for biodiesel production by glycerolysis: investigation and optimization of process parameters. Green Process Synth,. 2019;8(1):15–23.

[93] Faruque MO, Razzak SA, Hossain MM. Application of heterogeneous catalysts for biodiesel production from microalgal oil—a review. Catalysts. 2020;10(9):1025.

[94] Dantas J, Leal E, Cornejo DR, et al. Biodiesel production evaluating the use and reuse of magnetic nanocatalysts $Ni_{O.5}Zn_{O.5}Fe_2O_4$. Arab J Chem. 2020;13(1):3026–3042.

[95] Vasić K, Hojnik Podrepšek G, Knez Ž, et al. Biodiesel production using solid acid catalysts based on metal oxides. Catalysts. 2020;10(2):237–263.

[96] De Jesus de Oliveira C, Teleken JG, Alves HJ. Catalytic efficiency of the eggshell calcined and enriched with glycerin in the synthesis of biodiesel from frying residual oil. Environ Sci Pollut Res Int. 2020;27(15):17878–17890.

[97] Kondrat SA, van Bokhoven JA. A perspective on counting catalytic active sites and rates of reaction using x-ray spectroscopy. Top Catal. 2019;62(17-20):1218–1227.

[98] Sumari S, Fajaroh F, Suryadharma IB, et al. Zeolite impregnated with ag as catalysts for glycerol conversion to ethanol assisted by ultrasonic. IOP Conf Ser: Mater Sci Eng. 2019;515: 012075.

[99] Fattahi N, Konstantinos T, Rafael L, et al. Zeolite-based catalysts: a valuable approach toward ester bond formation. Catalysts. 2019;9(9):758.

[100] Karbul A, Yengejeh RJ, Mohammadi MK, et al. Synthesis and characterization of trimetallic Fe-Co-V/zeolite and Fe-Co-Mo/zeolite composite nanostructures. Mater Res. 2021;24(3):7.

[101] Liu L, Corma A. Metal catalysts for heterogeneous catalysis: from single atoms to nanoclusters and nanoparticles. Chem Rev. 2018;118(10):4981–5079.

[102] Alaya-Ibrahim S, Kovo AS, Abdulkareem AS, et al. Development of nano-silver doped zeolite a synthesized from Nigerian ahoko kaolin for treatment of wastewater of a typical textile company. Chem Eng Commun. 2020;207(8):1114–1137.

[103] Hashimoto S, Uwada T, Masuhara H, et al. Fabrication of gold nanoparticle-doped zeolite L crystals and characterization by optical microscopy: laser ablation- and crystallization inclusion-based approach. J Phys Chem C. 2008;112(39): 15089–15093.

[104] Zhu S, Xu L, Yang S, et al. Cobalt-doped ZnO nanoparticles derived from zeolite imidazole frameworks: Synthesis, characterization, and application for the detection of an exhaled diabetes biomarker. J Colloid Interface Sci. 2020;569:358–365.

[105] Gawande MB, Goswami A, Felpin F, et al. Cu and Cu-Based nanoparticles: Synthesis and applications in catalysis. Chem Rev. 2016;116(6):3722–3811.

[106] Southard J. Weathering, *geolibretexts*. 16:31; 2021, March 8 [2021 Retrieved June 25]. Available from https://geo.libretexts.org/@go/page/13466.

[107] Oyebanjo O, Ekosse G-I, Odiyo J. Physico-chemical, mineralogical, and chemical characterisation of cretaceous–paleogene/neogenekaolins within Eastern Dahomey and Niger Delta basins from Nigeria: possible industrial applications. Minerals. 2020;10(8):670–681.

[108] Dansarai MM, Bawa MA, Tokan A. Nigerian clay deposits for use as refractory materials in metallurgical industries – a review. Int J Eng Res Technol. 2020;9(6):1–12. https://www.ijert.org/nigerian-clay-deposits-for-use-as-refractory-materials-in-metallurgical-industries-a-review

[109] Kloprogge JT, Ponce CP. Spectroscopic studies of synthetic and natural saponites: a review. Minerals. 2021;11(2):112–129.

[110] Romero M, Padilla I, Contreras M, et al. Mullite-based ceramics from mining waste: a review. Minerals. 2021;11(3):332–350.

[111] Horri N, Sanz-Pérez ES, Arencibia A, et al. Effect of acid activation on the CO_2 adsorption capacity of montmorillonite. Adsorption. 2020;26(5):793–811.

[112] Zahid I, Ayoub M, Abdullah BB, et al. Activation of nano kaolin clay for Bio-Glycerol conversion to a valuable fuel additive. Sustainability. 2021;13(5):2631.

[113] Del Campo P, Martínez C, Corma A. Activation and conversion of alkanes in the confined space of zeolite-type materials. Chem Soc Rev. 2021;50(15):8511–8595.

[114] Novembre D, Gimeno D, Del Vecchio A. Synthesis and characterization of Na-P1 (GIS) zeolite using a kaolinitic rock. Sci Report. 2021;11:4872–5001.

[115] Almeida A, Ribeiro R, Mota JPB, et al. Extrusion and characterization of high Si/Al ratio ZSM-5 using silica binder. Energies. 2020;13(5):1201–1230.

[116] Al-Ani A, Haslam JJC, Mordvinova NE, et al. Synthesis of nanostructured catalysts by surfactant-templating of large-pore zeolites. Nanoscale Adv. 2019;1(5):2029–2039.

[117] Hartmann M, Thommes M, Schwieger W. Hierarchically-ordered zeolites: a critical assessment. Adv Mater Interfaces. 2021;8(4):2001841–2001869.

[118] Duan H, Tian Y, Gong S, et al. Effects of crystallite sizes of Pt/HZSM-5 zeolite catalysts on the hydrodeoxygenation of guaiacol. Nanomaterials. 2020;10(11):2246–2269.

[119] Jia X, Khan W, Wu Z, et al. Modern synthesis strategies for hierarchical zeolites: bottom-up versus top-down strategies. Adv Powder Technol. 2019;30(3):467–484.

[120] Pal N, Lee J-H, Cho E-B. Recent trends in morphology-controlled synthesis and application of mesoporous silica nanoparticles. Nanomaterials. 2020;10(11):2122–2137.

[121] Adrover AE, Pedernera M, Bonne M, et al. Synthesis and characterization of mesoporous SBA-15 and SBA-16 as carriers to improve albendazole dissolution rate. Saudi Pharm J. 2020; 28(1):15–24.

[122] Xu H, Zhu J, Zhu L, et al. Advances in the synthesis of ferrierite zeolite. Molecules. 2020;25(16):3722–3744.

[123] Smail HA, Rehan M, Shareef KM, et al. Synthesis of uniform mesoporous zeolite ZSM-5 catalyst for Friedel-Crafts acylation. Chem Eng. 2019;3(2):35–53.

[124] Bandura I, Panek R, Madej J, et al. Synthesis of zeolite-carbon composites using high-carbon fly ash and their adsorption abilities towards petroleum substances. Fuel. 2021;283: 119173–119195.

[125] Abdulridha S, Jiao Y, Xu S, et al. Mesoporous zeolitic materials (mzms) derived from zeolite y using a microwave method for catalysis. Front Chem. 2020;8:482.

[126] Hrachovcová K, Tišler Z, Svobodová E, et al. Modified alkali activated zeolite foams with improved textural and mechanical properties. Minerals. 2020;10(5):483–501.

[127] Valencia S. Zeolitic microporous materials and their applications. Molecules. 2021;26(3):730–755.

[128] Wang I, Shao Y, Li G, et al. Synthesis of high-micropore-volume pure-silica zeolites from a polymer near-neutral medium free of fluoride ions for VOCs capture. Microporous Mesoporous Mater. 2019;286:149–154.

[129] Pan T, Wu Z, Yip, A, CK. Advances in the green synthesis of microporous and hierarchical zeolites: a short review. Catalysts. 2019;9(3):274–299.

[130] Khaleque A, Alam MM, Hoque M, et al. Zeolite synthesis from low-cost materials and environmental applications: a review. Environ Adv. 2020;2:100019–101019.

[131] Xiong G, Meng F, Liu J, et al. Rapid hydrothermal synthesis of hierarchical ZSM-5/beta composite zeolites. RSC Adv. 2021; 11(35):21235–21247.

[132] Khan W, Jia X, Wu Z, et al. Incorporating hierarchy into conventional zeolites for catalytic biomass conversions: a review. Catalysts. 2019;9(2):127–150.

[133] Li J, Wang L, Zhang D, et al. One-step synthesis of hierarchical ZSM-5 zeolites and their catalytic performance on the conversion of methanol to aromatics. Reac Kinet Mech Cat. 2020; 130(1):519–530.

[134] Gackowski M, Datka J. Acid properties of hierarchical zeolites Y. Molecules. 2020;25(5):1044–1076.

[135] Zhang K, Fernandez S, Lawrence JA, et al. Organotemplate-free β zeolites: from zeolite synthesis to hierarchical structure creation. ACS Omega. 2018;3(12):18935–18942.

[136] Silva DSA, Castelblanco WN, Piva DH, et al. Tuning the brønsted and lewis acid nature in HZSM-5 zeolites by the generation of intracrystalline mesoporosity—catalytic behavior for the acylation of anisole. Molecular Catalysis. 2020;492: 111026–111136.

[137] Wang S, Tian R, He B, et al. The success of dual-functional templating for synthesizing hierarchical analcime zeolite. Appl Organometal Chem. 2019;33(11):e4711–4739.

[138] Feng J, Yan Z, Song J, et al. Study on the structure-activity relationship between the molecular structure of sulfategemini surfactant and surface activity, thermodynamic properties and foam properties. Chem Eng Sci. 2021;245:116857–111199.

[139] Feng G, Wen Z, Wang J, et al. Guiding the design of practical MTW zeolite catalysts: an integrated experimental-theoretical perspective. Microporous Mesoporous Mater. 2021;312: 110810–111118.

[140] Kalvachev Y, Todorova T, Popov C. Recent progress in synthesis and application of nanosized and hierarchical mordenite—a short review. Catalysts. 2021;11(3):308–330.

[141] Kim HS, Kang SK, Zhang H, et al. Al-ZSM-5 nanocrystal catalysts grown from silicalite-1 seeds for methane conversion. Energies. 2021;14(2):485–502.

[142] Zhang G, Fan Y, Huang J, et al. Decoupling nucleation from crystal-growth for the synthesis of nanocrystalline zeolites. Dalton Trans. 2020;49(21):7258–7266.

[143] Fang Y, Yang F, He X, et al. Dealumination and desilication for Al-rich HZSM-5 zeolite via steam-alkaline treatment and its application in methanol aromatization. Front Chem Sci Eng. 2019;13(3):543–553.

[144] Shamzhy M, Opanasenko M, Concepción P, et al. New trends in tailoring active sites in zeolite-based catalysts. Chem Soc Rev. 2019;48(4):1095–1149.

[145] Miyake K, Inoue R, Miura T, et al. Improving hydrothermal stability of acid sites in MFI type aluminosilicate zeolite (ZSM-5) by coating MFI type all silica zeolite (silicalite-1) shell layer. Microporous Mesoporous Mater. 2019;288:109523–109557.

[146] Auepattana-aumrung C, Márquez V, Wannakao S, et al. Role of Al in Na-ZSM-5 zeolite structure on catalyst stability in butene cracking reaction. Sci Rep. 2020;10(1):643–671.

[147] Li J, Wu Q, Wu J. Synthesis of nanoparticles via solvothermal and hydrothermal methods. In Aliofkhazraei M, editor. Handbook of nanoparticles. Cham: Springer; 2015. p. 1–28 https://doi.org/10.1007/978-3-319-13188-7_17-1

[148] Tran NBT, Duong NB, Le NL. Synthesis and characterization of magnetic Fe_3O_4/zeolite NaA nanocomposite for the adsorption removal of methylene blue potential in wastewater treatment. J Chem. 2021;2021:1–14.

[149] Ratnasari DK, Bijl A, Yang W, et al. Effect of H-ZSM-5 and Al-MCM-41 proportions in catalyst mixtures on the composition of Bio-Oil in Ex-Situ catalytic pyrolysis of lignocellulose biomass. Catalysts. 2020;10(8):868.

[150] Fawaz EG, Salam DAS, Rigolet S, et al. Hierarchical zeolites as catalysts for biodiesel production from waste frying oils to overcome mass transfer limitations. Molecules. 2021;26(16):4879.

[151] Qian S, Feng B, Zhai Y, et al. Catalytic pyrolysis of biodiesel surrogate over HZSM-5 zeolite catalyst. Chin J Chem Phys. 2021;34(1):102–111.

[152] Fereidooni L, Abbaspourrad A, Enayati M. Electrolytic transesterification of waste frying oil using Na+/zeolite–chitosan biocomposite for biodiesel production. Waste Manage (Oxford). 2021;127:48–62.

[153] AbuKhadra MR, Basyouny MG, El-Sherbeeny AM, et al. Transesterification of commercial waste cooking oil into biodiesel over innovative alkali trapped zeolite nanocomposite as green and environmental catalysts. Sustain Chem Pharm. 2020;17:100289.