Chemical Process Design Vol.4 No.2 (2025) 50-63

University of Sistan
and Baluchestan

Chemical Process Design

Available online at http://cpd.usb.ac.ir/

A Mini-Review on Biodiesel Production using Zeolite-based Catalysts

Mohammad Radi[1] , Ensie Bekhradinassab[2]✉

[1]Chemical Engineering Department, Faculty of Engineering, Behbahan Khatam Alanbia University of Technology, Behbahan, Iran. E-mail: mohammad.radii0078@gmail.com

[2] Corresponding Author, Chemical Engineering Department, Faculty of Engineering, Behbahan Khatam Alanbia University of Technology, Behbahan, Iran. E-mail: en.bekhradinassab@bkatu.ac.ir

ARTICLE INFO

Article type:
Review Article

Article history:
Received: 2025-05-01
Received in revised form: 2025-08-02
Accepted: 2025-08-03
Available online: 2025-08-03

Keywords: *Magnetic nanoparticles; Salen Ru(OTf)₂; Acetylation; Alcohol acetylation; Phenol acetylation; Schiff base; Recyclable Nano catalyst*

ABSTRACT

With increasing environmental concerns and the depletion of fossil fuels, biodiesel has emerged as a crucial renewable energy alternative. Among various production methods, zeolite-based solid catalysts have gained significant attention due to their high surface area, thermal stability, and reusability. Unlike traditional liquid alkaline catalysts, zeolites reduce soap formation, corrosion, and purification requirements, making them more efficient and environmentally friendly. However, challenges such as mass transfer limitations in micropores, sensitivity to feedstock impurities, and stability under harsh reaction conditions remain obstacles to their widespread adoption. This mini-review explores recent advancements in acidic, bi-functional, and basic zeolite catalysts for biodiesel production via esterification and transesterification. Strategies to overcome existing limitations, such as hierarchical pore design, surface modification, and composite formation, are discussed. Future research directions focus on nanostructure engineering and multifunctional composites to improve catalytic performance, durability, and cost-effectiveness. Despite current technical hurdles, zeolites demonstrate strong potential for sustainable biodiesel production. Continued innovation in catalyst design and process optimization could further enhance their efficiency, making them a viable solution for cleaner energy generation. The findings emphasize the importance of zeolite catalysts in advancing renewable fuel technologies while addressing environmental and economic concerns.

Cite this article: Radi, S., Bekhradinassab, E., (2025), A Mini-Review on Biodiesel Production using Zeolite-based Catalysts, *Chemical Process Design*, 4(2), 50-63. http//doi.org/10.22111/cpd.2025.51871.1056

Publisher: University of Sistan and Baluchestan.

1. Introduction

Considering the serious environmental problems and limitations in fossil fuel resources, the search for alternative and sustainable energy sources has become more important. Meanwhile, biodiesel, as a renewable fuel from natural resources such as vegetable oils and animal fats, can be a suitable alternative to fossil fuels. This fuel not only helps preserve the environment, but also reduces dependence on oil resources [1].

Biodiesel, which is an alkyl fatty acid ester, is created through transesterification or esterification processes that utilize catalysts. Homogeneous base catalysts like CH_3ONa, NaOH, and KOH are known for their high efficiency; however, they necessitate low levels of water and free fatty acids (FFAs) to prevent saponification [2]. On the other hand, acid catalysts such as H_2SO_4 and HCl are also employed, but they incur significant operational costs due to the need for purification and waste management. In contrast, heterogeneous catalysts provide advantages like straightforward recovery and reusability, making them more appropriate for continuous production methods. Therefore, choosing an effective and cost-efficient catalyst is essential for enhancing biodiesel production [3]. For example, heterogeneous zeolite catalysts achieve comparable conversion efficiencies (85-95%) while tolerating higher impurity levels (FFA <5%, water <1.5%), reducing wastewater generation by 60-80%, and maintaining >80% activity after 5-10 reaction cycles [4].

Zeolites are versatile materials with a wide range of structural and acidic properties. Their surface areas typically range from 350 to 700 m^2/g, and their pore volume is approximately 0.1cm^3/g. These features make zeolites effective catalysts due to their high surface area, substantial pore volume, and significant acidity. All zeolites contain Al, but they may also include Na or other monovalent or divalent metals. The monovalent or divalent ions, as well as Al ions, create Lewis acidic sites, and when these metals are bonded with OH groups, they generate strong Bronsted acid sites. Most of the pore volume in zeolites consists of micropores, which limits their use for large molecules like free fatty acids due to diffusion restrictions [5].

This mini-review systematically examines recent advances in zeolite-catalyzed biodiesel production, with particular focus on three critical aspects: (1) structure-activity relationships of acidic, basic, and bi-functional zeolites, (2) synthesis methods that overcome diffusion limitations, and (3) techno-economic challenges in industrial implementation. By critically analyzing over 50 recent studies, we highlight both fundamental breakthroughs and persistent gaps in catalyst stability and scalability. The discussion progresses from fundamental mechanisms to applied considerations, providing researchers with a balanced perspective on translating zeolite innovations into practical biodiesel technologies.

2. Biodiesel production process by zeolite-based catalyst

In order to investigate biodiesel production by zeolite-based catalyst, first, different and conventional types of zeolites are compared below:

- **H-ZSM-5 (MFI topology):**

Pore System: 3D network of 10-member ring channels (5.1×5.5 Å and 5.3×5.6 Å).

Advantages: High thermal stability (>500°C) and strong Brønsted acidity.

Performance: Effective for the esterification of small FFAs but suffers from diffusion limitations for bulky triglycerides (TGs) due to narrow pores [6].

- **H-Beta (BEA topology)**

Pore System: Interconnected 12-member ring channels (6.6 × 6.7 Å) [7].

Advantages: Larger pores accommodate triglycerides and FFAs efficiently; balanced Brønsted/Lewis acidity (NH_3-TPD confirmed).

Performance: Optimal for simultaneous esterification-transesterification (95.3% yield at 200°C with 55% Phosphotungstic acid (TPA)) [6].

- **H-Y (FAU topology)**

Pore System: 3D super cages (7.4 Å) accessible via 12-ring windows.

Advantages: Highest pore volume ($0.35\ cm^3/g$) for bulky molecules.

Performance: Excels in esterification but shows lower transesterification activity (32.7% yield) due to weaker acid strength.

Trade-offs: H-Beta's intermediate pore size and acidity resolve the limitations of H-ZSM-5 (diffusion constraints) and H-Y (moderate transesterification activity).

Hierarchical Design: As demonstrated by Baroi et al. (2014) [6], introducing mesoporosity (e.g., via TPA impregnation) in H-Beta improves triglyceride diffusion while preserving acidity, achieving 99.3% biodiesel yield under industrial conditions.

Stability: H-Y maintains crystallinity up to 850°C, whereas H-Beta requires stabilization (e.g., Zr-doping) above 550°C [6, 7].

Because zeolites are acidic catalyst, zeolite-based catalysts are applicable in esterification and transesterification reactions. Zeolite-based catalysts like zeolite-supported KOH present only basic sites due to the basic property of their collaborator components. In that case, it is appropriate only in the transesterification reaction. Consequently, zeolite-based catalysts are divided into three following sub-sections, whose reaction mechanism will be investigated in biodiesel generation reactions.

2.1. Acidic zeolite-based catalysts

Acidic zeolite-based catalysts are suitable for both esterification and transesterification reactions, particularly in biodiesel production. The reaction mechanism for biodiesel generation involves several stages. Initially, reactants migrate from the surrounding fluid to the external surface of the catalyst. Then, they move through the zeolite's pore structure. Once inside, the reactants are adsorbed onto the acidic sites of the zeolite. In the next step, a chemical reaction occurs between the adsorbed reactants, facilitated by the acidic sites. The products are then desorbed from the internal surface of the catalyst and exit through the pores to the external surface. Finally, the products return to the fluid phase [8].

As presented in Fig. 1(a), in the case of transesterification, triglycerides (TGs) are the feedstock. The acidic sites on the zeolite surface interact with the carbonyl group of the TG molecule, leading to bond formation. The carbonyl carbon in TG, seeking to balance its electron deficiency, attracts methanol through its electron pair. This results in the formation of an unstable intermediate, which eventually leads to the production of biodiesel and glycerol [9, 10]. For esterification reactions as presented in Fig. 1(b), where free fatty acids (FFAs) are the feed, the process is similar. The acidic sites on the zeolite interact with the oxygen in the carboxyl group of the FFA, pulling methanol into the reaction. An intermediate compound is formed, and water is released, resulting in the formation of biodiesel. In both esterification and transesterification reactions, zeolite-based catalysts facilitate the conversion of feedstock into biodiesel, with the zeolite structure providing the necessary acidic sites for the reaction to proceed efficiently [5].

2.2. Bi-functional zeolite-based catalysts

Bi-functional zeolite-based catalysts contain both acidic and basic sites, enabling them to facilitate both esterification and transesterification reactions. The acidic sites interact with FFAs and TGs in the same way as explained in the previous section, helping to create biodiesel by adsorbing reactants and promoting the reaction. On the other hand, the basic sites function differently. As presented in Fig. 1(c), they deprotonate alcohol, forming an alkoxide ion, which then attacks the carbonyl group of the triglycerides in a nucleophilic manner. This leads to the formation of an intermediate compound, where the double bond between the carbon and oxygen in the carbonyl group is converted to a single bond, and the oxygen gains a negative charge. The carbonyl carbon forms a new double bond, causing the removal of a biodiesel molecule from the intermediate compound. The oxygen that was bonded to the removed biodiesel takes a proton from the catalyst. The catalyst is then deprotonated, allowing the process to continue, resulting in the formation of three molecules of biodiesel and one molecule of glycerol [9, 11].

2.3. Basic zeolite-based catalysts

Some zeolite-based catalysts, depending on their synthesis method or the presence of strongly basic components, may exhibit dominant basic behavior, even if they originally possess acidic properties. If the active phase consists of basic catalysts, such as basic metal oxides, these catalysts are suitable for transesterification reactions, where the reaction occurs via basic sites. Zeolites are naturally acidic because of aluminum atoms in their framework. These atoms create negative charges that are balanced by exchangeable cations, leading to acidic sites. To add basicity. We replace the acidic protons (H^+) or other cations in the zeolite with alkali Metals (like Lithium, Sodium, Potassium, Rubidium, Cesium) and alkaline Earth Metals (like Magnesium, Calcium, Strontium, Barium) through a process called ion exchange. Larger alkali metal cations, like cesium or potassium, tend to create stronger basicity. In this type of catalyst, the basic sites facilitate the deprotonation of alcohol, which then leads to the formation of an alkoxide ion. This alkoxide attacks the carbonyl carbon of triglycerides in a nucleophilic manner, enabling the transesterification process to proceed [5, 12].

3. Effect of Zeolite Parameters and Technical Challenges in Biodiesel Production

The performance of zeolite-based catalysts in biodiesel production is strongly influenced by their structural and chemical properties. Firstly, pore size plays a critical role; zeolites with larger pores are more suitable for accommodating bulky triglyceride molecules. Recent studies demonstrate that hierarchical pore design (e.g., mesoporous ZSM-5 with 5-30nm channels) increases Brønsted acid site accessibility from 4% to 22%, boosting FAME yield from 68% to 95% [13]. Recent advances in hierarchical zeolite synthesis demonstrate that templating methods (hard/soft) can precisely tailor mesopore dimensions (5–50nm), significantly improving diffusion kinetics. For instance, carbon nanotube-templated mesopores (20-40 nm) in ZSM-5 reduce triglyceride Thiele modulus (Φ) by 60% via Pickering emulsion stabilization, achieving FAME yields up to 95% while mitigating coking. Soft-templating with CTAB further retains 85% microporosity while introducing 5–15nm mesopores, optimizing active site accessibility [14].

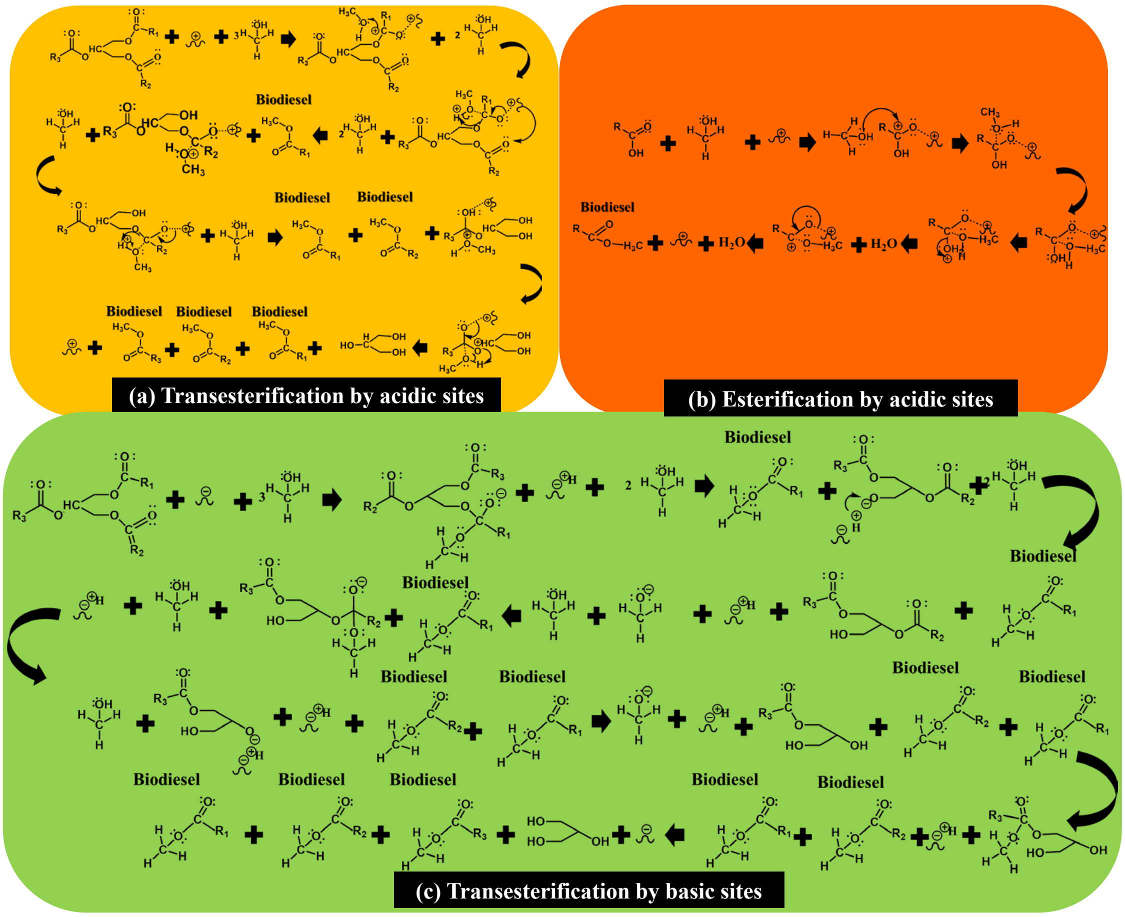

Fig. 1. Reaction pathways: (a) Transesterification by acidic sites; (b) esterification by acidic sites; and (c) transesterification by basic sites (Original)

Secondly, the Si/Al ratio is another key factor; lower values in the range of 10-20 enhance Brønsted acidity, which is beneficial for catalytic activity [15]. Notably, hierarchical zeolites with bimodal (micro-meso) pore systems can decouple acidity from Si/Al constraints.

Wang et al. (2024) report that even at high Si/Al (30–100), hierarchical ZSM-5 exposes 49% of Brønsted sites (vs. 4-6% in conventional zeolites) due to mesopore-assisted diffusion. This reconciles the trade-off between stability (high Si/Al) and acidity (low Si/Al), achieving 90-95% esterification yields under industrial conditions [14]. As explained before, zeolite catalysts face certain technical challenges. One major issue is mass transfer limitation (Thiele modulus $\Phi>5$ for triglycerides), which can be addressed by: (1) designing nanostructured zeolites with hierarchical porosity, where zeolite nanoparticles at oil-methanol interfaces reduce diffusion path lengths by 60% via Pickering emulsion stabilization, or (2) employing two-phase liquid-liquid systems [16]. Another challenge is the reduction in catalytic activity due to impurities in the feedstock. This can be mitigated through surface modification of the zeolite with hydrophobic groups (e.g., via silanolysis) [17] and pretreatment of oils to remove free fatty acids [18]. Moreover, another important property of zeolites is their high thermal and chemical stability. These properties allow zeolites to perform well in harsh industrial reaction conditions, including high temperatures and complex reaction environments, without reducing their performance. Zeolites are able to maintain their catalytic activity at high temperatures, even in acidic or basic chemical environments, due to their stable crystalline structure. This property makes zeolites more durable in biodiesel production processes, which are usually carried out under high temperatures and intense reaction conditions, and reduces the need for catalyst replacement [19].

3.1. Effect of Si/Al ratio on surface area, pore size, pore volume, and acid-base properties of zeolites

The Si/Al ratio has a significant impact on the structural and catalytic properties of zeolites. Increasing the Si/Al ratio generally leads to a decrease in the concentration of Al^{3+} in the zeolite framework, which results in a reduction in Brønsted acidity. Recent studies using advanced characterization techniques like FTIR with bulky probe molecules (e.g., 2,4,6-trimethylpyridine) reveal that accessibility of acid sites often limits catalytic performance more than total acidity. Hierarchical zeolites with bimodal (micro-meso) pore systems demonstrate 2-3×higher reaction rates by exposing up to 49% of Brønsted sites compared to 4-6% in conventional zeolites [13]. This decrease in acidity is due to fewer aluminum sites available for proton donation, which directly affects catalytic behavior, especially in acid-catalyzed reactions.

As the Si/Al ratio increases, the zeolite structure tends to be more silicon-rich, leading to a greater surface area and larger pore sizes. The higher Si/Al ratio also leads to a more robust and stable framework, which often results in increased thermal stability and resistance to framework collapse under harsh reaction conditions [20]. Additionally, the pore volume can decrease with higher Si/Al ratios as the framework becomes more rigid and compact, reducing void spaces. These structural and chemical modifications make zeolites with higher Si/Al ratios more suitable for reactions involving larger molecules, such as biodiesel production or hydrocarbon cracking [21]. The overall catalytic performance is also influenced by the acid-base properties of zeolites, which are determined by the Si/Al ratio. Zeolites with a low Si/Al ratio tend to have stronger acidic sites, while those with a high Si/Al ratio exhibit more neutral or weakly basic properties, making them more selective for certain catalytic applications, such as base-catalyzed reactions [21]. This balance between acidity and basicity is crucial for optimizing catalytic performance in various reactions, including esterification and transesterification processes [5].

Table 1 provides a quantitative comparison of how Si/Al ratios and hierarchical pore structures affect three critical catalyst properties: acid site accessibility, thermal stability, and biodiesel production efficiency. The data highlights the advantages of hierarchical zeolites in overcoming traditional trade-offs between acidity and stability. The data demonstrate that hierarchical zeolites uniquely combine: (1) high acid site accessibility (22-49%) through designed mesoporosity, (2) intermediate thermal stability (450˚C) via zirconium stabilization, and (3) superior esterification yields (90-95%). This resolves the conventional compromise between low-Si/Al (high acidity but poor stability) and high-Si/Al (high stability but weak acidity) zeolites [13].

Table 1. Comparative performance of zeolite catalysts: Effects of Si/Al ratio and hierarchical porosity

Parameter	Low Si/Al (10-20)	High Si/Al (30-100)	Hierarchical zeolites	Ref.
Bronsted acid sites accessibility	4-6% (Pyridine)	<5 %	22-49% (TIPB probe)	[13] [14]
Thermal stability	<400°C	>600°C	450°C (Zr-stabilized)	[13] [14]
Esterification yield	70-85 %	50-65 %	90-95%	[13] [14]
Coking resistance	Low	Moderate	High (40% reduction)	[14]

4. Methods for synthesizing zeolites

4.1 Hydrothermal synthesis

In this method, silica and alumina precursors are subjected to an alkaline environment at temperatures of 150-250˚C and autogenous pressure [22]. This process allows for precise control of the pore size and acid strength of the catalyst [11, 23]. Zeolites produced by this method have shown an efficiency of over 95% in transesterification reactions [24]. In this process, precursors such as sodium silicate (Na_2SiO_3) and sodium aluminate ($NaAlO_2$) are placed in an alkaline environment in the presence of water, in a closed reactor (autoclave), and heated at a temperature between 150 and 250°C and under spontaneous pressure for several hours to several days. During this process, zeolite crystals are formed whose structural properties, such as pore size, Si/Al ratio, and degree of crystallinity, can be precisely controlled [25].

- **Mechanistic insights:** The hydrothermal crystallization process occurs through four distinct phases:

  Precursor dissolution: Alkaline medium (pH 10-13) breaks down raw materials into reactive silicate ($SiO(OH)_3^-$) and aluminate ($Al(OH)_4^-$) species.

  Nucleation: Tetrahedral units organize into secondary building blocks (4-6 membered rings)

  Crystal growth: Progressive attachment of building units to crystal surfaces

  Ostwald ripening: Smaller crystals dissolve to feed growth of larger ones [26].

- **Key Parameters and Controls:**

  Precursor chemistry: Sodium silicate (Na_2SiO_3) and sodium aluminate ($NaAlO_2$) provide precise Si/Al control (1-∞)

  Alkali concentration: 1-5 M NaOH/KOH solutions mediate dissolution rates

  Crystallization time: Ranges from 6 hours to 14 days depending on desired morphology

  Temperature gradients: Typically 5°C/min heating ramps prevent defect formation

- **Structural Properties Achievable:**

  Pore sizes from 0.5nm (micropores) to 50nm (mesopores)

  Crystallinity >95% as verified by XRD

  Acid site densities of 0.4-1.5mmol/g

  Thermal stability up to 600°C

Table 2. Optimization of Hydrothermal Synthesis Parameters for Biodiesel Production [26]

Parameter	Typical range	Effect on properties	Optimal value for biodiesel catalysts	Characterization methods
Temperature	150-250°C	T → faster crystallization	180-200°C	XRD
Time	6 h - 14 days	↑t → larger crystals	48-72 h	Particle size analysis
Si/Al ratio	1-200	↓ratio → ↑acidity	10-20	ICP-OES, EDX
Alkali conc.	0.5-8 M	↑$[OH^-]$ → smaller particles	1-2 M NaOH	pH measurements
Precursor type	Various	Affects purity and cost	$Na_2SiO_3/NaAlO_2$	FTIR
Stirring rate	0-500 rpm	↑mixing → more uniform particles	200-300 rpm	FESEM
Aging time	0-48 h	Affects meso-porosity	24 h at 60 °C	

4.2. Surfactant-assisted synthesis

The use of surfactants allows the creation of mesoporous structures. These structures allow for better access of large triglyceride molecules to the active sites [27]. In this technique, surfactants such as CTAB (cetyltrimethylammonium bromide) are used as molecular templates to create mesoporous structures. The surfactant is incorporated into the zeolite structure during synthesis, and after the formation of the crystalline phase, it is removed by methods such as calcination or solvent extraction, leaving a stable mesoporous structure. The main advantage of this method is the increased permeability of bulky molecules such as triglycerides into the zeolite structure and, consequently, the increase in the reaction rate [28].

4.3. Template-assisted synthesis

Template-assisted synthesis has been widely utilized to modify the pore structures of zeolites, enhancing their suitability for catalytic applications such as biodiesel production. By employing various templating agents, researchers have successfully enlarged the pore sizes of zeolites, facilitating better diffusion of larger molecules like triglycerides. For instance, a study demonstrated the use of biodiesel-derived waste glycerol as a green template to create mesopores in ZSM-5 zeolites. This approach not only introduced mesoporosity but also maintained the zeolite's MFI structure, resulting in improved catalytic performance for aromatics production [29].

Another approach involved the dual-template synthesis of SSZ-13 zeolites using trimethyl-adamantanammonium hydroxide and a diquaternary-ammonium mesoporogen. This method induced significant mesoporosity without compromising the zeolite's microporosity, enhancing the accessibility of Brønsted acid sites and improving stability during methanol-to-olefins reactions [30]. Additionally, a sustainable method employed biomass-derived, monolithic N-doped carbonaceous templates to synthesize mesoporous ZSM-5 zeolites. This approach resulted in single crystals with intracrystalline mesopores ranging from 12 to 16nm, offering a cost-effective and flexible platform for synthesizing micro-/mesoporous crystalline zeolites [31].

4.4. zeolite-based composites

Recent research has shown growing interest in the development of zeolite-based composites to enhance the physicochemical and catalytic properties of traditional zeolites. These composites often involve the integration of zeolites with other inorganic materials such as bentonite or the incorporation of metal species like barium through methods such as hydrothermal synthesis or co-precipitation followed by calcination. The formation of such composites not only improves the textural and structural stability of the zeolite framework but also introduces new active sites or enhances existing ones, contributing to greater surface basicity, porosity, and thermal resistance. Additionally, the synergy between zeolites and co-components (e.g., clay minerals or alkaline earth metals) often results in materials with superior dispersion of active species and more accessible pore structures, which can be particularly beneficial in catalytic applications requiring larger reactant molecules. These modifications make zeolite-based composites promising candidates for use in environmentally relevant processes, including those involving biomass-derived feedstocks [32].

5. Uses of zeolite in biodiesel production

5.1. Zeolites in the transesterification process

In biodiesel production, the use of zeolite-based catalysts has attracted significant attention due to their unique properties such as high surface area, basic strength, and resistance to water and acid. Studies have shown that zeolite catalysts significantly improve the performance of the transesterification reaction. As shown in Table 3, for instance, in a study using CaO/NaY catalyst, the biodiesel yield reached 95% at 65°C with a reaction time of 3 hours [33]. In another study, the La_2O_3/NaY catalyst achieved a biodiesel yield of 84.6% from castor oil under optimized conditions of 70°C and 50 minutes [34]. Moreover, Zeolite Beta with a high Si/Al ratio achieved a conversion efficiency of over 90% in one hour for the transesterification of triolein [35]. Lastly, catalysts derived from natural diatomaceous earth exhibited excellent performance, achieving biodiesel yields of over 98% from soybean and palm oils [36].

Table 3. Zeolites in the transesterification process

Catalyst type	Oil source	Temperature (°C)	Time (h)	M:r Ratio	Yield (%)	Ref.
CaO/NaY	Soybean Oil	65	3	9:1	95	[33]
La_2O_3/NaY	Castor Oil	70	0.83	15:1	84.6	[34]
Beta	Triolein	63	1	-	>90	[35]
CAN	Soybean and Palm	63-70	12	-	>98	[36]

5.2. Zeolites in the esterification process

A variety of zeolite catalysts have been tested for the esterification of free fatty acids (FFAs) and bio-oil constituents to produce biodiesel, yielding varying results depending on the catalyst type, reaction conditions, and feedstock. As seen in Table 4, one study using zeolite Y prepared from Iraqi kaolin for esterification of oleic acid with ethanol achieved an 85% conversion at 70°C with a 5wt% catalyst loading and a 6:1 ethanol to oleic acid molar ratio after 60 minutes. In comparison, a commercial HY zeolite showed a lower conversion of 76% under similar conditions [37]. Another study focused on Al-MCM-41 mesoporous zeolites with Si/Al ratios of 8, 16, and 32 for esterification of palmitic acid with methanol, ethanol, and isopropanol. The highest conversion was obtained with the Al-MCM-41 zeolite at a Si/Al ratio of 8, achieving a satisfactory conversion with methanol, and the reaction was found to follow first-order kinetics [38].

For esterification of oleic acid in a fixed-bed reactor, the addition of Co-Ni-Pt to FAU-type zeolite increased the conversion to 93% in batch mode and 89% in continuous mode, exceeding results from similar studies [39]. Additionally, catalysts containing 12-tungstosilicic acid anchored to zeolite Hβ achieved an 86% conversion for oleic acid esterification, while transesterification of soybean oil reached a 95% conversion. The catalyst was recyclable for up to four cycles with no loss in performance [40].

A study using analcime zeolite from geothermal solid waste achieved an impressive biodiesel yield of 98.3% at 300°C with a 5wt% catalyst loading after one hour. Analcime (ANA) zeolite exhibits limited recyclability due to irreversible structural changes at high temperatures (300°C), consistent with prior reports [41]. While achieving high initial yields (~98%), its rapid deactivation after 3 cycles restricts practical use. For industrial applications, more stable zeolites (e.g., HY, Beta) with regenerable acid sites are preferable alternatives. The transformation from ‘stacked-book’ to ‘square-flake’ morphology after reuse confirms irreversible framework degradation. To address this, future work should focus on structural stabilization and acid-site preservation [41]. Finally, the esterification of acetic acid and o-cresol using microporous zeolites such as beta and FAU showed high ester formation yields, particularly when secondary meso-porosity was introduced to medium-pore ZSM-5, which alleviated diffusion constraints [42].

Table 4. Zeolites in the transesterification process

Catalyst	Feedstock	Temp. (°C)	M:O Ratio	Time (h)	Catalyst (wt.%)	Con. (%)	Ref.
Y	Oleic acid	70	6:1	1	5	85	[37]
HY	Oleic acid	70	6:1	1	5	76	[37]
FAU	Oleic acid	-	-	2	-	93	[39]
ANA	Fatty acids	300	-	1	5	98.29	[41]

5.3. Zeolites in simultaneous esterification and transesterification

A series of studies have explored the use of zeolite-based catalysts for biodiesel production through simultaneous esterification and transesterification processes, with varying results depending on catalyst type, concentration, and reaction conditions. In one study, catalysts containing 10-40 wt% of 12-tungstosilicic acid anchored to zeolite Hβ were used for esterification of oleic acid and transesterification of soybean oil. The maximum conversion achieved for oleic acid esterification was 86%, while the transesterification of soybean oil reached a 95% conversion [40]. The catalyst demonstrated excellent recyclability, maintaining conversion efficiency over four cycles. In a second study using analcime zeolite from geothermal solid waste, a biodiesel yield of 98.3% with 100% fatty acid alkyl ester (FAAE) content was achieved at a catalyst concentration of 5wt% and a reaction temperature of 300°C for one hour. However, the catalyst lost efficiency after three cycles, showing that regeneration was not feasible due to morphological changes [41]. A third study utilized Fe/Zeolite catalysts synthesized via a hydrothermal process from waste geothermal resources. The effect of catalyst concentration (ranging from 0.01g/g to 0.03g/g) and temperature (50°C to 70°C) was studied. The results indicated an increase in biodiesel yield with both higher catalyst concentration and reaction temperature, confirming the positive influence of these variables on the process [43].

5.3.1. Challenges in producing stable bi-functional zeolites

Producing stable bi-functional zeolites where both acidic and basic sites retain their activity over multiple reaction cycles presents several significant challenges:

Site stability and leaching: Both acidic and basic sites can be susceptible to leaching under harsh reaction conditions (e.g., high temperatures, presence of water, polar solvents). For example, highly acidic protons (Brønsted acid sites) can be exchanged with metal ions, or basic active species (like supported metal oxides or organic bases) can dissolve or detach from the zeolite framework. This loss of active sites directly reduces catalytic activity and limits recyclability [44].

Thermal stability: Zeolites themselves are generally thermally stable, but the incorporated acidic or basic functionalities might not be. High reaction temperatures, especially those used in some transesterification processes, can lead to sintering of basic metal oxides, dealumination of acidic zeolites (reducing acidity), or decomposition of organic basic groups. These changes alter the catalytic properties and can lead to irreversible deactivation [45].

Pore blocking and fouling: During reactions involving triglycerides and fatty acids, byproducts like glycerol and other heavy organic compounds can deposit on the catalyst surface and within the zeolite pores. This phenomenon, known as fouling or coking, can physically block access to both acidic and basic sites, reducing their effectiveness over time. This is a common issue in many heterogeneous catalytic processes, and zeolites, with their defined pore structures, can be particularly vulnerable [46].

Regeneration challenges: While some catalysts show good recyclability, regenerating bi-functional zeolites to restore both types of sites can be complex. Different regeneration methods (e.g., calcination to remove coke, acid washing to restore acidity) might preferentially damage or deactivate one type of site while trying to restore the other. Finding a mild and effective regeneration protocol that preserves both functionalities is crucial but difficult [47].

Synthesis control: Achieving a balanced distribution and optimal strength of both acidic and basic sites during synthesis is inherently challenging. The methods used to introduce one type of site might inadvertently affect the other, leading to a suboptimal catalyst. Precise control over precursor ratios, synthesis temperatures, and post-treatment procedures is essential to ensure the creation of stable and active bi-functional materials [48].

6. Economic considerations and comparative feasibility of zeolite catalysts

While zeolite-based catalysts offer significant advantages in biodiesel production, their economic viability must be critically evaluated against other heterogeneous catalysts. The synthesis cost of zeolites is indeed higher than that of conventional solid catalysts (e.g., CaO, MgO, or hydrotalcites) due to the energy-intensive hydrothermal processes and templating agents required for hierarchical pore design [13, 14]. However, the long-term economic benefits of zeolites arise from their:

Enhanced reusability: Zeolites exhibit superior stability under harsh reaction conditions (e.g., high temperatures, water presence) compared to low-cost metal oxides, which often leach or deactivate rapidly [44, 45]. For instance, CaO catalysts suffer from irreversible deactivation due to hydroxide formation, whereas zeolites retain >80% activity after 5 cycles [33, 36].

Feedstock flexibility: Zeolites can process low-quality feedstocks (e.g., waste cooking oil with high FFA content) without extensive pretreatment, reducing upstream costs [18, 41]. In contrast, base catalysts like CaO require stringent FFA limits (<1%) to avoid saponification [12].

Scalability potential: Recent advances in waste-derived zeolite synthesis (e.g., from kaolin or geothermal byproducts [37, 41]) have reduced raw material costs. Additionally, templating methods (e.g., surfactant-assisted synthesis) now enable mesopore creation without expensive organics [27, 28].

Comparative performance: Although metal oxides (e.g., CaO) show higher initial activity, zeolites outperform them in continuous processes due to resistance to pore clogging and sintering [46]. For example, hierarchical ZSM-5 achieves 95% FAME yield vs. 80% for CaO/Al_2O_3 under identical conditions [13].

Despite these advantages, further research is needed to optimize zeolite synthesis routes (e.g., microwave-assisted crystallization) and explore hybrid catalysts (e.g., zeolite-supported low-cost metals) to bridge the cost gap. A techno-economic analysis (TEA) comparing zeolites with other heterogeneous catalysts (e.g., hydrotalcites, sulfated zirconia) would provide clearer insights for industrial adoption.

6. Conclusion

Zeolites, especially when modified or synthesized from natural or waste materials, offer a promising alternative to traditional biodiesel catalysts. Their high surface area, tunable porosity, and acidity make them suitable for catalyzing both esterification of free fatty acids and transesterification of triglycerides, which are key steps in biodiesel production. One of the main advantages of zeolite catalysts is their ability to promote high conversion rates under mild reaction conditions. Additionally, zeolites have shown considerable stability and reusability, making them attractive for long-term use in biodiesel production. Their ability to catalyze reactions efficiently, even in the presence of water or free fatty acids, makes them suitable for processing low-quality feedstocks, such as waste oils or fats, without the need for extensive pre-treatment. While the catalytic performance of zeolites has been proven in several studies, there remain challenges regarding their long-term stability and the regeneration of their catalytic activity after multiple reaction cycles. Some zeolites show a decrease in activity due to changes in their structural integrity or acidity after prolonged use. However, modifications to zeolite structures, such as doping with metals or altering the framework, have been explored to improve their durability and efficiency.

In conclusion, zeolites offer a sustainable and efficient approach to biodiesel production, particularly when synthesized from waste materials or modified to improve their catalytic properties. Continued research into optimizing their structural stability, recyclability, and cost-effectiveness will be crucial for scaling their use in industrial biodiesel production processes. Moreover, integrating zeolite-based catalysts into biodiesel production can contribute to reducing environmental impact by repurposing waste materials and providing a greener alternative to conventional catalytic systems.

Future research should prioritize (1) bio-inspired templating to lower costs, (2) Mashine Learning-guided design of adaptive zeolites, and (3) 3D-printed monolithic catalysts for continuous flow systems. Emerging techniques like plasma-assisted synthesis and single-atom doping offer disruptive potential but require fundamental studies to address scalability constraints.

References

[1] Bekhradinassab, E., Tavakoli, A., Haghighi, M., Shabani, M., 2022. Catalytic biofuel production over 3D macro-structured cheese-like Mn-promoted TiO2 isotype: Mn-catalyzed microwave-combustion design. Energy Conversion and Management, 251, 114916. https://doi.org/10.1016/j.enconman.2021.114916

[2] Bekhradinassab, E., Ghasemi, I., 2025. Synthesis of Fe2O3-supported lightweight expanded clay aggregate (LECA) via solution combustion: An innovative and cost-effective catalyst for biodiesel generation. Surfaces and Interfaces, 106582. https://doi.org/10.1016/j.surfin.2025.106582

[3] Bekhradinassab, E., Haghighi, M., Tavakoli, A., Shabani, M., 2022. Mn-Fe catalyzed microwave combustion-plasma hybrid synthesis of 2D chips-like Mn-Fe boosted TiO2 architecture self-assembled of nano-walled honeycomb-like super-macroporous: Green fuel generation. Energy Conversion and Management, 270, 116178. https://doi.org/10.1016/j.enconman.2022.116178

[4] Sun, K., Lu, J., Ma, L., Han, Y., Fu, Z., Ding, J., 2015. A comparative study on the catalytic performance of different types of zeolites for biodiesel production. Fuel, 158, 848–854. https://doi.org/10.1016/j.fuel.2015.06.048

[5] Bekhradinassab, E., Haghighi, M., Shabani, M., 2025. A review on acidic metal oxide-based materials towards heterogeneous catalytic biodiesel production via esterification process. Fuel, 379, 132986. https://doi.org/10.1016/j.fuel.2024.132986

[6] Baroi, C., Mahto, S., Niu, C., Dalai, A.K., 2014. Biofuel production from green seed canola oil using zeolites. Applied Catalysis A: General, 469, 18–32. https://doi.org/10.1016/j.apcata.2013.09.034

[7] Arumugam, M., Goh, C.K., Zainal, Z., Triwahyono, S., Lee, A.F., Wilson, K., Taufiq-Yap, Y.H., 2021. Hierarchical HZSM-5 for catalytic cracking of oleic acid to biofuels. Nanomaterials, 11 (3), 747. https://doi.org/10.3390/nano11030747

[8] Ghasemi, I., Haghighi, M., Bekhradinassab, E., 2025. Microwave assisted combustion design and performance screening of NiM2O4 (M: Zn and Mn) spinels enhanced by lamellar porous graphene oxide nanosheets for biodiesel production. Journal of Environmental Chemical Engineering, 116263. https://doi.org/10.1016/j.jece.2025.116263

[9] Bekhradinassab, E., Tavakoli, A., Haghighi, M., Shabani, M., 2023. 2-Hydroxyethylammoniumsulfate ionic liquid performance as simultaneous fuel and sulfating agent in tablet-like manganese and iron incorporated titania synthesis: Biodiesel production from waste oil. Fuel, 340, 127402. https://doi.org/10.1016/j.fuel.2023.127402

[10] Ebrahimi, A., Haghighi, M., Ghasemi, I., Bekhradinassab, E., 2024. Design of highly recoverable clay-foundation composite of plasma-treated Co3O4/Kaolin to produce biodiesel from low-cost oil. Fuel, 366, 131267. https://doi.org/10.1016/j.fuel.2024.131267

[11] Shokrani, R., Haghighi, M., Mohammadpour, M., 2022. Influence of ultrasound irradiation power on surface design of CaO nanoparticles over secondary carbon-templated meso designed ZSM-5 for biofuel production from vegetable oil. Fuel, 323, 124387. https://doi.org/10.1016/j.fuel.2022.124387

[12] Ghasemi, I., Haghighi, M., Bekhradinassab, E., Ebrahimi, A., 2024. Ultrasound-assisted dispersion of bifunctional CaO-ZrO2 nanocatalyst over acidified kaolin for production of biodiesel from waste cooking oil. Renewable Energy, 225, 120287. https://doi.org/10.1016/j.renene.2024.120287

[13] Al-Ani, A., Freitas, C., Zholobenko, V., 2020. Nanostructured large-pore zeolite: The enhanced accessibility of active sites and its effect on the catalytic performance. Microporous and Mesoporous Materials, 293, 109805. https://doi.org/10.1016/j.micromeso.2019.109805

[14] Wang, X., Guo, S., Song, P., Xu, L., Zhang, X., Shen, B., 2024. Synthesis and catalytic performance of hierarchically porous catalysts during pyrolysis of lipids to produce liquid hydrocarbons: A review. Applied Catalysis A: General, 677, 119704. https://doi.org/10.1016/j.apcata.2024.119704

[15] Arhancet, J.P., Davis, M.E., 1991. Systematic synthesis of zeolites that contain cubic and hexagonal stackings of faujasite sheets. Chemistry of Materials, 3 (4), 567–569. https://doi.org/10.1021/cm00016a001

[16] Shokrani, R., Haghighi, M., 2020. Textural evolution of hierarchical nanostructured ZSM-5 via sono-hydrothermal design by various carbon shapes for efficient biodiesel production. Applied Catalysis B: Environmental, 271, 118940. https://doi.org/10.1016/j.apcatb.2020.118940

[17] Wang, C., Wang, L., Du, F., Yu, Q., Liang, X., 2023. A two-step organic modification strategy for improving surface hydrophobicity of zeolites. Advanced Powder Technology, 34 (11), 104228. https://doi.org/10.1016/j.apt.2023.104228

[18] Chai, M., Tu, Q., Lu, M., Yang, Y.J., 2014. Esterification pretreatment of free fatty acid in biodiesel production, from laboratory to industry. Fuel Processing Technology, 125, 106–113. https://doi.org/10.1016/j.fuproc.2014.03.025

[19] Al-Jammal, N., Al-Hamamre, Z., Alnaief, M., 2016. Manufacturing of zeolite based catalyst from zeolite tuft for biodiesel production from waste sunflower oil. Renewable Energy, 93, 449–459. https://doi.org/10.1016/j.renene.2016.03.018

[20] Li, J., Gao, M., Yan, W., Yu, J., 2023. Regulation of the Si/Al ratios and Al distributions of zeolites and their impact on properties. Chemical Science, 14 (8), 1935–1959. https://doi.org/10.1039/D2SC06010H

[21] Munthali, M.W., Elsheikh, M.A., Johan, E., Matsue, N., 2014. Proton adsorption selectivity of zeolites in aqueous media: Effect of Si/Al ratio of zeolites. Molecules, 19 (12), 20468–20481. https://doi.org/10.3390/molecules191220468

[22] Liu, M., Li, N., Cao, S., Wang, X., Lu, X., Kong, L., Xu, Y., Bu, X.-H., 2022. A "Pre-Constrained Metal Twins" strategy to prepare efficient dual-metal-atom catalysts for cooperative oxygen electrocatalysis. Advanced Materials, 34 (7), 2107421. https://doi.org/10.1002/adma.202107421

[23] Osatiashtiani, A., Puértolas, B., Oliveira, C.C.S., Manayil, J.C., Barbero, B., Isaacs, M., Michailof, C., Heracleous, E., Pérez-Ramírez, J., Lee, A.F., Wilson, K., 2017. On the influence of Si:Al ratio and hierarchical porosity of FAU zeolites in solid acid catalysed esterification pretreatment of bio-oil. Biomass Conversion and Biorefinery, 7 (3), 331–342. https://doi.org/10.1007/s13399-017-0254-x

[24] Yusuf, B.O., Oladepo, S.A., Ganiyu, S.A., 2023. Zr-modified desilicated ZSM-5 catalysts as highly active and recyclable catalysts for production of biodiesel from soybean oil: Insight into improved catalyst properties, acidity and dispersion through desilication. Fuel, 351, 128729. https://doi.org/10.1016/j.fuel.2023.128729

[25] Sadeghpour, P., Haghighi, M., 2018. High-temperature and short-time hydrothermal fabrication of nanostructured ZSM-5 catalyst with suitable pore geometry and strong intrinsic acidity used in methanol to light olefins conversion. Advanced Powder Technology, 29 (5), 1175–1188. https://doi.org/10.1016/j.apt.2018.02.009

[26] Derbe, T., Temesgen, S., Bitew, M., 2021. A short review on synthesis, characterization, and applications of zeolites. Advances in Materials Science and Engineering, 2021 (1), 6637898. https://doi.org/10.1155/2021/6637898

[27] Du, S., Li, F., Sun, Q., Wang, N., Jia, M., Yu, J., 2016. A green surfactant-assisted synthesis of hierarchical TS-1 zeolites with excellent catalytic properties for oxidative desulfurization. Chemical Communications, 52 (16), 3368–3371. https://doi.org/10.1039/C5CC08441E

[28] Cho, K., Na, K., Kim, J., Terasaki, O., Ryoo, R., 2012. Zeolite synthesis using hierarchical structure-directing surfactants: Retaining porous structure of initial synthesis gel and precursors. Chemistry of Materials, 24 (14), 2733–2738. https://doi.org/10.1021/cm300841v

[29] Wright, P.A., Maple, M.J., Slawin, A.M.Z., Patinec, V., Aitken, R.A., Welsh, S., Cox, P.A., 2000. Cation-directed syntheses of novel zeolite-like metalloaluminophosphates STA-6 and STA-7 in the presence of azamacrocycle templates. Journal of the Chemical Society, Dalton Transactions, (8), 1243–1248. https://doi.org/10.1039/A909249H

[30] Wu, L., Degirmenci, V., Magusin, P.C.M.M., Szyja, B.M., Hensen, E.J.M., 2012. Dual template synthesis of a highly mesoporous SSZ-13 zeolite with improved stability in the methanol-to-olefins reaction. Chemical Communications, 48 (76), 9492–9494. https://doi.org/10.1039/C2CC33994C

[31] White, R.J., Fischer, A., Goebel, C., Thomas, A., 2014. A sustainable template for mesoporous zeolite synthesis. Journal of the American Chemical Society, 136 (7), 2715–2718. https://doi.org/10.1021/ja411586h

[32] Abukhadra, M.R., Ibrahim, S.M., Yakout, S.M., El-Zaidy, M.E., Abdeltawab, A.A., 2019. Synthesis of Na+ trapped bentonite/zeolite-P composite as a novel catalyst for effective production of biodiesel from palm oil; Effect of ultrasonic irradiation and mechanism. Energy Conversion and Management, 196, 739–750. https://doi.org/10.1016/j.enconman.2019.06.027

[33] Wu, H., Zhang, J., Wei, Q., Zheng, J., Zhang, J., 2013. Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts. Fuel Processing Technology, 109, 13–18. https://doi.org/10.1016/j.fuproc.2012.09.032

[34] Du, L., Ding, S., Li, Z., Lv, E., Lu, J., Ding, J., 2018. Transesterification of castor oil to biodiesel using NaY zeolite-supported La2O3 catalysts. Energy Conversion and Management, 173, 728–734. https://doi.org/10.1016/j.enconman.2018.07.053

[35] Wang, Y.-Y., Chen, B.-H., 2016. High-silica zeolite beta as a heterogeneous catalyst in transesterification of triolein for biodiesel production. Catalysis Today, 278, 335–343. https://doi.org/10.1016/j.cattod.2016.03.012

[36] Đặng, T.-H., Nguyễn, X.-H., Chou, C.-L., Chen, B.-H., 2021. Preparation of cancrinite-type zeolite from diatomaceous earth as transesterification catalysts for biodiesel production. Renewable Energy, 174, 347–358. https://doi.org/10.1016/j.renene.2021.04.068

[37] Doyle, A.M., Albayati, T.M., Abbas, A.S., Alismaeel, Z.T., 2016. Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin. Renewable Energy, 97, 19–23. https://doi.org/10.1016/j.renene.2016.05.067

[38] Carmo, A.C., de Souza, L.K.C., da Costa, C.E.F., Longo, E., Zamian, J.R., da Rocha Filho, G.N., 2009. Production of biodiesel by esterification of palmitic acid over mesoporous aluminosilicate Al-MCM-41. Fuel, 88 (3), 461–468. https://doi.org/10.1016/j.fuel.2008.10.007

[39] Alismaeel, Z.T., Abbas, A.S., Albayati, T.M., Doyle, A.M., 2018. Biodiesel from batch and continuous oleic acid esterification using zeolite catalysts. Fuel, 234, 170–176. https://doi.org/10.1016/j.fuel.2018.07.025

[40] Narkhede, N., Patel, A., 2013. Biodiesel production by esterification of oleic acid and transesterification of soybean oil using a new solid acid catalyst comprising 12-tungstosilicic acid and zeolite Hβ. Industrial & Engineering Chemistry Research, 52 (38), 13637–13644. https://doi.org/10.1021/ie402230v

[41] Buchori, L., Widayat, W., Muraza, O., Amali, M.I., Maulida, R.W., Prameswari, J., 2020. Effect of temperature and concentration of zeolite catalysts from geothermal solid waste in biodiesel production from used cooking oil by esterification–transesterification process. Processes, 8 (12), 1629. https://doi.org/10.3390/pr8121629

[42] Milina, M., Mitchell, S., Pérez-Ramírez, J., 2014. Prospectives for bio-oil upgrading via esterification over zeolite catalysts. Catalysis Today, 235, 176–183. https://doi.org/10.1016/j.cattod.2014.02.047

[43] Muna, N.L., Mu'alimah, A.A., Pridiana, D.B., Widodo, A.K., Adiyar, S.R., Elinda, E.H., 2020. The production of biodiesel from waste cooking oil (Simultaneous esterification and transesterification using Fe/zeolite catalysts from waste geothermal). In: Materials Science Forum, Vol. 990, pp. 161–167. Trans Tech Publ. https://doi.org/10.4028/www.scientific.net/MSF.990.161

[44] Shi, Y., Xing, E., Wu, K., Wang, J., Yang, M., Wu, Y., 2017. Recent progress on upgrading of bio-oil to hydrocarbons over metal/zeolite bifunctional catalysts. Catalysis Science & Technology, 7 (12), 2385–2415. https://doi.org/10.1039/C7CY00574A

[45] Ahmedzeki, N.S., Al-Tabbakh, B.A., Antwan, M.B., Yilmaz, S., 2018. Heavy naphtha upgrading by catalytic reforming over novel bi-functional zeolite catalyst. Reaction Kinetics, Mechanisms and Catalysis, 125 (2), 1127–1138. https://doi.org/10.1007/s11144-018-1432-y

[46] Fawaz, E.G., Salam, D.A., Rigolet, S., Daou, T.J., 2021. Hierarchical zeolites as catalysts for biodiesel production from waste frying oils to overcome mass transfer limitations. Molecules, 26 (16), 4879. https://doi.org/10.3390/molecules26164879

[47] Ennaert, T., Van Aelst, J., Dijkmans, J., De Clercq, R., Schutyser, W., Dusselier, M., Verboekend, D., Sels, B.F., 2016. Potential and challenges of zeolite chemistry in the catalytic conversion of biomass. Chemical Society Reviews, 45 (3), 584–611. https://doi.org/10.1039/C5CS00859J

[48] Rahman, N.J.A., Ramli, A., Jumbri, K., Uemura, Y., 2019. Tailoring the surface area and the acid–base properties of ZrO2 for biodiesel production from Nannochloropsis sp. Scientific Reports, 9 (1), 16223. https://doi.org/10.1038/s41598-019-52771-9