MILs as Heterogeneous Catalysts for Biodiesel Production

Shaimaa K. Mohamed[1],*, E. A. El-Sharkawy[1], Hamdy A El-Kady[2], Eman M.A. Ali[2]

[1]Department of Chemistry, Faculty of Science, Suez University, Suez, Egypt

[2]Department of Petroleum Refining and Petrochemical Engineering, Faculty of Petroleum and Mining Engineering, Suez University, Suez, Egypt

ABSTRACT

The fossil fuel supply is being depleted daily due to rising energy usage. Fossil fuels emit greenhouse gases, which contribute to global warming and have many other negative consequences on the environment. The flexible and environmentally friendly biodiesel has become a popular replacement for fuels made from fossil sources. Esterification and transesterification reactions have been used to produce biodiesel using homogeneous and heterogeneous catalysts. During the production of biodiesel, heterogeneous catalysts can overcome the problems that homogeneous catalysts had. To increase the catalytic activity, scientists are currently investigating several catalysts supports because heterogeneous catalysts associated with a deficiency of active sites. Among heterogeneous catalysts, Materials of Institute Lavoisier frameworks (MILs) which is a family of metal organic frameworks has gained the most attention due to its large specific surface area, flexible pore structure, Uniformity in pore size and functional groups. In this review various types of MILs have been discussed. In addition, the different preparation methods of MILs, factors affecting biodiesel production, and properties of produced biodiesel are reviewed.

1. Introduction

Globalization and population density are both increasing quickly, which has led to an excessive use of fossil fuels like petroleum, coal, and gases [1]. This causes environmental problems, global climate change, harmful health consequences from pollution, and an increase in fuel prices, all of which are likely to have an impact on the value of produced goods and the country's economy [2]. The global concern of fossil fuels drawbacks' stem from the proven facts that they are non-renewable, unsustainable, unfavorable as it emits toxic gases and it contributes to the rise in CO2 emissions linked to the greenhouse effect and global warming [2-4]. Biodiesel is an ideal alternative to fossil fuel due to its biodegradability, sustainability, lack of toxic substances and suitability for use in vehicle engines [5]. Other unique qualities of biodiesel includes engine compatibility, greater cetane number, greater combustion efficiency, excellent lubricity and reduced sulfur and aromatic content, which render it as an attractive potential replacement for mineral diesel (Petro-diesel) [6]. By definition, biodiesel is a fuel made of long-chain fatty acid mono-alkyl esters that are obtained from either vegetable oil or animal fats[7, 8] . Since biomass is used to make biodiesel, biodiesel is seen as a renewable resource with the ability to serve as a consistent and dependable energy source.

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* Corresponding author at Suez University

E-mail addresses: shaimaa.mohamed@sci.suezuni.edu.eg (Shaimaa K. Mohamed)

The process to generate biodiesel emits very little waste. Biodiesel has trace levels of nitrogen and no sulfur and oxygen content of 10–11%. Engine combustion efficiency can be enhanced by biodiesel's oxygen concentration[8].

2. The feedstocks for biodiesel production

The properties, composition and concentration of biodiesel depend on the feedstock selection since different natural sources contain different oils and fatty acids. The main feedstocks used to produce biodiesel are divided into the following categories: edible oils, non-edible oils, waste cooking oils, animal fats and algae[9-11]. Fig (1) shows the different sources of feedstock for biodiesel production

2.1. Edible oils resources

Edible oils are known as first generation feedstocks for biodiesel production. Sunflower, soybeans, rapeseed, palm oil and coconut are examples of edible oil resources. The main disadvantage of using edible oil for biodiesel production is the competition between biodiesel production and traditional crops for food which affecting on food security[9, 11].

2.2. Non-edible oils resources

Non-edible oils are known as second generation feedstocks for biodiesel production. Using non-edible oils is a potential method for lowering the amount of edible oils used in the manufacture of biodiesel. Non-edible oils resources include castor bean seed, jatropha, rubber seed, jojoba and rice ban. There are many advantages for using

non-edible oils as a feedstock for biodiesel production: 1) they are incredibly economical in comparison to edible oil, 2) generate beneficial byproducts, 3) they remove competition for fuel and food since they are unfit for human use, 4) they are readily available, renewable, biodegradable, and contain less sulfur and aromatic ingredients [9, 11].

2.3. Waste cooking oil and animal fats

There are several advantages for the environment, the economy, and food security when cheap cooking oil waste is used. Animal fats that might be utilized as feedstock include chicken fat and tallow. Animal fat waste also has economical price for biodiesel production[11].

2.4. Microalgae

They are microbial organisms with the ability to photosynthesis. Because of their basic multicellular or unicellular construction, these bacteria can develop quickly and exist in hard environments. Compared to crops, forests, and aquatic plants, microalgae grow more quickly and take up less space. But the disadvantages of this type of feedstocks are the extraction process of microalgae oil takes time, more pretreatment techniques are required and microalgae biodiesel is less stable due to unsaturated lipids [9, 11].
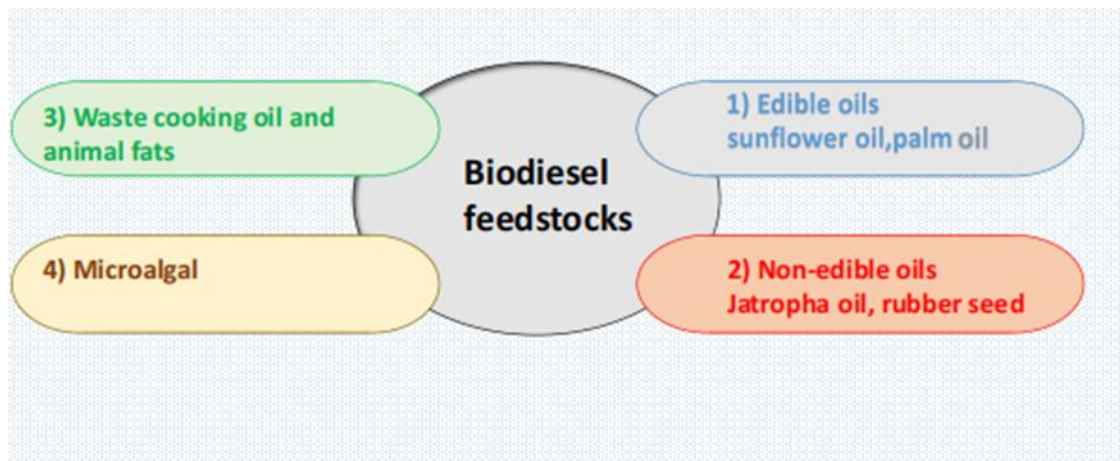

Fig (1): Different sources of feedstocks for biodiesel production

3. Biodiesel Production method

Biodiesel can be produced via a variety of techniques, such as pyrolysis, catalysis, and micro-emulsion. To make oil appropriate for use as diesel engine fuel, all of these techniques seek to lower oil viscosity, improve volatility, and enhance stability against oxidation[12-14].
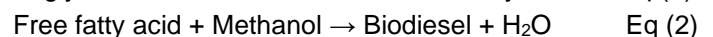
The process of pyrolysis involves the heat decomposition of larger organic molecules into smaller ones without the presence of oxygen or air. The fuel obtained through thermal decomposition is probably going to reach close to diesel fuel. For moderate throughput, the cost of the thermal cracking devices is high[12].

micro-emulsion is the technique for blending the feedstock with appropriate solvents[15]. The commonly utilized solvents in current research include 1-butanol, ethanol, and methanol[9, 13]. Vegetable oils' viscosity was reduced by micro-emulsion but massive carbon deposits were the outcome[12]. Microemulsions are less efficient in producing heat than diesel fuels because of their high alcohol concentration[9].

Typically, the production of biodiesel by chemical catalysis involves transesterification and/or esterification with the use of a homogeneous or heterogeneous catalyst [14].

When vegetable or animal fat (triglycerides) and alcohol are transesterified with the help of a catalyst, a sequence of fatty acid alkyl esters called biodiesel (fatty acid alkyl ester) (FAAE) is produced Eq(1) [16]. Also, biodiesel can be produced through the esterification of free fatty acids such as oleic acid and palmitic acid with methanol or ethanol (Eq (2)) with acid/ alkali catalyst [17].

Triglyceride + Methanol $\rightarrow$ Biodiesel + Glycerol   Eq (1)

Free fatty acid + Methanol $\rightarrow$ Biodiesel + H_2O Eq (2)

Transesterification is used to create biodiesel from the majority of edible oils, including soybean, sunflower, and rapeseed [18, 19]. Esterification is used when the feedstock oil has a high level of free fatty acids (FFA), which react with alcohol to produce FAAE and H_2O [16]. The choice of homogeneous catalysts can be either basic or acidic and the selection between them depend on the feedstock's FFA and water content. The most popular homogeneous alkaline catalysts are sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide (CH_3ONa), and they are utilized for oils that have a low content of FFA [19]. These catalysts have a number of benefits, including Strong catalytic activity, rapid reaction times, easy availability and low performing conditions. However, homogeneous base catalysts are extremely sensitive to water and free fatty acids. Thus, during the reaction, they produce soap and enormous amounts of wastewater, which raises the cost of manufacturing and operation. These characteristics simultaneously make these catalysts unfavorable to the environment [20]. besides recycling the catalyst is not

possible for homogenous alkaline catalyst [21]. In high FFA feedstock like waste cooking oil, homogeneous acid catalysts such as sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), and hydrochloric acid (HCL) better than homogeneous base catalysts. But homogeneous acid catalysts have a very acidic and corrosive character and require further neutralization procedures [20, 22]. Furthermore, homogeneous acidic catalysts need longer time and higher temperature to turn oil into biodiesel than homogeneous alkaline catalysts do [23]. Because of this, homogeneous acidic catalysts are not very appropriate for commercial use [24].

Heterogeneous catalysts, which have their active sites in distinct phases from the reactants, are non-corrosive, ecologically benign, and recoverable. Consequently, they considered to be superior than homogeneous catalysts and significantly increasing the economic and technological viability [5, 25] through the ability to regenerate catalysts, produce biodiesel of high quality, and separate products with ease. Scholars investigated heterogeneous acids such as zeolites, sulfated metal oxides, ion exchange resins, Metal- organic frameworks (MOFs) and sulfonated carbon [26].

Due to their remarkable adaptability, Metal-Organic Frameworks (MOFs) have lately attracted increasing attention as heterogeneous catalysts. The key factors that make prospective MOFs as viable heterogeneous catalysts include their high surface area, high porosity, ease of functionalization, crystallinity and adjustable pores [27]. MOFs consisted of metallic nodes that are connected by organic linkers [28]. There are many applications for MOFs, including gas storage and separation, sensing, optics, drug delivery, and magnetism (Fig. (2)) [2, 18].
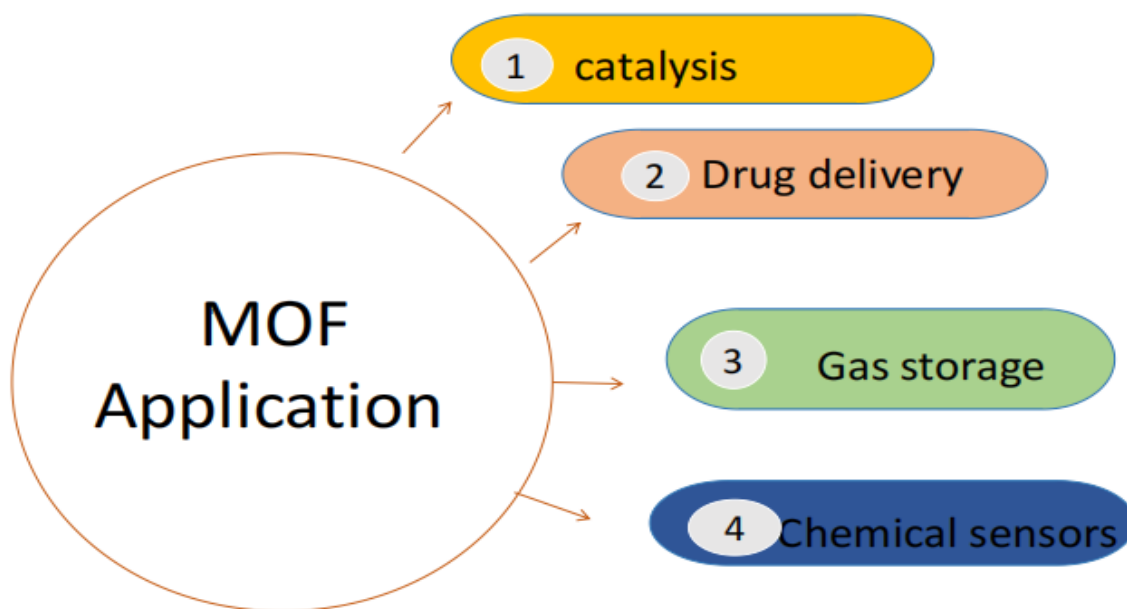

Fig (2): Several applications of MOFs.

4. MILs as promising heterogenous catalysts

Materials of Institute Lavoisier (MILs) are a prominent class of MOFs because of their great stability, persistent porosity, and incredibly high specific surface area. MILs are identified by the institution's abbreviation where the first prepared MIL was developed by Férey [29] and his colleagues by hydrothermally treating terephthalic acid and chromic nitrate nonahydrate. Modern MILs generally are made of carboxylate and trivalent cations such chromium (III), aluminum (III), vanadium (III), gallium (III) andiron (III) [29, 30]. Table (1) provides a summary of the various MILs cited in literature.

Table (1): Summary of the various MILs cited in literature.

MIL	Central metal	Organic ligand	Ref.
MIL-100	Cr, Al, Fe	H_3BTC	[29, 31, 32]
MIL-101	Cr, Al, Fe	H_2BDC	[29, 33]
MIL-53	Cr, Al, Fe	H_2BDC	[29, 33]
MIL-88A	Fe	Fumaric acid	[29]
MIL-88B	Fe	H_2BDC	[29, 34]
MIL-125	Ti	H_2BDC	[29, 35]
MIL-68	In, Ga, Fe, V	H_2BDC	[29]
MIL-47	V	H_2BDC	[36]

H_3BTC:1,3, 5 benzene tricarboxylic acid; H_2BDC: 1, 4 benzene dicarboxylic acid.

4.1. Preparation methods of MIls

For the synthesis of MILs with various active metal sites and organic linkers, many techniques have been devised. The most popular ones employed for MILs among them include solvothermal, ultrasonic, electrochemical, microwave-assisted, and mechanochemical syntheses [29].

4.1.1. Hydro (Solvo) thermal method

Utilizing a hydro (solvo) thermal method, products can self-assemble from soluble precursors. Typically, closed vessels (autoclaves) are used to carry out the reactions in polar solvents. In general, the working temperature range of an autoclave under autogenously pressure is 80-260°C above the boiling point of the solvent. However, in many cases, lengthy reaction durations (up to several days for solvothermal and hydrothermal procedures) are required[37]. The morphology of the crystals is also influenced by temperature, and longer reaction durations may cause the final product to decompose. Solvents with high boiling points are most often employed. In general, MeOH, EtOH, dimethylformamide (DMF) and diethylformamide (DEF) are used. Solvothermal synthesis is an easy, practical approach that may be used for MIL laboratory experiment designs. The fact that the synthesized MILs have uniform size, high crystallinity, a large specific surface area, and adjustable structure and morphology is among the solvothermal method's most important benefits.

However, the solvothermal approach also has several drawbacks, including a dangerous chemical, poor yield (< 50%) a high reaction temperature, and a prolonged reaction time. For instance, MIL-53(Fe) synthesized by Horcajada et al.[29] needed the energy-intensive process of 15 hours at 150 °C, in addition to the use of the cancer-causing organic solvent N, N-Dimethylformamide (DMF). Also, The technique used for production of MIL-101(Cr) by Férey et al. [29] was not very ecologically benign because of low product yield and HF being considered as is a harmful contaminant [29, 38].

4.1.2. Microwave method

In these processes, the temperature of the solution can be increased using microwaves to produce metal's nanosized crystals. Nonetheless, they are an essential tool for high-speed synthesis. Additionally, this technique can effectively regulate the shape and size of the resultant particles. The reaction time of the microwave synthesis of MILs is substantially shorter than that of conventional solvothermal synthesis, ranging from a few minutes to an hour. When using microwave heating instead of conventional heating, the time needed for the synthesis of MIL-100(Cr) was cut to 4 h instead of 4 days. Because microwave synthesis employs the same chemicals as solvothermal synthesis, it should be noted that it might have certain drawbacks including low yield, risky reagents, and high reaction temperature [29, 37].

4.1.3. Electrochemical method

MOF powders are produced on an industrial scale using an electrochemical method. In comparison to solvothermal synthesis, this technique has a number of advantages, including the avoidance of anions such nitrates from metal salts, lower reaction temperatures, and incredibly rapid synthesis. In this method, an electrolyte solution with organic ligands is used to electrolyze the metal anode, forming metal ions, which are then used to build MOFs. The electrochemical approach was used to successfully produce MIL-100(Al), MIL-53(Al), and NH_2-MIL-53(Al). But this approach also has significant disadvantages, such the use of dangerous chemicals and expensive equipment that need frequent repair [29, 37].

4.1.4. Mechanochemical method

In mechanochemical synthesis, intermolecular bonds are broken mechanically before a chemical reaction occurs. A combination of metal salt and organic linker is ground without the use of a solvent using a mortar and pestle or a ball mill. After grinding, the mixture is gently heated to evaporate any water or other volatile molecules that were produced as byproducts in the reaction mixture. Reactions may be carried out at room temperature in solvent-free environments, which is very helpful in situations when we can avoid using organic solvents. It is possible to produce products with a minimal number of components and to achieve quantitative yields in a short reaction time (10–16 min)[37]. Instead of a solvent, mechanical forces are used in this process to create coordination bonds at ambient temperature using manual grinding or a ball mill. It's a green chemical process that's safe for the environment and creates materials with high purity and efficiency in less time [38].

According on whether solvents are involved in the process, three general approaches to the mechanochemical synthesis of MILs may be distinguished; 1) neat grinding (NG) is a technique that doesn't employ any solvent; 2) liquid-assisted grinding (LAG) is technique that uses a little quantity of solvent and 3) ion-and-liquid assisted grinding (ILAG) employs minimal solvents and a little salt as additions. Pilloni et al.[39] employed a vibrating ball-mill to create MIL-100 (Fe) where a grinding jar was filled with H_3BTC, $Fe(NO_3)_3$-$9H2O$, and many 3 mm-diameter balls and were ground for 1h with 5ml of tetramethyl ammonium hydroxide. The main benefit of mechanical synthesis of MILs is the absence of or seldom use of solvents, which makes the procedure environmentally benign. The main benefit of mechanical synthesis of MILs is the absence of or seldom use of solvents, which makes the procedure environmentally benign. Additionally, new ligands that are poorly soluble in common solvents can be used, expanding the family of MILs. However, the resultants MILs frequently have low purity, and solvents are still required for the purification. The difficulty of controlling the end product's particle size, which is frequently quite fine owing to the grinding, is another possible drawback of the mechanochemical production of MILs [29, 40, 41].

4.1.5. Ultrasonic method

This technique is concerned with the chemistry that takes place in a reaction mixture when high-energy ultrasound is used. Ultrasound is a cyclic mechanical vibration with a frequency of 10 MHz, which is between 20 kHz and the maximum limit of human hearing. The primary goal of Ultrasonic synthesis in MOF research is developing a technique that is rapid, energy-efficient, ecologically friendly, simple to use, and applicable at room temperature[37]. When a reaction solution is exposed to ultrasonic radiation, bubbles are generated that quickly become localized hot spots with high temperatures and pressure, promoting chemical reactions and the rapid production of crystallization nuclei. The ultrasonic approach was used to successfully create the MIL-53(Cr-Fe) sample. Low product yields, dangerous chemicals, and unsuitability for industrial manufacturing are some of the drawbacks of ultrasonic techniques [29, 38].

4.2. Types of MIls according to active sites

By using MOF as a carrier for different groups with catalytic features, several issues related to homogeneous acidic and basic-catalysts can be resolved. Changing the functions and pore size of MOF structures allows them to regulate their basic and acidic characteristics. Because of their massive surface area, MOFs offer a powerful interaction between organic ligands and metal ions. Consequently, MOF has strong attachments between its active sites, which minimizes leaching issues and improves catalytic activity overall. Because MOF composites can supply sites for both the acidic and basic functionalized groups, they are an ideal carrier for bifunctional catalysts[2]. When metal ions or clusters are coordinated with rigid organic linkers in the presence of solvents to create MOF structures, the resultant structures are put together to form three-dimensional structures. During this process, there are weakly restricted solvent molecules present in the metal nodes aid in the formation of the MOF structure when these solvents are thermally activated, they may be easily removed without changing the crystal structure resulting in Lewis acid site production. Lewis acid sites can serve as active sites for a variety of organic reactions such as esterification and transesterification[42].

MILs can be acidic, basic, bifunctional depending on active sites that are present on it.

4.2.1. Acidic catalyzed MIL

Waste cooking oil and other oils with a high acid value might react more easily in the Prescence of solid acid catalysts [2]. It has been reported that acid MOFs catalysts have the advantages of facilitating esterification of FFA with alcohols in addition to catalyzing transesterification [16]. As mentioned before, Lewis acid sites are simply created inside MOF structural frameworks[42]. It is possible to functionalize MOF composites with both the Lewis acid and Brønsted acid catalysts such as ionic liquids, Heteropoly acid (HPA), sulfated compounds and polyoxometalate (POM)[2].

Liu et al. [43], produced a highly stable sulfonated catalyst (MF-SO$_3$H) by functionalizing MIL-100(Fe) with sulfonic acid (-SO$_3$H) and employed acidic catalyst in oleic acid esterification process. According to their study, there are several Lewis and Brønsted acid sites at a temperature of 70 °C. They were able to reach 95.86% yield of biodiesel produced by the catalyst with excellent reusability.

Zhang et al. [44], employed H$_4$SiW/MIL-100 (Fe) catalyst to produce biodiesel by esterification of lauric acid with methanol. The catalyst was prepared using the hydrothermal technique whereH$_4$SiW encapsulated in the cages of MIL-100(Fe). The maximum conversion was 80.3

Xie and Wang [34],functionalized CoFe$_2$O$_4$/MIL-88B(Fe)-NH$_2$ catalyst by inserting POM-based sulfonated ILs containing Brønsted-Lewis acid sites. the catalyst proved excellent activity in the esterification of FFAs and the transesterification of soybean oil

Chen et al. [45], modified the structure of MIL-101(Cr) by SO$_3$H-functionalized ionic liquid (SIL) and phosphotungstic acid (HPW) which was used as a connector. The prepared SIL-PW/MIL-101(Cr) showed good catalytic activity for the oleic acid-methanol esterification process reaching 94.3% at 70◦C with good reusability.

4.2.2. Basic catalyzed MIL

For the production of biodiesel, several alkali and alkaline earth metal oxides as well as basic ionic liquids have been used as solid heterogeneous base catalysts. [2]. The active sites in the solid catalyst continue to leach, which is a major problem. Utilizing MOF materials will help to greatly prevent leaching of active sites. Due to the properties and structure of MOF, the modification with basic function groups can be easier [16].

The basic catalyst is generally favorable due to the moderate reaction conditions, i.e., lower temperature and shorter time, even if basic catalysts might produce saponification with low-quality raw oils[18].

If MOFs can be applied as a support to limit metal oxide leaching, they might be a superior option[18]. The low stability of alkaline MOFs to FFA is one of their drawbacks, which limits their use, especially with cooking oil waste that has a high acid value.

There are many functional groups can be added to MOF structure to increase its basic character, like the work of Abdelmigeed et al [28], in which a magnetized zeolitic imidazolate framework (ZIF-8) was created and then impregnated with sodium hydroxide. The prepared catalyst was then studied for the production of biodiesel through the ethanolysis of vegetable oil. With the new catalyst, the ethanolysis reaction produced an oil conversion of 70%. However, MILs functionalized with basic catalytic sites are not reported yet in literature.

4.2.3. Bifunctional MIL

Esterification and transesterification of low-quality raw oils have been proposed as potential applications for bifunctional MIL catalysts having both acidic and basic active sites [18]. As bifunctional MIL that contains both acidic and basic sites combines features of both types. Because of their large surface area, adjustable structure, and tunable properties, studies have demonstrated that MOFs can be essential in the development of bifunctional catalysts. By modifying their ligands and functionalities, MOFs might potentially alter their active sites and behave as bifunctional catalysts [2].

Heteropoly acid and the acid/alkaline ionic liquid are ideal for encapsulation in MOFs. Furthermore, the coordination structure of MOFs might be modified to include an acid (-SO3H) or an alkaline (-NH2) group via making use of the advantage of flexible ligands. By doing this, the active site may be evenly distributed while maintaining the fundamental structure of MOFs not change. Based on this, a bi-functional catalyst might be created by encapsulating an acid or alkaline active site that is linked to MOFs by an ionic and covalent bond [16]. Hassan et al. [46] , prepared bifunctional catalyst by incorporating Zr(IV)-Sal Schiff base complex into aminofunctionalized MIL-101(Cr) framework. The catalytic activity of the catalyst was tested in esterification reaction of oleic acid with methanol with maximum conversion 74.1% of methyl oleate. the catalytic activity was assigned to basic sites arising from amino-functionalized MIL-101(Cr) along with Lewis acid sites steaming from the chromium (III) coordinative unsaturated metal sites (CUSs) as Lewis acid sites in the structure besides the extra Lewis acid sites provided by Zr (IV). Table (2) showed catalytic performance of different MIL catalysts reported in literature.

Table (2): catalytic performance of different MIL catalysts.

Biodiesel feedstock/ Alcohol	Catalyst	Biodiesel synthesis Method	Surface area $m^2\ g^{-1}$	Reaction conditions					Type	Ref.
				ATOR	Catalyst (wt.% or g)	Temp (°C)	Time (h)	Biodiesel Yield (%)		
OA/Methanol	MF-SO$_3$H	Esterification	0.0618	10:1	8 wt.%	70	2	95.86	Acidic	[43]
LA/ Methanol	H$_4$SiW/MIL-100(Fe)	Esterification	-	12:1	0.3 g	160	3	80.3	Acidic	[44]
SO/ Methanol	CoFe$_2$O$_4$/MIL-88B(Fe)-NH$_2$	Transesterification	35.44	30:1	8wt%	140	8	95.6	Acidic	[34]
OA/ Methanol	SIL-PW/MIL-101(Cr)	Esterification	323.4	12:1	8wt%	70	3	94.3	Acidic	[45]
PO/ Methanol	CAM750	Transesterification	0.9001	9:1	4wt%	65	2	95.07	Basic	[21]
PO/ Methanol	MM-SrO	Transesterification	66.88	12:1	8wt%	65	0.5	96.19	Basic	[2]
OA/ Methanol	NH$_2$-MIL-101(Cr)-Sal-Zr	Esterification	473	10:1	4wt%	60	4	74.1	Bifuna-tional	[18]

ATOR: Alcohol to oil ratio; Wt.: Weight; OA: Oleic acid; SO: Soybean oil; PO: palmitic acid; LA: lauric acid.

5. Factors affecting biodiesel production

The optimal conversion during transesterification or esterification would depend on a number of processing parameters and variables including reaction temperature, alcohol type, catalyst amount, alcohol: oil molar ratio, water content and reaction time[16].

5.1. Catalyst amount

A key to achieving the best trans-esterification process is the selection of an appropriate catalyst. well-defined mesostructured, Strong Brønsted and/or Lewis acid groups at a high density and improved surface hydrophobicity to shield the Lewis acidic sites from the water-poisoning impact are characteristics of an ideal solid catalyst for biodiesel generation according to Su & Guo [6] and Santacesaria et al. [47].

Increasing the catalyst quantity often results in an increase in the active catalytic site, which enhancing conversion. However, once equilibrium is attained, a further increase in catalyst dosage would not improve conversion. Extra catalyst causes saponification, particularly for the alkaline catalyst[16]. At a study by Li et al.[21] , As CaO was added to MIL-100(Fe) during their inquiry to catalyze the transesterification of palm oil and methanol. When the catalyst dose was raised from 1 wt.% to 4 wt.%, the transesterification conversion improved correspondingly from 47.92% to 95.07%. However, once the catalyst quantity was increased to 8 wt.%, it was dropped to 92.05%.

5.2. Alcohol type

Biodiesel is made using monohydric alcohols with various carbon numbers, including methanol, ethanol, propanol, and butanol. In a study by Hanh et al. [48], They contrasted how different kinds of alcohol affected the conversion of transesterification containing methanol, ethanol, 2-propanol, 2-butanol, 2-hexanol, 2-octanol, and 1-decanol. The transesterification rate produced by various

alcohols specifically followed the sequence of methanol > ethanol > 2-propanol > 2-butanol > 2-hexanol > 2-octanol > 1-decanol. They discovered that as the length of an alcohol's carbon chain increased, the rate of transesterification steadily reduced. This was caused by the difference in polarity, where the alcohol's polarity decreased with increasing number of carbons. Additionally, the normal-chain alcohol has less steric hindrance than the secondary alcohol with the same carbon. Consequently, because to their minimal steric hindrance, short-chain alcohols like methanol and ethanol are the most often utilized. In an investigation done by Meneghetti et al., [16] Castor oil was transesterified using methanol and ethanol, respectively. Results showed that ethanol needed a longer reaction time than methanol did to accomplish the same transesterification conversion.

5.3. Reaction temperature

Transesterification and esterification are endothermic reactions, and external heat is necessary to move the process in the desired direction. The viscosity of the feedstock oil is typically reduced by raising the reaction temperature, which lowers the mass transfer limitations between the feedstock oil, alcohols, and catalyst. The preferred reaction temperature is often close to the boiling point of the chosen alcohols. Alcohols in the reaction system will be vigorously evaporated as the reaction temperature rises over the boiling point, producing many bubbles on the catalyst surface. Since transesterification and esterification took place on the catalyst surface, this is harmful to the liquid-solid reaction system. Meanwhile, the high temperature consumes a lot of energy [16, 22]. Zhang et al. [49] Kaur, and Ali [50] verified that when methanol was employed as the alcohol, the ideal temperature was 65 ^{o}C.

5.4. Alcohol to Oil or FFA Molar ratio

Theoretically, the molar ratios of methanol to oil in transesterification and esterification are respectively 3:1 and 1:1. In order to obtain greater FAAE, additional alcohols are needed to move the equilibrium point in a forward direction as transesterification and esterification are reversible reactions. But excessive alcohol consumption is not favored. Due to the fact that excessive alcohol would dilute the catalyst's concentration and fewer active sites would be accessible for reactants, which would decrease the rate of transesterification / esterification conversion [16, 18].

Li et al. [51] in their study of SrO /MIL-100(Fe) found that when the molar ratio of methanol/oil changed from 3 to 12, the transesterification conversion increased proportionally from 44.27% to 98.65%. But the conversion decreased to 95.31% when the molar ratio increased to 15, Zhang et al. [49] also confirmed similar results.

5.5. Reaction time

The amount of catalyst, type of alcohol, alcohol to oil molar ratio, and reaction temperature all affect reaction time**.** This indicates that the previously mentioned parameters confirm the transesterification/ esterification equilibrium point. Reaction time is somewhat less significant than the previously listed factors. The transesterification/esterification conversion would be enhanced with a longer reaction time with other preset parameters. The ideal equilibrium time is at that point since the conversion does not alter with reaction time. Alkaline catalyst often needs less time to complete the same conversion than acidic catalyst [16].

5.6. Free water

Free water can exist in feedstock, such as waste cooking oil, which is not desired for transesterification if there is of an alkaline/acid solid catalyst. The feedstock oil would undergo saponification, especially with the alkaline catalyst therefore slowing the reaction. By forming fatty acid salt, or soap, from the feedstock oil, the reaction would be impeded because the soap would stick to the catalyst's surface. Furthermore, experts confirmed that water would poison the active site [6, 16, 34]. Ramachandran et al. demonstrated that an acid active site like -SO3H would rapidly leach into water [52].

6. Fuel properties of biodiesel

The resulting biodiesel must go through specific characterization steps before being used commercially. The designations supplied by the American Society of Testing and Materials (ASTM)-D6751 and the United States Environmental Protection Agency (EPA) standards. Viscosity (mm^2/s), cloud point (^{o}C), pour point (^{o}C), iodine value, saponification value, density, flash point (^{o}C), cetane number, and other characteristics must all meet the requirements of the aforementioned standards. The cetane number is determined by the carbon number and the FAME concentration. A high cetane number is preferred for easy fuel and engine operation, which also minimizes the formation of white smoke. Cetane number is used to assess the fuel's flammability index. For biodiesel, the optimal cetane number should be at least 47. The maximum amount of water content is 0.05% volume, as specified by ASTM standard D6751. Excessive water contents can lead to microbiological development in equipment used for handling, storing, and transporting fuel. For the purpose of ensuring fire safety, the flashpoint (^{o}C) must have a minimum value of 130 or above. Typically, low viscosity is required for optimal fuel combustion, with the usual value for biodiesel being 1.9-6.0 mm^2 s^{-1}. Higher viscosity gasoline can result in big droplets during injection, requiring more energy to pump and inefficient combustion resulting in the release of greenhouse gases. For improved performance, the low-temperature cloud point is often assumed for biodiesel. Biodiesel's saponification value is linked to low production and low quality. 312 mg KOH g^{-1} is determined to be the highest estimated value of biodiesel saponification. The pour point provides information about the fuel's pumping ability. Specified values for the previous parameters according to EPA and ASTM (Table 3) [2, 53, 54].

Table 3: Standard biodiesel properties

Fuel properties	Unit	ASTM/EPA limits
Kinematic viscosity at 40 ° C	mm^2/s	1.9–6
Specific density of a fuel at 40 °C	g cm^{-3}	0.82-0.90
Acid value	mg KOH g^{-1}	0.5
Cetane number		>47
Flash point	°C	>120
Boiling point	°C	182 to 338
Pour point	°C	-15 to 16
Cloud point	°C	-3 to 15
Ash content	Wt.%	Max 0.02
Carbon content	Wt.%	Max 0.3
Water content	% vol.	0.05%
Methanol content	Wt.%	Max 0.2
Sulfur content	Wt.%	0

7. Concluison

MIL series a family of MOF composites are found to be promising support for catalyzing esterification and transesterification reactions. There are many synthesis processes for MIL series, the most common one is solvothermal and hydrothermal method. There are many factors affecting on biodiesel production such as alcohol type, reaction time, reaction temperature, catalyst amount, alcohol to oil / FFA molar ratio. Before being apply commercially, biodiesel must go through specific characterization steps according to the ASTM-D6751 and EN-14214 standards.

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