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Fumarate Based Metal–Organic Framework: An Effective Catalyst for the Transesterification of Used Vegetable Oil

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Abstract: Advancement of technology for the sustainable production of biodiesel is of significant importance in fighting against rising fuel costs due to the fast depletion of fossil fuels. In this regard, the application of highly efficient MOFs (metal–organic frameworks)-based materials as acidic, basic, or supported heterogeneous catalysts plays a crucial role in enhancing the efficiency of biodiesel production processes. In this report, we demonstrate the synthesis and catalytic application of Zr-fumarate-MOF (also known as MOF-801) as a heterogeneous catalyst for the transesterification reaction of used vegetable oil (UVO) for the production of biodiesel. The formation of MOF-801 and its structural stability is confirmed by a variety of characterization techniques including XRD, SEM, EDX, FT-IR, BET, and TGA analyses. The results revealed the formations of highly crystalline, cubic MOF-801 possessing thermal stability below 500 °C. The MOF-801 catalyst demonstrated moderate catalytic activity during transesterification of UVO (~60%) at 50 wt.% of methanol: oil, 10 wt.% catalyst loading, 180 °C reaction temperature, and 8 h of reaction time. Furthermore, the catalyst has exhibited adequate reusability with a slight reduction in the reaction yield of up to ~10% after three cycles.

Keywords: metal–organic framework; Zr-fumarate-MOF; catalyst; transesterification; vegetable oil

1. Introduction

Due to the fast depletion of oil reserves, the demand for alternative energy resources has increased tremendously [1]. Among various renewable energy resources, biofuels have found decent consideration and have been applied progressively as a suitable alternative to traditional fossil fuels [2]. Biofuels have greatly contributed in controlling the emission of greenhouse gases, which can cause a serious threat to the environment and human life [3,4]. Particularly, biofuels generated from renewable energy resources including plants and other naturally abundant materials have been appreciated due to their non-toxic and biodegradable nature [5]. For instance, biodiesel that is comprised of fatty acid methyl esters is typically obtained from various renewable resources, such as animal fats and vegetable oils, etc., have found several applications [6]. Biodiesel is generally obtained from the natural feedstock through the process of transesterification using suitable catalysts [7]. This type of fuel is less dangerous to the environment due to the low emission of greenhouse gases while burning including SO₂, SO₃, CO, etc. In addition, biodiesel is more lubricious and easier to handle and contains lower amounts of carcinogenic substances when compared to the traditional fossil fuels [8,9].

Typically, transesterification of triglycerides present in used or edible oils is carried out in alcohols using acid or base catalysts to produce biodiesel. This process is usually performed under homogeneous conditions at mild temperatures using KOH, NaOH, etc., as catalysts [10]. However, acid catalysts such as HCl or H₂SO₄, etc., are more preferred for the triglycerides of used oils which effectively activate the substrates through the
electrolytic process [11]. Particularly, for the triglycerides with low free fatty acid (FFA) contents, homogeneous basic catalysts deliver relatively more efficient catalytic activities when compared to the acid catalysts [12]. However, the applications of homogeneous catalysts are largely inhibited due to their high cost on separations and environmental hazards. Moreover, these types of catalysts also require long reaction times and suffer from saponification and corrosion problems [13].

Alternatively, heterogeneous catalysts are less expensive, more stable at high temperature and pressure, readily available, and easy to separate [14]. Therefore, these types of catalysts offer a suitable alternative to the conventional homogeneous catalysts for the production of biodiesel [15]. Indeed, there is a continued urge among researchers for the development of advanced heterogeneous catalysts for the sustainable production of biodiesel at a minimal cost [16]. To date, various studies have been published on the transesterification of glycerides using different types of heterogeneous catalysts during the production of biodiesel. However, the shortage of raw materials and high production costs still make the biodiesel more expensive when compared to conventional fossil fuels [17].

To overcome this problem, appropriate feedstock selection from renewable wastes, including non-edible crops, animal fats, used vegetable oils (UVO), etc., is highly desirable [18]. However, these types of renewable wastes often contain high free fatty acid (FFA) contents, which generally require a large amount of catalysts and higher purification costs [19,20]. Therefore, the conversion of cheap renewable wastes and non-edible fats into biodiesel products through simple economic and environmentally friendly processes using effective and low-cost heterogeneous catalysts is highly required [21]. Usually, the FFA contents are converted to their alkyl esters counterparts in the presence of different types of heterogeneous catalysts including acid, base, and bifunctional (acidic–basic character) catalysts [22]. Both solid acid and base catalysts have their own merits and demerits, such as the acid catalysts can effectively catalyze the esterification of FFAs even in the presence of large water and FFA contents [23].

Thus, heterogeneous catalysts are promising candidates for biodiesel production from renewable wastes including used vegetable oils [24]. Thus far, a variety of heterogeneous catalysts such as metal and metal oxides, carbonaceous materials, and metal–organic frameworks (MOFs) based catalysts have been applied successfully and their activity for transesterification has been studied [25–27]. In this regard, MOFs based catalysts have been given significant attention due to their remarkable skeleton structure, which offers immense possibilities of generating diverse basic functionalities [28,29]. MOFs combine the respective beneficial properties of both organic and inorganic components and can incorporate a variety of active sites in their structure, which can be introduced by the proper selection of the constituents involved [30]. Additionally, they offer huge porosity, uniform pore size, controllable functional groups, and structural tenability which are potential characteristics of a catalyst required for the production of biodiesel [31]. Among several MOFs, zirconium-based MOFs have recently gained decent attention in heterogeneous catalysis due to their unique thermal, mechanical and chemical properties [32,33].

Till date, a variety of Zr-based MOFs such as, NU-1000, MOF-808, etc., have been applied for several important catalytic reactions, particularly UiO-66 MOF has gained vast attention [34–37]. The porous crystalline network of UiO-66 typically consists of the imperfect framework with missing linkers leading to the formation of active defects which not only facilitate the adsorption of substrates but also enhance the interactions between reactants [38]. Moreover, the vacant sites on nodes in MOFs with missing linkers, such as in UiO-66, potentially generate Lewis acid sites which further enhance the catalytic properties of Zr-based MOFs [39]. However, there are several other Zr-based MOFs that are not yet explored for their catalytic potential, such as MOF-801. Therefore, in this report, we present the synthesis and catalytic application of fumarate-based MOFs (MOF-801) (Scheme 1), which contains a unique microporous Zr-based 3D structure consisting of Zr₆ nodes connected by fumarate linker.
Scheme 1. Graphical representation of transesterification of UVO to biodiesel utilizing the synthesized fumarate-based MOFs (MOF-801) catalyst.

2. Materials and Methods

2.1. Preparation of MOF-801

In this study, the synthesis of MOF-801 is carried out as per the previously published literature [40]. Briefly, 0.8 g of ZrOCl$_2$·8H$_2$O was dissolved in 15 mL of DMF-formic acid (v/v = 20:7) mixture in a 50 mL round bottom flask. To this solution, 0.29 g of fumaric acid was added and the mixture was left for stirring for 30 min until a clear solution was obtained. Subsequently, the resultant solution was transferred to a 50 mL Teflon cup, which was fixed into a hydrothermal/solvothermal autoclave reactor. The reactor was kept in an oven for 6 h at 130°C. Thereafter, the product was isolated via centrifugation and washed repeatedly with DMF and ethanol (3 times), and dried overnight under vacuum at 100°C.

2.2. Transesterification of Used Vegetables Oil (UVO)

The UVO for the transesterification was obtained from a fast-food center in Riyadh (KSA). The catalytic reaction was performed in methanol using 3 g of UVO, 1.5 M of methanol, and 0.3 g of MOF-801 (10 wt.% of oil). All the reactants were thoroughly mixed in a 100 mL beaker via rigorous stirring, and subsequently, the mixture was transferred into a 100 mL Teflon cup that was fixed into a steel autoclave. The autoclave reactor was heated to 180°C in a muffle furnace for 8 h. Thereafter, the reaction was stopped, and the autoclave was allowed to cool down at room temperature. The catalyst was isolated from the mixture via centrifugation at a speed of 8000 RPM. From the resultant reaction mixture, excess methanol was evaporated using a rotary evaporator, which leads to the formation of two separate layers. The upper layers consisted of unreacted oil and transesterification products, while the lower contained glycerol. Using a separating funnel, the lower layer was separated, while the upper layer was processed using a rotary evaporator to collect unreacted oil and transesterification products. The conversion of UVO to esters was confirmed via $^1$H NMR. All the details about sample preparation for characterization and other technical information about the instruments used during this study is provided in a separate Supplementary Materials file.

3. Results and Discussions

3.1. X-ray Powder Diffraction (XRD) Analysis

MOF-801 is a three-dimensional, microporous Zr-based MOF consisting of fumarate linkers in which each secondary building unit (SBU) is comprised of six Zr ions. Every Zr ion is surrounded by eight oxygen ions, while each SBU is connected with 12 linkers. MOF-801 is considered as a stable MOF due to the presence of strong covalent bonds and excellent coordination between each SBU. SBUs in MOF-801 are slightly tilted due to the presence of non-linear fumarate ions. It contains three different kinds of pores including two types of tetrahedral pores with a diameter of 5.6 and 4.8 Å, and octahedral pores with...
7.4 Å diameter [41]. Such types of small pores are convenient for the proper adsorption of small molecules which is very helpful during catalytic reactions. The preparation of MOF-801 and its crystallinity is confirmed by powder X-ray diffraction as shown in Figure 1. The XRD patterns showed well-defined reflection at ~10°, 13.9°, 19.9°, and 21.7°, which can be assigned to the (200), (222), (420), and (440) planes. These distinct reflections correspond to the most prominent and characteristic diffraction peaks of the simulated crystalline MOF-801 structure reported in a previously published study (Figure S1) [40]. XRD pattern measured for the as-prepared MOF-801 in Figure 1 matched and exhibited a good agreement to the XRD data presented in a previously published study which pointed towards the existence of the cubic (fcc topology) crystalline MOF-801 (Zr-fumarate) [42].

![Figure 1. XRD analysis of MOF-801.](image)

### 3.2. Fourier-Transform Infrared Spectroscopy (FT-IR) Analysis

FT-IR is employed to identify the functional groups of MOF-801, and the spectrum is presented in Figure 2. The peaks in the IR spectrum of MOF-801 are identical and matched with previously published data for Zr MOFs [41]. A broad peak at ~3400 cm⁻¹ represents a characteristic peak of the OH group. The absorption at 1650 cm⁻¹ is attributed to the C=O stretching of DMF, and 1578 cm⁻¹ is attributed to the asymmetric stretching of O–C–O belonging to the carboxylic group of ligands, C-H symmetrical and asymmetrical stretching appeared in the range of 3100–2800 cm⁻¹, whereas the symmetric stretching of the same group appears at 1403 cm⁻¹. On the other hand, peaks at 1211, 983, and 796 cm⁻¹ can be attributed to C–N stretching, CH₃ skeletal vibrations, and C–C–H out-of-plane bending. Furthermore, the two sharp peaks at 655 and 491 cm⁻¹ can be assigned to vibrations of Zr₆(OH)₄O₄ and asymmetric stretching of the Zr-(OC) group of MOF-801 [43].
3.3. Thermogravimetric Analysis (TGA)

In order to measure the thermal stability of MOF-801, the sample was subjected to TGA analysis (Figure 3), which revealed weight loss up to ~500 °C in three steps. The initial weight loss of ~25% occurred below 125 °C, which is attributed to the removal of moisture from the sample. Subsequently, another 25 to 30% weight loss between 125 to 350 °C occurred due to the evaporation of guest molecules, such as solvent molecules from the cavities of the sample. Upon further continuation of heating above 350 °C, the sample started to disintegrate and it was completely decomposed at ~500 °C due to the breaking of the carboxylate groups network; this indicates the high thermal stability of the sample [44].

3.4. Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray (EDX) Analysis

The morphology of the as-prepared MOF-801 was analyzed by SEM, as shown in Figure 4a; dense and defect-free morphology is observed in the micrograph. EDX was further measured to investigate the elemental composition of the sample. Figure 4b clearly demonstrates the presence of carbon, oxygen, and zirconium in the sample, which is reflected by the peaks at ~0.28, 0.55, and 2.1 keV, respectively.
3.5. N₂ Isotherm Analysis

N₂ adsorption–desorption isotherm analyses were performed in order to find out the Brunauer–Emmett–Teller (BET) specific surface area and Barrett–Joyner–Halenda (BJH) pore size distribution of MOF-801. The adsorption–desorption behavior, porosity, and surface area of the as-prepared MOF-801 were examined (cf. Figure 5a) which revealed type-I adsorption behavior, and the calculated BET surface area of 750.11 m²/g. The pore size distribution curves demonstrate the presence of micropores with large pores distribution of ~20 to 100 nm as shown in Figure 5b. These pores are relatively larger than the triglyceride molecules which enable them to trap the substrate and bring it closer to the active sites in the catalytic system.

3.6. Catalytic Evaluation of MOF-801

MOF-801 was used as a catalyst during the transesterification reaction of UVO. The progress of the reaction was monitored using ¹H NMR spectroscopy and was based on the yield of glycerol, which facilitated the estimation of the conversion of UVO. For the sake of simplification, a graphical illustration of the transesterification of triglycerides with CH₃OH (methanol) is depicted in Figure 6. Typically, the presence of glycerol moieties in triglycerides is ascertained by the appearance of ¹H NMR peaks at 4.1 to 4.3 and 5.1 ppm, which are associated with the coupling of –CH₂– and –CH– groups, respectively. Notably, the intensities of the ¹H peaks belonging to the triglycerides in the sample collected after reaction (cf. Supplementary Materials Figure S1), decreased significantly which indicated the transformation of the starting materials to the transesterification product. In addition, the ¹H spectrum of triglycerides also consists of several other peaks (peaks at 1.30, 1.60, 1.95, 2.30, and 2.63 ppm) because of the interaction of the –CH₂– group with other moieties. Other ¹H peaks in triglycerides and fatty acid methyl esters, which commonly exist due to the conjugated and non-conjugated proton resonances appear at 5.30, 5.35, and 6.03 ppm. Apart from triglycerides, mono- and di- glycerides are also present in UVO; however, they do not appear in the ¹H spectrum, due to their solubility in CH₃OH fraction, which is already separated during processing [45]. Apart from all the aforementioned peaks, the ¹H
spectrum of UVO after transesterification also contains a characteristic $^1$H peak at 3.65 ppm, which is associated with the methoxy group of fatty acid methyl ester. This peak is used to calculate the conversion of triglycerides to biodiesel due to the transesterification reaction using the following Equation (1).

$$\text{Conversion (\%)} = 100 \times \frac{2A_{CH_3}}{3A_{\alpha-CH_2}}$$  \hspace{1cm} (1)

where $A_{CH_3}$ = area of methoxy protons in the methyl esters, and $A_{\alpha-CH_2}$ = area of the methylene protons adjacent to the carbonyl group.

Figure 6. Graphical illustration of the transesterification of triglycerides with methanol.

The transformation of UVO using MOF-801 as catalysts was analyzed by changing the amount of catalyst. The transesterification of UVO was performed in methanol by varying the amount of catalyst between 5 to 20 wt.% of the UVO used during the reaction (Figure 7a). The details of the reaction are given in Table 1. The conversion of the UVO was ascertained by $^1$H NMR given in Supplementary Materials (Figures S2–S18). MOF-801 (10 wt.%) rendered ~60% conversion of UVO in 8 h of time at a temperature of 180 °C with a CH$_3$OH:oil weight percent of 50. Expectedly, in the absence of catalyst, under similar reaction conditions, the conversion of UVO did not occur. To test the effect of the amount of catalyst of the yield of glycerol, several experiments were performed by changing the amount of catalyst. The result revealed that the amount of catalyst (5–20 wt.%) had slightly influenced the catalytic properties of the catalyst. For instance, with increasing the amount of catalyst from 5% to 10%, the yield of the glycerol had increased between ~36% to ~60%, respectively. However, when the amount of catalyst was further increased from 10% to 15% and 20%, the change of the yield of glycerol was negligible, and almost remained the same (cf. Table 1).

Table 1. The transesterification reactions of UVO in CH$_3$OH using different amounts of oil.

| Catalyst       | Oil (g) | Amount of Catalyst | Product Yield (g) | Conversion (%) |
|----------------|--------|--------------------|-------------------|----------------|
|                |        | wt.% to Oil | Amount (g) | Biodiesel | Glycerol | $^1$H-NMR | Yield of Glycerol |
| MOF-801        | 1.5    | 5         | 0.075     | 1.311    | 0.055    | 40.3      | 36.1             |
| MOF-801        | 10     | 10        | 0.150     | 1.406    | 0.091    | 59.8      | 58.7             |
| MOF-801        | 15     | 15        | 0.225     | 1.399    | 0.090    | 59.6      | 58.1             |
| MOF-801        | 20     | 20        | 0.300     | 1.394    | 0.087    | 57.4      | 56.1             |
| MOF-801/HCl    | 10     | 10        | 0.150     | 1.482    | 0.107    | 70.0      | 69               |

Reaction conditions: Temperature—180 °C, Methanol to oil (50 wt.%), and time 8 h.
Figure 7. Conversion of UVO in the presence of MOF-801 as catalysts using different reaction parameters (a), at varying catalyst loading. (Green line conversion based on NMR and red line conversion based on the yield of glycerol) and (b) using different amounts of CH$_3$OH with respect to oil.

Theoretically, 3 mol of CH$_3$OH is sufficient to produce 1 mol of triglyceride, but to prevent the reversible reaction, an excess amount of CH$_3$OH is used to improve the reaction rate in the forward direction. To investigate the effect of CH$_3$OH, several experiments were performed by varying the amount of CH$_3$OH with respect to oil. For this purpose, the amount of CH$_3$OH was used from 30 to 60 weight percent (wt.%) with respect to reactant (UVO) as shown in Figure 7b. With increasing the amount of CH$_3$OH up to 15 wt.% in the order of 30, 40, and 50 wt.% (CH$_3$OH:oil), the conversion was also increased to ~20, 48, and ~60%, respectively. However, when the amount of CH$_3$OH was further increased to 60 wt.%, the conversion was decreased to ~56%, which indicated that the optimum amount of CH$_3$OH is 50 wt.% of UVO for this reaction. To optimize the time of the reaction, the conversion of UVO was monitored in various reactions by changing the time from 2 to 8 h. Initially, in 2 h of reaction time only ~35% of conversion was obtained due to the lower dispersion of oil in CH$_3$OH. However, as the time of the reaction was increased, the conversion was also increased, and finally at 8 h of reaction time a maximum of ~60%, which is considered as optimum reaction time (Figure 8a). Furthermore, the effect of temperature on the reaction which is known to influence the kinetics of the reaction is also investigated. To do this, different experiments were performed by varying the temperature of the reaction from 140 to 200 °C, while keeping all the other parameters constant. These experiments have revealed an optimum temperature of 180 °C, which has produced the maximum amount of product as shown in Figure 8b.

Figure 8. Transesterification of UVO over MOF-801, (a) at a different time interval. (Green line conversion based on NMR and red line conversion based on the yield of glycerol) and (b) at different temperatures.
Previous reports suggested that the oxygen ions (O\(^{2-}\)) in catalysts typically promote the reaction in the forward direction and help in enhancing the yield of transesterification products [46]. These oxygen ions are highly negative and tend to function as the Brønsted bases, which could potentially enhance the activity of the catalyst [47]. Typically, in mixed metal oxide based catalysts, the basicity of the catalyst is affected by the electron transfer of the metal groups [48]. Considering this assumption, the positive metal ions (Zr (IV) cation) in MOF-801 may facilitate the electron transfer to the oxygen anions (O\(^{2-}\)) leading to an enhanced electron density at the sites [49]. These highly negative sites become susceptible to nucleophilic attack, and thus function as Bronsted bases. These basic sites tend to adsorb CH\(_3\)OH (methanol) molecules leading to the formation of CH\(_3\)O\(^-\) (methoxide anions) and H\(^+\) (hydrogen cations). During the reaction, the former reacts \(\text{CH}_3\text{O}^-\) with triglycerides to produce biodiesel. To ascertain this, the pH of the reaction is slightly changed by adding a little amount of HCl (10% \(v/v\)). Surprisingly, the conversion of the reactant (UVO) is further enhanced to ~70%. This could be attributed to the inherent catalytic activity of HCl, which effectively acts as a catalyst during homogeneous transesterification reactions to produce biodiesel [50]. Finally, the reusability of catalyst was also investigated under optimized reaction conditions, i.e., 10 wt.% of catalyst and 50 wt.% of UFO with respect to oil, while the reactions were performed for 8 h at 180 °C temperature. Over these reactions, up to three cycles, the efficiency of catalyst has slightly reduced, and at the end of the 3rd cycle the yield of the product has decreased up to ~10%, as shown in Figure 9 in 8 h of time.

![Figure 9. Reusability study of the MOF-801 catalyst for the transesterification of UVO.](image)

4. Conclusions

Herein, we have successfully demonstrated the preparation of MOF-801 catalyst under solvothermal conditions at an optimum temperature of 130 °C. Detailed characterization of catalysts was performed to recognize the formation and stability of the as-prepared catalyst. XRD analysis has indicated the formation of crystalline and cubic Zr-fumarate based MOF-801. SEM and EDX have confirmed the elemental identity of the sample, while TGA exhibited the thermal stability until 500 °C, which is sufficient for the biodiesel production processes. The as-prepared sample (MOF-801) is applied for the transesterification of UVO for the production of biodiesel, which has demonstrated moderate catalytic activity under facile conditions. The activity of the catalyst may be attributed to the catalytically active ionic sites in the crystal structure including cationic Zr and anionic O\(^{2-}\) sites. These results can be further used towards the application of MOFs as heterogeneous catalysts in biodiesel production from UVO on a larger scale.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst12020151/s1. Figure S1: (a) Comparison of the simulated MOF-801 from the previously published data [1] and (b) as-synthesized XRD patterns of MOF-801; Figure S2: 1H-NMR spectrum of used vegetable oil (UVO); Figure S3: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (5 wt.% to oil) at 180 °C in 8 h with methanol to oil 50 wt.%; Figure S4: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 8 h with methanol to oil 50 wt.%; Figure S5: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (15 wt.% to oil) at 180 °C in 8 h with methanol to oil 50 wt.%; Figure S6: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (20 wt.% to oil) at 180 °C in 8 h with methanol to oil 50 wt.%; Figure S7: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 8 h with methanol to oil 30 wt.%; Figure S8: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 8 h with methanol to oil 40 wt.%; Figure S9: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 8 h with methanol to oil 50 wt.%; Figure S10: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 8 h with methanol to oil 60 wt.%; Figure S11: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 2 h with methanol to oil 50 wt.%; Figure S12: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 4 h with methanol to oil 50 wt.%; Figure S13: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 6 h with methanol to oil 50 wt.%; Figure S14: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 8 h with methanol to oil 50 wt.%; Figure S15: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 140 °C in 8 h with methanol to oil 50 wt.%; Figure S16: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 160 °C in 8 h with methanol to oil 50 wt.%; Figure S17: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 180 °C in 8 h with methanol to oil 50 wt.%; Figure S18: 1H-NMR spectrum of biodiesel synthesized by transesterification of UVO using MOF-801 catalyst (10 wt.% to oil) at 200 °C in 8 h with methanol to oil 50 wt.%. 

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