

**Supported Metal-Oxide Catalysts for More Efficient
Conversion of Waste Vegetable Oils into Biofuel**

BY

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|Dedicated to my family |

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LIST OF ABBREVIATIONS

FAME	:	Fatty Acid Methyl Esters
FFA	:	Free Fatty Acid
WCO	:	Waste Cooking Oil
SEM	:	Scanning Electron Microscopy
TGA	:	Thermogravimetric Analysis
XRD	:	X-Ray Diffraction
TEM	:	Transmission Electron Microscope
TPD	:	Temperature-Programmed Desorption
FTIR	:	Fourier Transform Infrared Spectroscopy
MRMO	:	Molar Ratio of Methanol to Oil
MREO	:	Molar Ratio of Ethanol to Oil
TEAOH	:	Tetraethyl ammonium hydroxide
DMF	:	Dimethylformamide
SDA	:	Structure-directing agent
BET	:	Brunauer, Emmett, and Teller
BJH	:	Barrett, Joyner and Halenda
GC-MS	:	Gas Chromatography-Mass Spectroscopy
NMR	:	Nuclear Magnetic Resonance
TMS	:	Tetramethylsilane
ASTM	:	American Society for Testing and Materials

IUPAC	:	International Union of Pure and Applied Chemistry
XRF	:	X-Ray Fluorescence
MOFs	:	Metal-organic frameworks
NH₃-TPD	:	Ammonia- Temperature-Programmed Desorption

ABSTRACT

Full Name : [Basiru Olayinka Yusuf]
Thesis Title : [Supported Metal-Oxide Catalysts for More Efficient Conversion of Waste Vegetable Oils into Biofuel]
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[Due to environmental concerns and resources exhaustion of the traditional fossil fuel, more attention has been paid to renewable energy sources. Biodiesel has become one of the foremost renewable energy sources to replace conventional fossil-derived diesel. It is a renewable, biodegradable and non-toxic fuel which can be easily produced through transesterification reaction. This research intends to contribute towards enhancing the biodiesel production from low-cost feedstocks. This was achieved through a novel system of solid acid catalyst design using metal oxides deposited on mesoporous zeolites support and metal organic frameworks (MOFs) support. All the catalysts were synthesized using wet impregnation technique. The physical and chemical properties of the catalysts were characterized using N₂-physiosorption for surface area and pore structure determination, X-ray diffraction (XRD) for crystallinity and phase purity, Fourier transform infrared spectroscopy (FTIR) for functional groups identification, pyridine-FTIR for Bronsted and Lewis acidic sites, thermogravimetric analysis (TGA) for thermal stability, scanning electron microscope (SEM) for morphologies, transmission electron microscope (TEM) for active phase distribution, ammonia-temperature programmed desorption (NH₃-TPD) for acidic property, X-ray fluorescence (XRF) for elemental composition. The as-developed catalysts were tested on a waste cooking oil (WCO) in a Parr batch reactor. The

biodiesel was analyzed using Nuclear Magnetic Resonance (^1H and ^{13}C NMR) and Gas Chromatography-Mass Spectroscopy (GC-MS). The effect of various process conditions such as reaction time, the ratio of methanol to oil, catalyst loading, and temperature were investigated and optimized. The fuel properties of the prepared biodiesel are excellent, for they are consistent with ASTM D6751 standards. A plausible mechanism has been proposed for the simultaneous transesterification and esterification reactions that govern the conversion of WCO to biodiesel. Kinetic studies were done to provide better understanding of the catalytic performance and to estimate kinetic parameter (activation energy). The results revealed that the reactions followed the pseudo first-order kinetic model, with an activation energy (E_a) >25 kJ/mol. These results are consistent with the previous studies on similar systems and the E_a suggest that the reactions are chemically-controlled, not mass transfer-controlled. |

ملخص الرسالة

الاسم الكامل: بشير اولينكا يوسف

عنوان الرسالة: محفزات أكسيد المعادن المدعومة من أجل تحويل نفايات الزيوت النباتية بكفاءة أكبر إلى وقود حيوي

التخصص: كيمياء

تاريخ الدرجة العلمية: مايو 2023

بسبب الاهتمام المتزايد بالمصادر المتجددة للطاقة نظرًا للقلق البيئي ونضوب موارد الوقود الأحفوري التقليدي، أصبح الوقود الحيوي أحد أهم مصادر الطاقة المتجددة لاستبدال الديزل التقليدي المستمد من الوقود الأحفوري. يعتبر الوقود الحيوي وقود متجدد وقابل للتحلل الحيوي وغير سام يمكن إنتاجه بسهولة عن طريق تفاعل تبادل الاسترة. تهدف هذه الدراسة إلى المساهمة في تعزيز إنتاج الوقود الحيوي من مواد خام ذات تكلفة منخفضة. تم تحقيق ذلك من خلال نظام جديد لتصميم محفز حمض صلب باستخدام أكاسيد المعادن المرسبة على سطح مادة الزيولايت المسامية ودعم الإطارات العضوية المعدنية. .

تم تحقيق ذلك من خلال نظام جديد لتصميم محفز حمض صلب باستخدام أكاسيد المعادن المرسبة على الدعم من مواد الزيولايت المتسامية وهياكل الإطارات العضوية المعدنية. تم تحضير جميع المحفزات باستخدام تقنية التشريب الرطب. تم توصيف الخصائص الفيزيائية والكيميائية للمحفزات باستخدام تقنية الامتصاص الفيزيائي للنتروجين لتحديد المساحة السطحية وهيكल المسامات، وتقنية تشتت الأشعة السينية لتحديد بلورة ونقاوة الطور المتكون، وطيف الأشعة تحت الحمراء مع التحويل الفوري لتحديد المجموعات الوظيفية، وطيف الأشعة تحت الحمراء مع البيريدين لمواقع برونستد ولويس الحمضية، وتحليل الوزن الحراري للاستقرار الحراري، والمجهر الإلكتروني الماسح للتشكيلات، المجهر الإلكتروني النافذ لتوزيع الطور النشط، الامتصاص المبرمج لدرجة حرارة الأمونيا للخاصية الحمضية، مطافية الأشعة السينية للتكوين الأولي

تم اختبار المحفزات المتطورة على نفايات زيت الطهي (WCO) في مفاعل دفعي Parr. كما تم تحليل الوقود الحيوي باستخدام الرنين المغناطيسي النووي للهيدروجين والكربون 13 والتحليل الطيفي الكتلي للغاز. تم فحص وتحسين

تأثير ظروف العملية المختلفة مثل وقت التفاعل ونسبة الميثانول إلى الزيت وتحميل المحفز ودرجة الحرارة. تعتبر خصائص الوقود للديزل الحيوي المحضر ممتازة ، لأنها تتوافق مع معايير ASTM D6751. تم اقتراح آلية معقولة لتفاعلات الأسترة التبادلية والأسترة المتزامنة التي تحكم تحويل منظمة الجمارك العالمية إلى وقود الديزل الحيوي. أجريت الدراسات الحركية لتوفير فهم أفضل للأداء الحفاز ولتقدير طاقة التنشيط. أظهرت النتائج أن التفاعلات اتبعت النموذج الحركي الزائف من الدرجة الأولى ، بطاقة تنشيط $E_a > 25$ كيلو جول / مول. تتوافق هذه النتائج مع الدراسات السابقة على أنظمة مماثلة ، وتشير طاقة التنشيط إلى أن التفاعلات خاضعة للتحكم الكيميائي ، وليست مضبوطة بنقل الكتلة. |

CHAPTER 1

INTRODUCTION

1.1 Background Information

The increased demand for fossil fuels and the need for a sustainable environment have become areas of great global concern. The world depends on the availability of fuels for its burgeoning population, which in turn desires a better quality of life. The yearly world consumption of primary energy is about 12.5 billion toe (tonne of oil equivalent; 1 toe = 41.87 GJ), and with the growing population would increase the price of crude oil and directly affect the global economy [1-2]. At present, petroleum-based fuels account for about 85% of primary energy consumption, 58% of this is utilized in the transport sector [3-4]. The mass utilization of non-renewable energy sources has raised concern for the option of renewable energies because of the detrimental environmental consequences, which incorporate global warming and serious climate changes [5]. The combustion of fossil-derived fuels produces approximately 98% of carbon emissions [6]. If the world continues to use non-sustainable energy sources for energy generation, it will not be wrong to assume there will be a time when this world will not be an ideal place to live. Therefore, in order to preserve our environment for future generations, it is necessary to take some measures in curtailing our demand for fossil fuels.

Sustainable development is the key issue, which has attracted significant attention and concern over the last few decades. Researchers are interested in developing potential renewable energy sources because of the declining fossil fuel reservoirs with an increase in crude oil prices and relatively rapid growth in the global population. For long-term environmental and economic growth, transitioning from energy dominated by fossil fuel

to sustainable technologies based on renewable energy sources is now essential. This transition would not only be challenging for researchers, but it would also have economic and environmental implications [7]. The diversification of energy sources by transitioning from fossil-fuel-dominated energy to an energy portfolio covering a variety of renewable fuels, would meet global energy demand [8]. Biodiesel has gotten a lot of attention as a green fuel because of its clean combustion characteristics and its sustainable sources [9-10]. In addition to being biodegradable, it is free of sulfur, has lower exhaust emission, and is free of aromatics [10]. Biodiesel production is a rapidly increasing biofuel technology since it provides a set of environmental advantages over traditional fossil fuels. Biofuel is employed as a first-generation fuel. According to a survey published by Zion Market Research, the global biofuel market is estimated to be about \$219 billion in 2022 [11]. Biodiesel is obtained from natural fats and oils and could be used in place of conventional fossil-based diesel without modifying the current diesel engines.

To produce biodiesel from fats and oils, four distinct methods are used: pyrolysis, hydrocarbon blending dilution, transesterification, and emulsification [8]. The transesterification method is mainly used to produce biodiesel from different kinds of fats and oils worldwide because the transesterification method produces fuel that is highly compatible with the diesel engines that are currently in use [7]. The key purpose of transesterification process is to bring the oil's viscosity down to that of conventional diesel fuel [9]. Transesterification is a method of producing biodiesel that involves the reaction of triglycerides, recycled oil waste, or fats with alcohol in the presence of an effective catalyst to generate alkyl esters (biodiesel) while glycerol is produced as a byproduct (Fig. 1.1) [12-13]. In general, three sequential reversible reaction steps occur during this transesterification reaction. First, diglyceride is formed through the conversion of triglyceride to diglyceride, and then diglyceride is converted to monoglyceride. The process of converting monoglyceride to glycerol follows. At each step of the reaction, a fatty acid methyl ester (FAME, biodiesel) is produced. Therefore, the method produces a total of three fatty acid methyl esters [13]. Figure 1.2 illustrates the complete chemical reaction used to produce biodiesel. In general, for triglyceride transesterification reaction, methanol is the favored alcohol because it is less costly and can react quickly with

triglycerides owing to its advantages, which include high polarity and being the alcohol with the shortest alkyl chain [14].

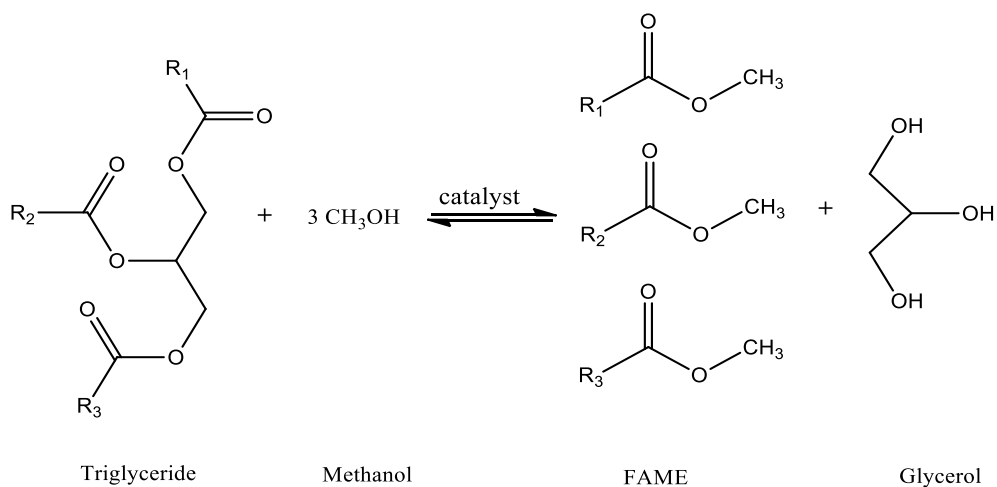


Figure 1.1 Overall transesterification reaction

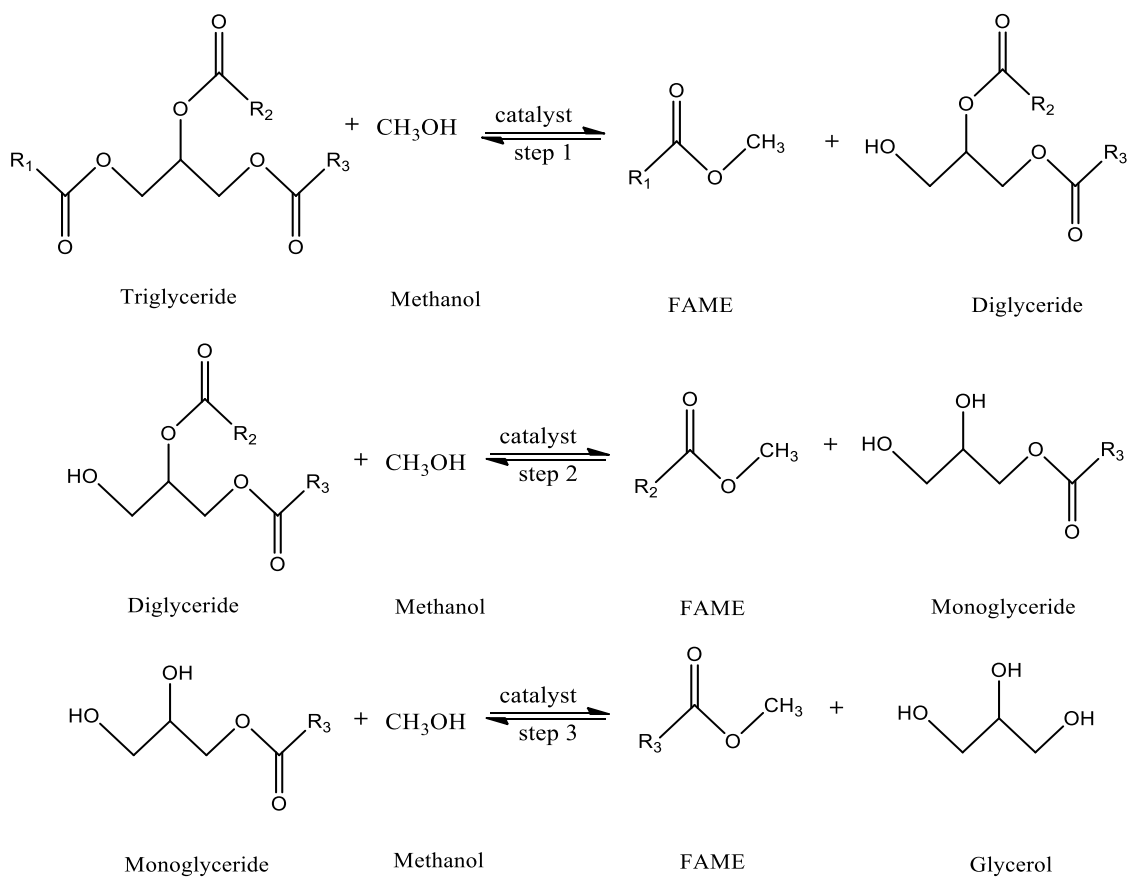
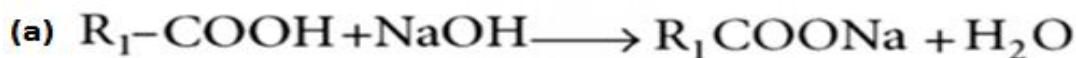


Figure 1.2 Transesterification reaction (sequential reaction)

The waste cooking oil could be used as a feedstock in the production of biodiesel instead of using virgin vegetable oil. Waste cooking oil is released directly into the waterway or accumulated on the ground in most cafeteria, hotels, and other service industries. The generation of biodiesel from used oil is environmentally friendly since it recycles waste cooking oil and provides renewable energy with fewer emissions. It replaces some amount of imported petrochemical oil and also reduces waste management costs. Producing biodiesel from waste cooking oil has three solutions: environmental, waste management and economic [14]. Moreover, when biodiesel burns, fewer contaminants are released. There are also no aromatic and sulfur compounds in the combustion outlet [15]. If vegetable oil contains free fatty acid, soap and water would be formed when a homogeneous base catalyst is used. The saponification side reaction is described in Figure 2. The key downside in this reaction is catalyst usage and increased difficulties in the separation process, which contributes significantly to the production cost. Besides that, water formation in the product can inhibit the reaction as well. Also, water produced in the side reaction (saponification reaction) can produce more free fatty acid by hydrolyzing triglycerides (Figure 1.3). In order to prevent saponification reactions (soap formation when free fatty acid (FFA) reacts with a homogeneous base catalyst), waste vegetable oil can be pre-treated with an acid catalyst. The acid catalyst would esterify the free fatty acid into esters of free fatty acid (biodiesel) [15]. This reaction is quite helpful when there is a high proportion of free fatty acids in the feedstocks. But this is a slower reaction than the transesterification reaction catalyzed by the base (Figure 1.3).



FFA Sodium hydroxide Soap Water

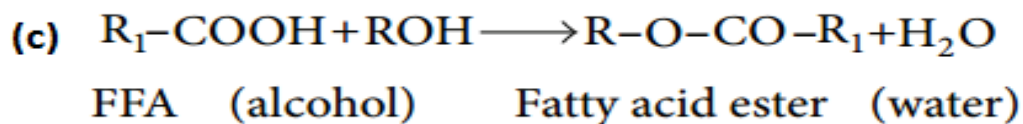
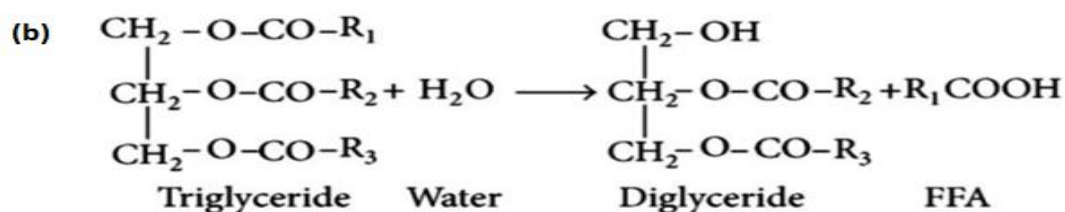


Figure 1.3 (a) Saponification side reaction. (b) Hydrolysis reaction. (c) Esterification

The most significant challenges for waste cooking oil biodiesel production is the development of a cost effective catalyst with a high activity, stability and long lifetime, due to its crucial impact on the conversion of products. Heterogeneous catalysts have attracted much attention compared to homogeneous catalysts because of their separation and reusability. The most effective catalysts from all the numerous areas of heterogeneous catalysis are metal oxide-based catalysts because mesoporous or porous metal oxides allow a large number of catalytic processes. The importance of catalysts based on metal oxide lies in their successful catalysis of various reactions, e.g. catalysis of acid-base, oxidation reactions, conversion of biomass and photocatalysis. Due to their large number of active acid sites, some metal oxides have higher catalytic activity, thus increase the catalytic surface area. These properties improve the yield of reactions and reduce reaction times [32]. Most of these metal oxides-based catalysts originate from transition metals group,

such as titanium oxides (TiO_2), zirconium oxides (ZrO_2), tin oxides (SnO_2), tungsten oxides (WO_3), iron oxides (Fe_2O_4) and zinc oxides (ZnO). Among all these acid catalysts, CaO-zirconia, tungsten-zirconia, and sulfonated-zirconia are promising for transesterifying triglycerides into alkyl esters [33]. The careful design of strong, effective, and reliable acid catalysts that can significantly enhance the efficiency of biodiesel production still remains a major challenge. The suitable heterogeneous acid catalyst for transesterification reactions should have features including hydrophobic surface, unique porosity, and strong Brønsted / Lewis acid properties [34]. Also, it is important to avoid poisoning, deactivation, and leaching of acid sites in the reaction medium.

1.2 Statement of the Problem

Recently, energy demand has increased to a large extent because of industrial development and population growth. Therefore, the development of renewable sources of energy for sustainable development and economic growth has become a priority in many countries. Biodiesel production has drawn considerable attention around the world, and it can dramatically minimize global warming and reliance on conventional fuels. About 95% of biodiesel production today comes from refined vegetable oils [6]. The extensive utilization of refined vegetable oils for biodiesel production can cause serious food issues in developing countries. It is therefore necessary to search for alternative low-cost feedstock for production of biodiesel for sustainable development. Waste cooking oil could be a promising feedstock to produce low-cost biodiesel. By using waste cooking oil (WCO), the cost of biodiesel production can be effectively reduced to 70% [6]. In addition, the production of biodiesel from the WCO would solve the problems of waste disposal and also prevent competition of the same oil resources for food and fuel.

Generally, in the commercial production of biodiesel, homogeneous catalysts are used in the transesterification process [17]. Homogeneous catalysts (acid or base) have several advantages including mild reaction conditions and high activity (reaction complete within one hour). The use of homogeneous catalysts, however, results in many process problems such as reactor corrosion, soap production, higher energy consumption, problems with

handling multiple feedstocks and production of significant quantities of wastewater, thereby increasing the overall cost of production of biodiesel.

A promising material for biodiesel production from different feedstocks is heterogeneous catalysts. Heterogeneous catalysts overcome the problems faced by the traditional homogenous catalysts. Heterogeneous catalysts have many advantages: they are environmentally friendly, efficient conversion, and compared to homogeneous catalysts, there are fewer issues with disposal. However, the major problems associated with heterogeneously catalyzed biodiesel production are their inability to withstand high FFA and water content of the feedstocks, which in turn leads to deactivation. This drawback becomes the main driving force to design a catalyst of proper configuration to achieve highly effective biodiesel production from low-cost feedstocks.

1.3 Research Objectives

Heterogeneous catalysts have drawn significant attention in the production of biodiesel because of high temperature tolerance, lack of toxicity, ease of recycling and reusability. The overall goal of this research is to design novel and effective heterogeneous catalysts for efficient biodiesel production from low-cost feedstocks.

The main objectives of this research are:

1. To explore new catalysts that can catalyze simultaneously esterification-transesterification reactions for efficient biodiesel production. Catalysts represented in the scheme: e.g. S-M-Z and M-Z (where S represent sulfate. M represent ZrO₂, CuO, ZnO, and Z represent ZSM-5, beta-zeolite, UiO-66 MOF and Cu-BTC MOF). Sulfated-Zn, Zr, Cu and Zn supported on Beta-zeolite, desilicsted ZSM-5, UiO-66 MOF and Cu-BTC MOF, respectively.
2. To investigate the physico-chemical properties of the prepared catalyst utilizing various techniques like scanning electron microscope (SEM), thermogravimetric analysis (TGA), surface area and porosity analysis (BET), X-ray diffraction (XRD), temperature-programmed desorption (TPD), transmission electron microscope

(TEM), fourier transform infrared spectroscopy (FTIR), pyridine-FTIR, X-ray fluorescence (XRF).

3. To investigate the activity of the as-developed catalyst by transesterification-esterification of low-cost feedstocks using Parr batch reactor and to examine the role of different reaction parameters like catalyst weight, reaction time and temperature, and methanol:oil ratio on the biodiesel conversion to identify the optimum process conditions for effective biodiesel production.
4. To study the reaction kinetics of a selected catalyst for investigating the feasibility of the biodiesel production using low-cost feedstock, test fuel properties and regenerate spent catalysts for economic and environmental viability.

1.4 Organization of the Thesis

The structure of this PhD thesis is based on the manuscript-style to ease the reading and understanding. Thesis introduction is given in Chapter 1, following this chapter, Chapter 2, presents literature reviews for biodiesel production. It also includes different types of catalysts used for upgradation techniques. In Chapter 3, the experimental sections procedures are discussed including all the materials, catalyst synthesis, reaction processes, and characterization techniques used to characterize catalyst and biodiesel.

Chapter 4 of the study, investigated biodiesel production from waste cooking oil using sulfated- zinc oxide supported on Beta zeolite catalysts. The effects of process parameters such as reaction time, temperature, catalyst loading and methanol to oil molar ratio are investigated. The surface acidity and its influence on the activity of pure Beta zeolite, ZnO/Beta zeolite and Sulfate/ZnO-Beta zeolite were also investigated. Zeolite-supported ZrO_2 catalyst ($\text{ZrO}_2/\text{ZSM-5}$) and a series of desilicated zeolite-supported ZrO_2 catalyst [$\text{ZrO}_2/\text{ZSM-5}(0.1\text{-}0.3\text{M})$] were successfully synthesized by impregnation method and used

as novel catalysts for the production of biodiesel in Chapter 5. The structure-performance characteristics of the catalysts were probed via different characterization techniques.

In chapter 6, we synthesized a series of Cu supported on a UiO-66 MOF (5-10%Cu/UiO-66) catalysts and utilized those catalysts to produce biodiesel from waste cooking oil with methanol. Furthermore, the influence of various process parameters, including methanol/WCO molar ratio, catalyst loading, reaction temperature and time were studied to optimize the reaction. In addition, the reaction kinetic parameters and catalyst reusability were explored. Zn supported on a Cu-BTC MOF (4-10%Zn/Cu-BTC) catalysts were prepared and utilized as new heterogeneous catalyst to produce biodiesel from WCO with methanol in chapter 7. Also, plausible mechanism to produce biodiesel through transesterification and esterification are described. The overall conclusions and recommendation from this dissertation are provided in Chapter 8. the references, appendices and authors resume at the later end. |

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel production feedstock

Recently, energy demand has increased to a large extent because of industrial development and population growth. Therefore, the development of renewable sources of energy for sustainable development and economic growth has become a priority in many countries. Biodiesel production has drawn considerable attention around the world, and it can dramatically minimize global warming and reliance on conventional fuels. A wide variety of feedstock can be used to produce biodiesel. The feedstock cost account for approximately 75% of the total biodiesel production costs [15]. So, the main issues surrounding biodiesel commercialization were feedstock prices and production costs [16]. Thus, in order to achieve low biodiesel production costs, it is important to choose suitable feedstock that are fairly cheap to produce biodiesel.

Biodiesel feedstock comes in a variety of forms: non-edible oil, edible oil, algal lipid, and waste cooking oil (Figure 2.1) [17-20]. Currently, almost all biodiesel production begins with edible oil as a feedstock because it is widely available from the established agricultural sector. In Malaysia, Europe, and the United States, edible oils are the main feedstock utilized in biodiesel production. However, the vast cultivation of edible oil for biodiesel production can put the entire world at risk, in which the slightest planning error can have a significant impact on food supply and the economy [1]. The limited agricultural land typically available for growing food would be compromised when the fuel economy and the food economy are both in competition for the same resources. Based on these circumstances, the production of biodiesel using edible food crops as a feedstock can cause

serious food supply issues in developing countries due to competition for the same resources [21].

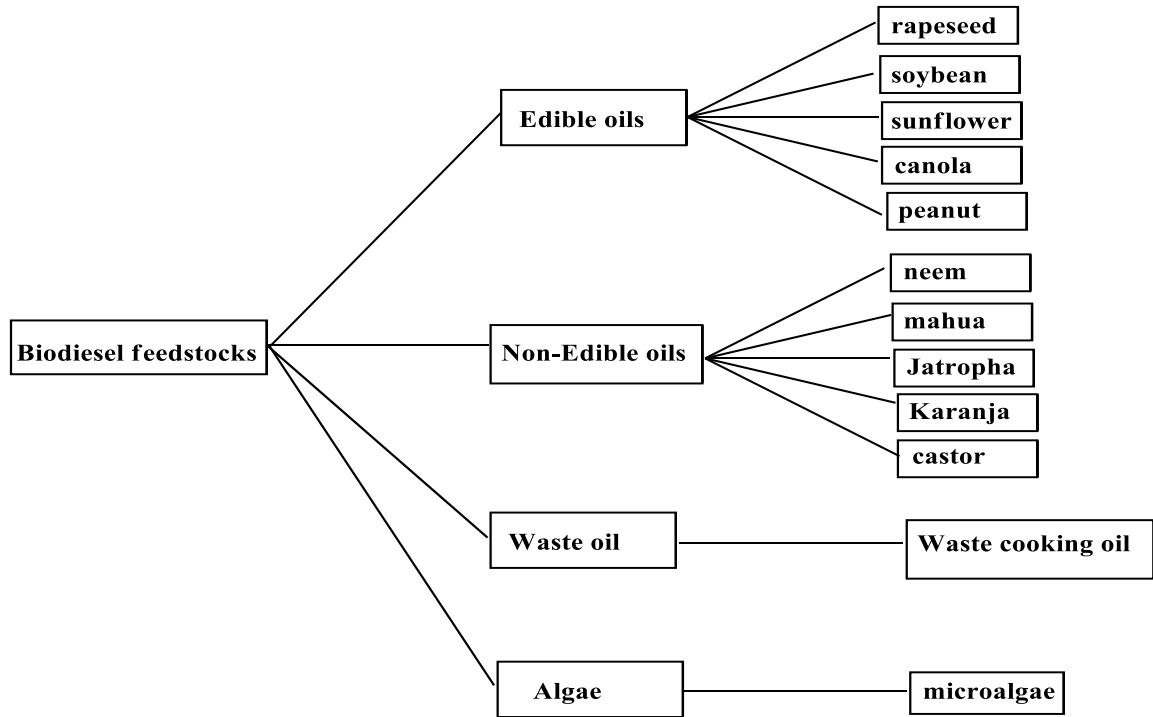


Figure 2.1 Types of biodiesel feedstock

Non-edible oils like Neem, Jatropha, Karanja, Castor, and Mahua has been identified as suitable feedstock for producing biodiesel [22]. Non-edible oil biodiesel may be deemed to have good prospects such as acceptable fuel quality, excellent engine efficiency, and desirable exhaust emission properties [23]. But biodiesel produced from non-edible oil incorporates both favorable and unfavorable attributes. Biodiesel is produced using non-edible oil as a feedstock because of its ready availability, lower aromatic content, biodegradability, and lower sulfur content [24]. However, non-edible is unfavorable as biodiesel feedstock due to the higher reactivity of its unsaturated fatty acid chains, lower volatility, higher viscosity, and carbon residue [24]. Micro algae are becoming increasingly popular as a feedstock for the production of biodiesel around the world [25].

It has become a key feedstock for producing biodiesel because of its various benefits, including higher oil productivity, rapid growth rate than conventional crops, which are of course augmented by limited available land [25].

Waste cooking oil (WCO) could be used as a biodiesel feedstock instead of edible oil. WCO is released directly into the waterway or accumulated in the ground in most cafeterias, hotels, and other service industries [26]. Producing biodiesel from WCO offers three possible solutions: environmental, waste management, and economic [27]. It is environmentally friendly to produce biodiesel from WCO because it recycles used oil and also provides sustainable energy with lower emissions. It also reduces waste management costs. By utilizing WCO, the expense of producing biodiesel could be decreased by up to 70% [6]. Also, waste disposal concerns could be solved by producing biodiesel from WCO.

2.2 Types of Catalyst

As mentioned previously, transesterification of vegetable oil, animal fat, and recycled waste oil with methanol in the presence of a suitable catalyst produces methyl ester of long-chain fatty acid (biodiesel), with glycerol as a byproduct [28]. During the transesterification reaction, a catalyst plays a key role in providing an active site for the reactants and reduce the reaction's total activation energy. In general, in the production of biodiesel, different kinds of catalysts are used to transesterify triglycerides: homogeneous catalysts, heterogeneous catalysts, and biocatalysts (Figure 2.2).

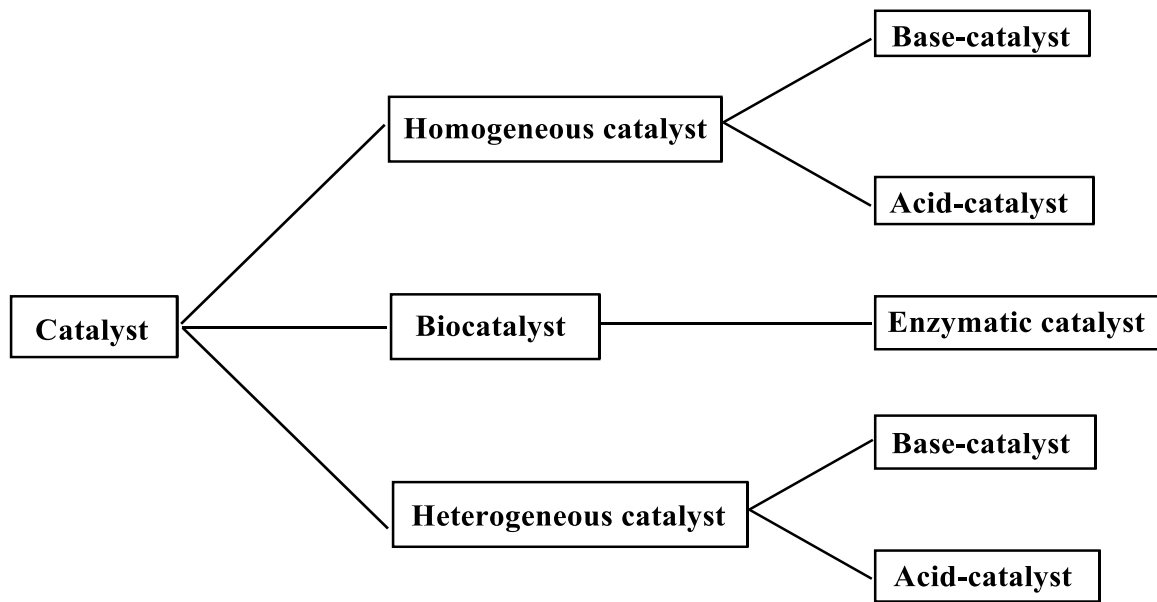


Figure 2.2. Classification of biodiesel catalyst

2.3 Homogeneous Catalyst Utilized in the Production of Biodiesel

Conventionally, homogeneous catalysts are employed in biodiesel production from various oils. For industrial biodiesel production, the most commonly utilized catalyst is homogeneous catalyst, as it is easy to use and less time is required to obtain a complete reaction. Homogeneous catalysts, which generally may be liquid or gaseous, and reactants are both in the same phase [29-30]. Homogeneous catalysts are classified into two categories: acidic catalysts and alkaline catalysts [31].

2.2.1 Homogeneous Base-Catalysts

For triglyceride transesterification, homogeneous base catalysts are typically utilized. The base catalysts are metal-based oxide and alkaline liquids such as potassium methoxide, sodium methoxide, carbonates, sodium hydroxide, and barium hydroxide [32]. The catalytic activity of homogenous base catalysts is very high in transesterification [32]. Metallic hydroxide is often used as homogenous base catalysts in transesterification because of lower prices, but they usually have lower activity in transesterification than alkoxide [33]. In transesterification reaction, alkoxide species are highly basic and have a high activity which then attacks the triglyceride carbonyl group to form long-chain fatty acid (biodiesel) and glycerol [6].

Many researchers have studied the homogeneous base-catalyzed transesterification reactions of triglycerides. In 2008, Rashid et al. [34] used homogeneous base catalyst potassium hydroxide (KOH) to produce rapeseed oil biodiesel. The authors discovered that potassium hydroxide can achieve a yield of 96% with a 1 wt% catalyst loading. Phan et al. showed that potassium hydroxide can produce promising results with maximum biodiesel yields of up to 90% at a 0.75 wt% catalyst concentration [35]. However, when the catalyst amount was raised to 1.5 wt% potassium hydroxide, only 75% of biodiesel yield was achieved. This declining trend is explained by saponification, which happens when catalyst loading is high, resulting in a lower biodiesel yield and increases reactant viscosity. The performance of different KOH catalyst loading in the transesterification of croton megalocarpus oil was examined by Kafuku et al. [36]. They observed that the use of a 0.50 wt.% catalyst loading led to a decreased biodiesel conversion (50%). However, the biodiesel conversion increased significantly and reached a maximum value of 88% at a catalyst amount of 1.0 wt.%. Furthermore, they discovered that increasing the catalyst loading above the optimal catalyst concentration of 1.0 wt.% reduced biodiesel conversion, and soap was discovered in greater quantities due to excess catalysts that favor the saponification process.

Sivakumar et al. [37] carried out research to optimize biodiesel yield using KOH catalyst. Their results showed that 1.2 wt.% KOH catalyst at 75 °C can be considered as an optimum condition for transesterification of waste scum. A yield of 96.7% was achieved for these process conditions in 30 min. KOH catalyst was utilized by Dueso et al in the catalytic transesterification of sunflower oil [38]. Under the reaction conditions of 60 °C temperature, 1 wt.% catalyst loading and 6:1 molar ratio of methanol to oil (MRMO), a biodiesel yield of 98.6% was obtained in 3 h with the KOH catalyst.

Transesterification of *Elaeagnus angustifolia* seed oil in methanol utilizing potassium methoxide catalyst was investigated by Kamran et al. [39]. At a reaction condition of temperature $T = 60$ °C, time $t = 60$ min, 1.0 wt% of catalyst, and 9:1 MRMO, the optimal biodiesel yield of 95% was achieved. Also, in the work of Wakil et al. [40] on transesterification of rice bran using sodium hydroxide (NaOH) catalyst, 80% yield was obtained at 0.9 wt% NaOH catalyst, reaction temperature of 60 °C in 2 h at 6:1 MRMO.

When compared to homogeneous acid-catalyzed processes, the homogeneous base-catalyzed process with sodium methoxide and potassium methoxide catalyst and edible oils like sunflower, soybean, and canola is four thousand times faster than that of homogenous acid-catalyzed reaction [33]. Unfortunately, this approach has a few drawbacks, including the fact that the catalyst is not recycled, and must be removed from the product streams [30]. The catalyst can also react with oil impurities to produce soap, especially free fatty acids [31]. The effective use of homogeneous base catalysts is confined to refined oils containing a FFAs of less than 0.5 weight percent [31]. In addition, these catalysts are removed after the reaction is complete by washing the biodiesel with water, which could lead to the loss of alkyl esters, consumption of energy, and the production of significant quantities of wastewater [41]. Therefore, it is important to explore the possibility of replacing homogeneous base catalysts with some other suitable transesterification reaction catalysts in order to establish an environmentally friendly and low-cost biodiesel production method.

2.3.2 Homogeneous Acid-Catalysts

The homogeneous acid-catalyzed transesterification process offers a considerable advantage over the homogeneous base-catalyzed transesterification process because the presence of FFAs in the feedstock has no effect on the acid catalyst and both esterification and transesterification can be catalyzed at the same time [42]. The most widely employed catalysts for acid-catalyzed transesterification are sulfuric acids, hydrochloric acids, and sulfonic acids [42]. Homogeneous acid-catalysts produce very high alkyl ester yields. However, compared to base-catalyzed transesterification reactions, the reactions are slower, making the process costly as a result of high energy consumption [43]. Acid-catalyzed transesterification reaction has the same problems of separation as the base-catalyzed process.

To optimize biodiesel production, several researchers have made attempts to investigate the homogeneous acid-catalyzed transesterification of triglycerides. Freedman et al. [44] conducted extensive research on the catalytic activity of sulfuric acid (H_2SO_4) in the production of soybean oil biodiesel. They demonstrated that a biodiesel conversion of >90% can be obtained with a 1 mol % catalyst and 30:1 MRMO for 69 h. Using sulfuric acid and hydrochloric acid catalysts, biodiesel is produced from castor oil by Meneghetti et al. [45]. The authors found that biodiesel can be produced by transesterifying castor oil using ethanol or methanol. By using either ethanol or methanol, they obtained almost similar biodiesel yields, but they noticed that when methanol was used, the transesterification process proceeded very fast. Crabbe et al. [46] transesterified crude palm oil with methanol over H_2SO_4 catalyst. The authors found that a biodiesel yield of 97% can be achieved by using a 5 wt.% catalyst and 40:1 MRMO at 95 °C in 9 hours. Similarly, Wang et al. [47] used H_2SO_4 catalyst for WCO transesterification. The authors observed that the sulfuric catalyst shows enhanced transesterification activity and provided a maximum methyl ester conversion of 90% at a reaction temperature of 95 °C, 20:1 MRMO, and sulfuric acid loading of 4 wt.% in 10 h. The homogeneous acid-catalyzed biodiesel production process is effective to convert low-cost feedstock to biodiesel, but not so economical because large quantities of catalysts and a long reaction time are required to obtain a high biodiesel yield. Homogeneous acid-catalysts are preferred for low-cost feedstock because the catalysts are insensitive to the presence of FFAs and water, while

the presence of FFAs and water in the feedstock has an effect on homogeneous base catalysts. Therefore, it is very important to search for a catalyst that has the potential of overcoming issues related to homogeneous catalyst biodiesel production for sustainable energy processes. Table 2.1 depicts a comparison of various homogeneous catalysts utilized by several research studies to convert different feedstock into biodiesel.

Table 2.1

Some studies on biodiesel production utilizing homogeneous catalysts

Catalyst	Feedstock	Reaction conditions (reaction time, temperature, catalyst amount, and alcohol to oil molar ratio)	Conversion	Ref.
KOH	Croton megalocarpus oil	1 h, 60 °C, 1.0 wt.%, 30:1	88%	36
Potassium methoxide	Elaeagnus Angustifolia seed oil	1 h, 60 °C, 1 wt.%, 9:1	95%	39
NaOH	Rice bran oil	2 h, 60 °C, 0.9 wt.%, 6:1	80%	40
KOH	Waste scum	30 min, 75 °C, 1.2 wt.%, 6:1.	96.7%	37
H ₂ SO ₄	Soybean oil	69 h, 65 °C, 1 wt.%, 30:1	>99%	44
H ₂ SO ₄	Crude palm oil	9 h, 95 °C, 5 wt.%, 40:1	97%	46
H ₂ SO ₄	Used cooking oil	10 h, 95 °C, 4 wt.%, 20:1	90%	47

2.4 Heterogeneous catalysts utilized in the production of biodiesel

Heterogeneous catalysts are in different phases compared to the reactants and products [48]. Because of its availability and short reaction time, homogeneous catalysts are becoming more common in the biofuel industry [49]. However, in the esterification and transesterification processes, the use of a homogeneous catalyst causes many problems. For instance, when sulfuric acid is used in esterification, it causes reactor corrosion and high sulfur content in biodiesel products. For homogeneous base catalysts such as KOH and NaOH, product separation, liquid catalyst recovery, and product washing are required through the acid neutralization steps, which could lead to the production of a high amount of wastewater, higher energy consumption, thereby increasing the biodiesel production costs. It is expected that using heterogeneous catalysts rather than homogeneous catalysts will overcome the issues related to homogeneous catalysts. In comparison with homogeneous catalysts, heterogeneous catalysts offer various benefits, including easy regeneration, elimination of product washing step, less corrosiveness, efficient conversion, environmental friendliness, and fewer disposal issues. Heterogeneous catalysts can handle multiple feedstock in a single step [50]. However, the major problems associated with heterogeneously catalyzed biodiesel production include a higher ratio of alcohol to oil and higher temperature. Another disadvantage of heterogeneous catalysts is that they react with alcohol and oil to form three phases, which limits dispersion and hence reduces reaction rate [50]. The difficulty of mass transfer is resolved by the use of co-solvents such as heptane, ethanol, and tetrahydrofuran, which enables oil and alcohol miscibility, as a result of which the reaction rate is increased [51]. The use of catalyst supports is another way to overcome mass transfer difficulty [52]. The supports will offer the active species with increased pores and precise surface area in which they could attach and react with bulky triglycerides [52]. Heterogeneous catalysts are further subdivided into two categories: acidic catalysts and alkaline catalysts [48].

2.4.1 Heterogeneous base-catalysts

Heterogeneous base catalysts with alkaline properties on their surface are excellent candidates to substitute a homogeneous base catalyst for the transesterification process. Heterogeneous base catalysts have the tremendous potential to address the major challenges encountered in the biodiesel production industry. These catalysts offer several advantages, which include easy regeneration, environmental friendliness, and fewer disposal issues [53]. Furthermore, during heterogeneous base-catalyzed transesterification reactions, only small amount of wastewater is produced. Heterogeneous base catalysts are typically more resistant to FFAs and water in the economical feedstock, which includes waste cooking oil and fat as compared to homogeneous base catalysts [54]. Longer catalyst life, renewability, selectivity, and higher activity can all be achieved with heterogeneous base catalysts [55]. Heterogeneous base catalysts are further subdivided into six groups. Supported alkali earth metal or supported alkaline earth metal, hydrotalcite, zeolite, metal oxide, mixed metal oxide, and non-oxide are the six groups of heterogeneous base catalysts [56].

Several heterogeneous base catalysts for biodiesel production have been documented in the literature over the last few decades. Liu et al. [57] transesterified soyabean oil using strontium oxide (SrO) catalyst. The author found that a biodiesel yield of 95.0% can be obtained with 12:1 MRMO and 3 wt.% catalyst at 65 °C for 30 minutes. Moreover, after ten cycles of reusing strontium oxide catalyst, the biodiesel yield was only reduced marginally. Kim et al [58] transesterified soybean oil with methanol over Na/NaOH/ γ -Al₂O₃ catalyst. The biodiesel yield achieved was 94% at 1 wt.% catalyst loading and 9:1 MRMO at 60 °C after 2 h. Liu et al [55] documented the use of calcium oxide (CaO) catalyst in the production of biodiesel. The specific surface area (m²/g) of the catalyst was determined using The Brunner–Emmett–Teller (BET) technique. The total surface area of a solid catalyst is measured by BET surface area analyzers. A powdered analyte is suspended in an inert gaseous bath, and the surface adsorption of gas molecules is measured. The CaO catalyst BET surface area was 0.56 m²/g. At a process condition of T= 65 °C, t = 3 h, 8 wt.% of CaO catalyst, and 12:1 MRMO, the maximum biodiesel yield of 95% was achieved. They also investigated the comparative activity of calcium oxide

with $\text{K}_2\text{CO}_3/\gamma\text{Al}_2\text{O}_3$ and $\text{KF}/\gamma\text{Al}_2\text{O}_3$ solid catalyst. They found that CaO catalyst maintained activity after repeated use for twenty cycles and the yield remained unaffected, while biodiesel yield was reduced when $\text{K}_2\text{CO}_3/\gamma\text{Al}_2\text{O}_3$ and $\text{KF}/\gamma\text{Al}_2\text{O}_3$ solid catalyst are subsequently reused for 20 cycles. This is due to the dissolution of alkali metal compounds in alcohol, which decreases the catalytic activity and thus reduces the yield in the subsequent reaction. The activity of a CaO catalyst in biodiesel production from sunflower oil was investigated by Granados et al. [59]. They demonstrated that with catalyst amount and temperature of 1.0 wt.% and 60 °C, respectively, 13:1 MRMO in 90 min, biodiesel yield of 94% was achieved. The BET pore size diameter of the CaO catalyst was 30 nm and the surface area of the CaO catalyst was 32 m²/g. During their investigation, they found that the active site of the catalyst was poisoned by atmospheric gases (H_2O and CO_2). Consequently, the catalyst was subjected to high-temperature activation treatment before reaction to enhance its activity. Even though the key poison species, carbonate group, was removed from the surface by this treatment, active species leaching was also observed. But the amount of leaching did not result in a substantial decrease in activity and the catalyst maintained activity after repeated use for 8 cycles [59]. However, biodiesel conversion reduced from 94% in the first cycle to 80% in the second cycles, and the yield remained unaffected after that. Veljkovic et al. [60] studied the kinetics of calcium oxide catalyst in the transesterification of sunflower oil using methanol. A biodiesel yield of 98% was achieved with 1 wt.% catalyst content at 60 °C, and 6:1 MRMO in 2 h reaction time. Kaur et al [61] used a lithium doped calcium oxide (Li/CaO) catalyst in the production of jatropha and karanja oil biodiesel. X-ray diffraction, BET, and transmission electron microscopy were used to characterize the catalyst. The catalyst, under an optimized reaction condition of 12:1 MRMO, 5 wt% catalyst at 65°C, produced the highest conversion of >99% in 1 h and 2 h reaction time for karanja and jatropha oil, respectively. Kouzu et al. [62] transesterified soyabean oil utilizing CaO catalyst and methanol. The authors found that the catalyst shows excellent transesterification performance, where biodiesel yield of 93% was obtained with 0.78 g catalyst, a reaction time of 1 h, and mixing speed of 500 rpm. Mootabadi et al. [63] evaluated the performance of different catalysts in the production of palm oil biodiesel: calcium oxide (CaO), strontium oxide (SrO), and barium oxide (BaO). They recorded biodiesel yield of 95.2% (for BaO), 95.2% (for SrO),

and 77.3% (for CaO) by using 3 wt.% catalyst in 1 h. The catalysts activity order was BaO > SrO > CaO. In another related study, Salamatinia et al. [64] studied the performance of BaO and SrO in the production of palm oil biodiesel. A biodiesel yield of 69.44% and 66.93% were achieved using 1.0 wt.% catalyst at 50 °C, and 9:1 MRMO in 30 min reaction time for BaO and SrO, correspondingly. They reported that optimized biodiesel yield obtained with MRMO of 9:1 and catalyst loading of 3.0 wt% in 50 min for SrO and BaO were >94% and 95.17%, respectively.

Laskar et al. [65] employed waste snail shells as a heterogeneous base catalyst in the production of soybean oil biodiesel. The use of waste materials as a catalyst source reduces the overall cost of producing biodiesel. It also allows for the recycling of natural mineral sources, making the process environmentally friendly. The waste snail shells main component calcium carbonate (CaCO_3) is transformed into calcium oxide (CaO) catalyst by calcination in air for 5 hours at 900 °C [65]. They obtained 98% biodiesel yield from soybean oil using 6:1 MRMO at ambient temperature and 3.0 wt.% catalyst amount in 7 h reaction time. Moreover, the catalyst maintained activity after reuse for 8 reaction cycles. Also, Viriya-empikul et al. [66] used waste eggshells as a heterogeneous catalyst in biodiesel production from palm olein oil. The waste eggshells major component CaCO_3 is transformed into CaO catalyst by calcination in the air for five hours at 800 °C. With a 10 wt.% catalyst and 12:1 MRMO, a biodiesel yield of >90% was achieved at 60 °C for 2h. Nair et al. [67] investigated the use of clamshell as a catalyst in the transesterification of waste frying oil for biodiesel production. The CaO catalyst, which was synthesized from clamshell successfully transesterified waste frying oil, and >89% of biodiesel yield was obtained with 6.03:1 MRMO at 60 °C and 3 wt.% catalyst for 3 h. Birla et al. [68] reported a 87.28% biodiesel yield from WCO with 8.45:1 MRMO, 2 wt.% of catalyst at 60 °C in 7 h using a heterogeneous base catalyst such as snail shells. Xie et al. [69] transesterified soybean oil using NaX Zeolite/KOH heterogeneous solid base catalyst. They reported that the NaX Zeolite/KOH catalyst showed good transesterification performance, where a maximum biodiesel yield of 85.6% was obtained with 10:1 MRMO and 3.0 wt.% of catalyst loading at 65 °C for 8 h. In the transesterification of soybean oil with methanol, Fabbri et al. [70] employed a Na_2PEG (300), as a base catalyst in the production of soybean

oil biodiesel with dimethyl carbonate. They reported that the catalyst provided a conversion of approximately 99% at 5 wt.% catalyst amounts and 90 °C reaction temperature after 5 hours reaction time. Elsewhere, Tan et al. [71] transesterified used cooking oil over chicken eggshells and ostrich eggshells as a catalyst. A biodiesel yield of 94% and 96% were achieved using 1.5 wt.% catalyst at 65 °C, and 12:1 MRMO in 2 h reaction time for chicken eggshells and ostrich eggshells, correspondingly. Also, Xu et al. [72] investigated the catalytic performance of KF/Zn(Al)O catalyst in the production of biodiesel from soybean oil. According to the authors, the synthesized catalyst is more reactive than that of Zn-Al hydrotalcite. In their study, the reaction was conducted for 3 h with 3 wt.% catalyst and 6:1 MRMO at 65 °C. A biodiesel yield of about 95% was achieved at these conditions within 3 h. Navajas et al. [73] studied Mg-Al hydrotalcite catalytic activity in the transesterification of sunflower oil. The co-precipitation method was used to produce the catalyst with Mg:Al molar ratio of 5. They obtained a 92% biodiesel yield at 60 °C temperature, 48:1 MRMO, and 2 wt.% catalyst loading for 24 h. They attributed the Mg-Al hydrotalcite catalytic activity to the existing basic sites at the crystal edge. Trakarnpruk et al. [74] reported a high biodiesel yield by utilizing a K-loaded Mg-Al hydrotalcite catalyst in palm oil biodiesel production. The authors conducted the reaction with 7.0 wt.% catalyst and 30:1 MRMO at 100 °C for 7 hours. A biodiesel yield of approximately 86.6% was obtained at these conditions. Hernandez et al. [75] transesterified sunflower oil and WCO over Na-Mg-Al hydrotalcite catalyst. The optimum MRMO was 15:1 for sunflower oil and 9:1 for WCO. The catalyst produces the highest yield of 88% and 67% for sunflower oil and WCO, respectively, at 60 °C for 8 h by using 7 wt.% catalyst (hydrotalcite impregnated with 5% of sodium for sunflower oil and 10% of sodium for WCO). Yan et al. [76] used Zn₃La₁(Lanthanum modified ZnO) for biodiesel production from WCO. An optimum yield of 93.7% was achieved with 3 wt.% catalyst and 26:1 MRMO at 200 °C for 3 h. Agarwal et al. [77] transesterified WCO with KOH/Al₂O₃ catalyst. They reported that the catalyst showed excellent transesterification performance, where yield of 96.8% was obtained with catalytic loading of 15 wt.% and 9:1 MRMO at 70 °C for 2 hours. Moreover, when KOH/Al₂O₃ catalyst was subsequently reused for 3 cycles, the catalyst resulted in a reasonable conversion rate (83%). Molaei et al. [78] reported a 92.1% biodiesel yield from WCO with 10.0 wt.% catalyst and 30:1 MRMO at 65 °C in 2 h using CaO-ZrO₂ catalyst.

They observed that the stability of CaO-ZrO₂ catalyst declined as the Ca/Zr molar ratio increases, such that high stability was achieved by catalyst prepared with low concentration of CaO.

In view of the literature presented above, it may therefore be argued that the heterogeneous base-catalyzed method is an efficient method of producing biodiesel with low cost and negligible environmental consequences. However, this process is sensitive to the FFAs composition of feedstock used to produce biodiesel. Hence, the inability of heterogeneous base catalysts to withstand high FFAs of the economical feedstock under mild reaction conditions is the main limitation associated with their development. Table 2.2 shows a comparison of different heterogeneous base catalysts utilized by several research studies, in terms of biodiesel yield, process conditions, and feedstock.

Table 2.2

Some studies on biodiesel production utilizing heterogeneous base catalysts

Catalyst	Feedstock	Reaction conditions (reaction time, temperature, catalyst amount, and alcohol to oil molar ratio)	Performance	Ref.
SrO	Soyabean oil	30 min, 65 °C, 3 wt.%, 12:1	95%	57
Na/NaOH/ γ Al ₂ O ₃	Soyabean oil	2 h, 60 °C, 1 wt.%, 9:1	94%	58
CaO	Soyabean oil	3 h, 65 °C, 8 wt.%, 12:1	95%	55
CaO	Sunflower oil	100 min, 60 °C, 1 wt.%, 13:1	94%	59

CaO	Sunflower oil	2 h, 60 °C, 1 wt%, 6:1	98%	60
Snail shell	Waste cooking oil	7 h, 60 °C, 2 wt.%, 8.45:1	87.28%	68
BaO	Palm oil	1 h, 50 °C, 3 wt.%, 9:1	95.2%	63
SrO	Palm oil	1 h, 50 °C, 3 wt.%, 9:1	95.2%	63
CaO	Palm oil	1 h, 50 °C, 3 wt.%, 12:1	77.3%	63
BaO	Palm oil	60 min, 50 °C, 3 wt.%, 9:1	95.17%	64
SrO	Palm oil	60 min, 50 °C, 3 wt.%, 9:1	>94%	64
Waste snailshells	Soyabean oil	7 h, 3 wt.%, 6:1	98%	65
Waste eggshells (CaO)	Palm olein oil	2 h, 60 °C, 10.0 wt.%, 12:1	>90%	66
KOH/Al ₂ O ₃	Waste cooking oil	2 h, 70 °C, 15 wt.%, 9:1	96.8%	77
Li/CaO	Jatropha oil karanja oil	2 h, 65 °C, 5 wt.%, 12:1 1 h, 65 °C, 5 wt.%, 12:1	>99	61
Ostrich eggshells	Used cooking oil	2 h, 65 °C, 1.5 wt.%, 12:1	96%	71
Chicken-eggshells	Used cooking oil	2 h, 65 °C, 1.5 wt.%, 12:1	94%	71
NaX Zeolite/KOH	Soyabean oil	8 h, 65 °C, 3 wt.%, 10:1	85.6%	69

Na ₂ PEG (300)	Soyabean oil	5 h, 70 °C, 6 wt.%, 30:1	99%	70
KF/Zn(Al)O	Soyabean	3 h, 65 °C, 3 wt.%, 6:1	95%	72
Mg-Al hydrotalcite	Sunflower oil	24 h, 60 °C, 2 wt.%, 48:1	92%	73
K- loaded Mg-Al hydrotalcite	Palm oil	7 h, 100 °C, 7 wt.%, 30:1	86.6%	74
Na-Mg-Al hydrotalcite (HT-Na)	Waste cooking oil	8 h, 60 °C, 7 wt.%, 9:1	67%	75
Zn ₃ La ₁ (Lanthanum modified ZnO)	Waste cooking oil	3 h, 200 °C, 3 wt.%, 26:1	93.7%	76
CaO (Clamshell)	Waste frying oil	3 h, 60 °C, 3 wt.%, 6.03:1	>89	67
CaO-ZrO ₂	Waste cooking oil	2 h, 65 °C, 10 wt.%, 30:1	92.1%	78

2.4.2 Heterogeneous acid-catalysts

Heterogeneous acid catalysts have an enormous potential to simultaneously carry out both esterification of free fatty acid and transesterification of triglycerides using low-cost feedstock, thus lowering the cost of producing biodiesel. Heterogeneous acid catalysts can usually withstand more extreme operating conditions and cause less corrosion problems compared to homogeneous acid catalysts [79]. These catalysts have many acid sites of various Brønsted or Lewis acidity strengths. Biodiesel is usually produced from feedstock with high FFAs using heterogeneous acid catalysts. However, the benefits of

heterogeneous acid catalysts including: easy separation from the finished product, and their being recyclable for repeated use. Therefore, heterogeneous acid catalysts offer a more economical path to the biodiesel production process [80-81]. Nevertheless, to achieve good conversion yield, higher temperatures, higher catalyst loading, and longer reaction times are required for heterogeneous acidic catalysts [82]. Also, in some cases, soap formation is observed using heterogeneous acid catalysts, and purification is required in most cases to ensure the appropriate fuel quality. In addition, it is important to avoid poisoning, deactivation, and leaching of acid sites. Low-cost feedstock, for example, waste cooking oils, have been described as promising feedstock with the potential to decrease the cost of production and thus enhance biodiesel production economic viability. Heterogeneous acid catalysts are usually non-sensitive to water and free fatty acid. Thus, free fatty acid esterification and triglycerides transesterification into biodiesel can be catalyzed more efficiently with a solid acid catalyst. In addition, the acid-catalyzed process is cost-effective and can also address waste disposal problems because heterogeneous acid catalysts can produce biodiesel directly low-cost feedstock [83]. The most effective catalysts from all the numerous areas of heterogeneous catalysis are metal oxide-based catalysts because mesoporous or porous metal oxides allow many catalytic processes. The importance of catalysts based on metal oxide lies in their successful catalysis of various processes, e.g. catalysis of acid-base, oxidation reactions, conversion of biomass, and photocatalysis. Due to their vast number of active acid sites, some metal oxides have higher catalytic activity, thus increase the catalytic surface area. These properties improve the yield of reactions and reduce reaction times [84]. Most of these metal oxides-based catalysts originate from transition metals groups, such as titanium oxides (TiO_2), zirconium oxides (ZrO_2), tin oxides (SnO_2), tungsten oxides (WO_3), iron oxides (Fe_2O_3), and zinc oxides (ZnO). Among all these acid catalysts, sulfonated-zirconia, tungsten-zirconia, and CaO -zirconia are suitable for transesterifying triglycerides into alkyl esters [85]. A suitable heterogeneous acid catalyst for transesterification reactions should have features including hydrophobic surface, interconnected large pores, and strong Brønsted/Lewis acid properties [86]. A myriad of studies on the utilization of the heterogeneous acid catalyst in biodiesel production have been conducted. Jitputti et al. [87] showed that sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) can produce promising results with biodiesel yields of up to 86.3% and 90.3%, with

crude coconut and palm kernel oils, respectively. However, biodiesel yield was only 48% (crude coconut oil) and 63% (palm kernel oil) when unsulfated zirconia was used as a catalyst instead of sulfated zirconia. The results showed that sulfated zirconia demonstrated the highest catalytic conversion (86.3% for coconut oil and 90.3% for palm kernel oil) in optimized conditions of 200 °C temperature, 6:1 MRMO, and 1.0 wt.% catalyst for 4 h. This essentially demonstrates that the main factor in achieving high triglyceride conversion is the modification of metal oxide surface acidity. Ibrahim et al [88] explored the esterification of waste cooking oil using ZrO₂ loaded on various supports (TiO₂, SiO₂, Fe₂O₃, and Al₂O₃). The hybrid sol-gel auto combustion approach was used to synthesize the catalyst. The esterification process was conducted with 120:1 MRMO and 0.1 wt.% catalyst at 120 °C for 3 hours. Optimal biodiesel conversion (48.6%) was achieved with ZrO₂/SiO₂ catalyst within 3 hours. Park et al. [89] performed esterification of WCO with ZrO₂, in which tungstate (WO₃) was integrated into ZrO₂ instead of sulfuric acid (H₂SO₄). WO₃/ZrO₂ was found to be more stable than SO₄²⁻/ZrO₂, thus preventing acid sites from leaching into the reaction media. The authors discovered that after 1 hour at 75 °C, 93% of FFAs conversion was achieved using 9:1 MRMO [89]. Despite the high acidity of sulfated-zirconia, during liquid-phase transesterification reaction, it is known to suffer substantial deactivation due to sulfate leaching [90]. By dissolving the freshly prepared SO₄²⁻/ZrO₂ catalyst in water, catalyst leaching has been tested [90]. Hydrolysis of the sulfate groups to H₂SO₄ and HSO₄ rapidly lowers the pH of the suspension. This will induce transesterification through homogeneous acid catalysis, thereby obstructing heterogeneous catalytic activity. SO₄²⁻/ZrO₂ was prepared using chlorosulfonic acid, HSO₃Cl rather than impregnation with H₂SO₄. The prepared catalyst (SO₄²⁻/ZrO₂) exhibited a very high catalytic activity and no leaching of sulfates was noted. Chlorosulfonic acid is a very dangerous chemical, and also exposure for a very short period may lead to death or serious trauma [91].

The esterification of methanol-induced FFA using SO₄²⁻/SnO₂-ZrO catalyst was conducted by Enascuta et al. [92]. They reported that the esterification process involves Brønsted and Lewis acid sites. A biodiesel yield of 82.58% was achieved using the following conditions: 5.0 wt.% of catalyst and 6.5:1 of molar ratio of ethanol to oil (MREO) at 78 °C for 6 hours. A number of new SO₄²⁻/ZrO₂-based catalysts were obtained from MCM-41 silica-

supported calcined zirconium sulfate (ZrX-MCM-41, where X represents zirconia sulfate precursor weight percentage) have been studied by Jiménez et al in the production of biodiesel using sunflower oil having high water and FFA content [93]. They reported that optimized ethyl esters yield of 91.5% was obtained with 14:1 MREO and 14.6 wt.% of catalyst at 200 °C in 5 h. In addition, as-prepared catalysts are stable (without sulfate species leaching) with consistent catalytic activity after three catalytic cycles. Elsewhere, Gopinath et al. [94] used mesoporous sulfated Zr-KIT-6 to produce biodiesel from oleic acid and jatropha oil. The catalyst was synthesized using a hydrothermal process. Sulfated Zr-KIT-6 catalyst is produced by loading various amount of zirconia into a fixed gel in an acidic medium and then sulfating it (see Figure 2.3). The authors found that biodiesel conversion of 85% and 96% were achieved from jatropha oil and oleic acid, respectively, with 4 wt.% catalyst and 20:1 MRMO at 120 °C in 6 h.

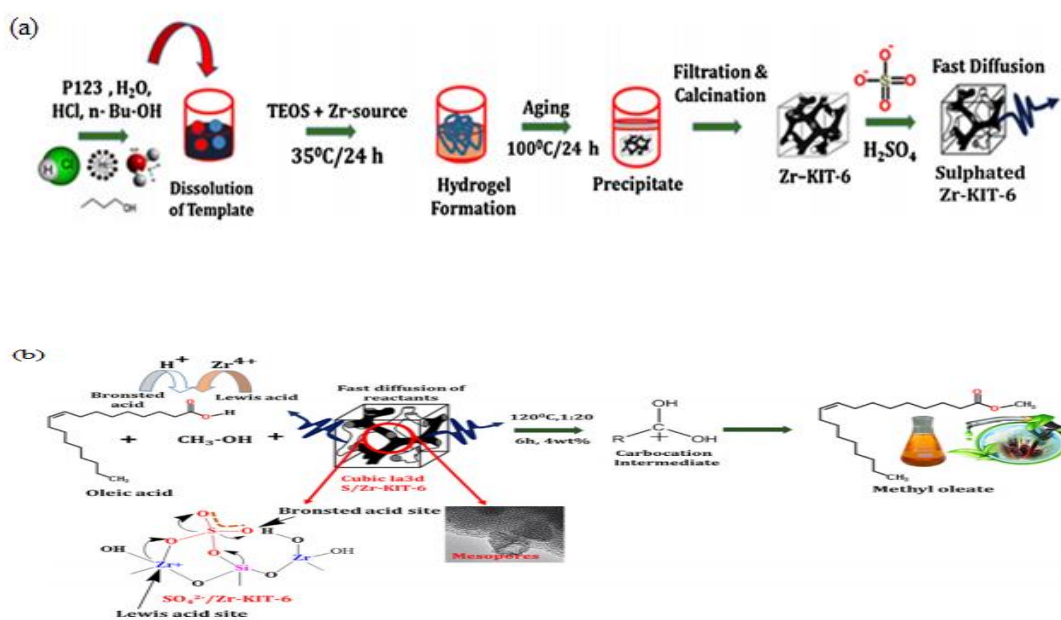


Figure 2.3 (a) Schematic diagram of synthetic strategy of mesoporous Sulfated Zr-KIT-6

(b) Esterification of oleic acid by mesoporous Sulfated Zr-KIT-6. (Reprinted from ref. 94.).

Fatimah et al. [95] conducted transesterification of soybean oil with Zr_2O -supported bamboo leaf ash ($\text{Zr}_2\text{O}/\text{BLA}$) as a catalyst. The catalyst was synthesized using the impregnation technique and the catalyst had a 20 wt% metal content. It is noted that the $\text{Zr}_2\text{O}/\text{BLA}$ catalyst showed excellent transesterification performance, where biodiesel yield of 89.99% was achieved under optimal process condition (12 wt.% of catalyst and 15:1 MRMO at 50 °C for 0.5 h). Wang et al [96] applied a zirconium-based carbonaceous ($\text{Zr-SO}_3\text{H@CMC}$) catalyst to produce biodiesel from oleic acid. They reported that a maximum of 99.1% biodiesel yield was obtained at 90 °C for 2h, using 5.0 wt.% catalyst amount, and 20:1 MRMO.

Guldhe et al. [97] evaluated the catalytic activity of tungstated zirconia (WO_3/ZrO_2) in the transesterification of S. Obliquus lipids with methanol. The Fourier transform infrared spectroscopy characterization of the WO_3/ZrO_2 indicated that Brønsted and Lewis acid sites are present. Transesterification of S. Obliquus lipids was carried out with 15 wt.% catalyst loading and 12:1 MRMO at 100 °C for 3 hours. The maximum biodiesel conversion under this condition was 94.58%. Also, Sun et al. [98] explored the transesterification of sunflower oil using ZrO_2 loaded on La_2O_3 support ($\text{ZrO}_2/\text{La}_2\text{O}_3$) synthesized by wet impregnation, in the production of biodiesel (Figure 2.4). The authors reported optimum biodiesel conversion of 84.9% with 5 wt.% catalyst loading and 30:1 MRMO at 200 °C for 5 h.

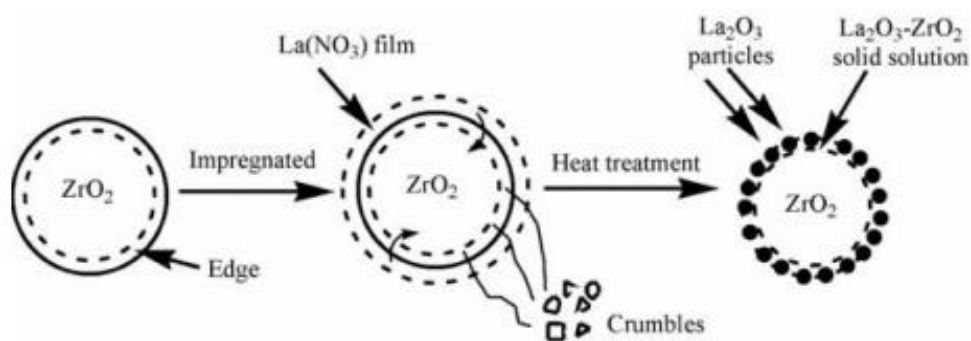


Figure 2.4 Schematic of $\text{ZrO}_2/\text{La}_2\text{O}_3$ catalyst surface solid-state reaction (Reprinted from ref. 98.)

Malhotra et al. [99] used Sodium/ZnO-loaded SBA-15 in the production of virgin cotton seed oil biodiesel. The catalyst was synthesized under atmospheric conditions by the wet impregnation method. Cotton seed oil is converted to biodiesel via transesterification process using the following conditions: 12 wt.% catalyst amount, 65 °C temperature, and 24:1 MRMO in 4 h. A yield of 98% was obtained under these conditions. After reuse for five reaction cycles, the catalyst maintained activity and no substantial reduction in catalytic performance [99]. Elsewhere, the application of manganese-doped zinc oxide was reported by Baskar et al. [100] to produce biodiesel using Mahua oil. It is noticed that 97% yield was achieved with 8 wt.% catalyst amounts and 7:1 MRMO at 50 °C in 50 min. Another study from the same research group focused on using nickel-doped zinc oxide in castor oil transesterification (Figure 2.5) [101]. They reported optimal biodiesel yield of 95.20% in 60 min for nickel-doped zinc oxide catalyst, at 11 wt% catalyst loading, 8:1 MRMO at 55 °C [101].

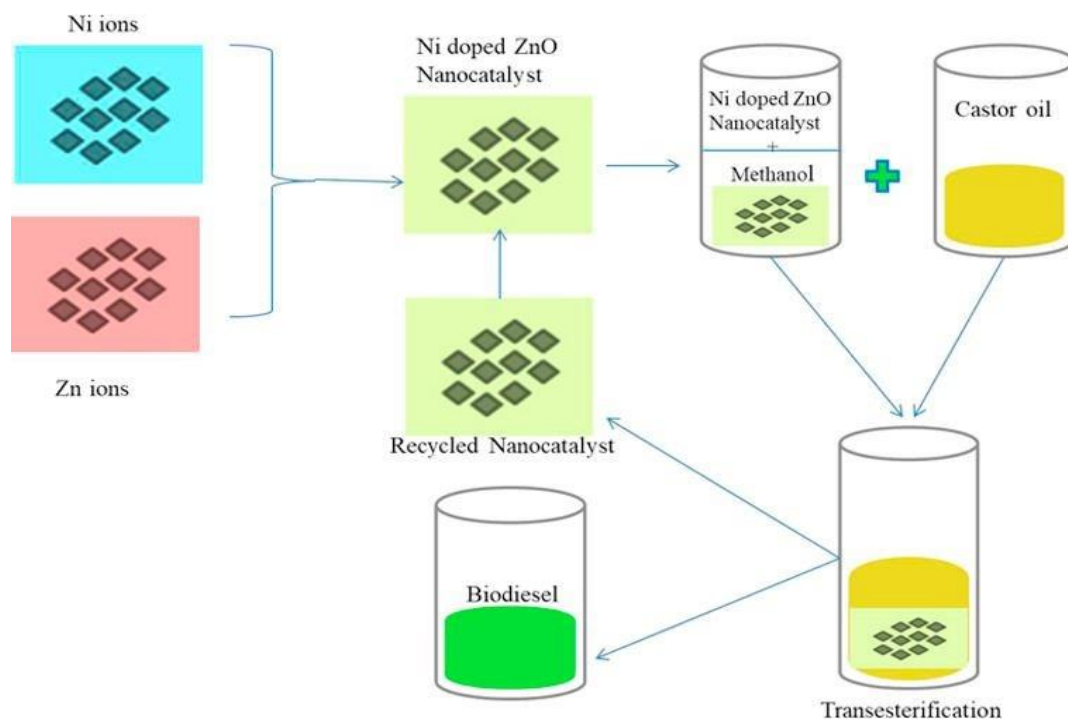


Figure 2.5 Transesterification of castor oil by Ni-doped ZnO nanocatalyst. (Reprinted from ref. 101.)

Borah et al. [102] investigated transesterification of *Mesua ferrea* oil with cobalt-doped zinc oxide catalyst. The optimized reaction was conducted with 2.5 wt.% catalyst and 9:1 MRMO at 60 °C for 3 h, and a maximum conversion of 98.03% of the feed stock was obtained. Soltani et al. [103] explored the transesterification of palm fatty acid distillate using mesoporous $\text{SO}_3\text{H-ZnAl}_2\text{O}_3$ catalyst. A microwave irradiation heating system was

used to synthesize the catalyst. They reported that the $\text{SO}_3\text{H-ZnAl}_2\text{O}_3$ catalyst showed excellent esterification performance, where an optimal yield of 94.59% was achieved with 1.5 wt.% catalyst loading and 9:1 MRMO at 60 °C in 20 min. AlSharifi et al. [104] used lithium/zinc composite supported waste chicken bone, synthesized by the wet impregnation method to produce biodiesel from waste canola oil. The authors reported that the optimum biodiesel conversion of 98% using different metal ratios and reaction conditions of 18:1MRMO and 4.0 wt.% catalyst loading at 60 °C in 3.5 hours.

Tin oxide (SnO_2) is a semiconductor material with a broad bandgap (approximately 3.7 eV). Generally, it is possible to obtain SnO_2 in mesostructured form by hydrolyzing inorganic precursors in the presence of surfactants as a structure director [105]. During calcination, most of the SnO_2 mesostructure collapses because they are not stable. An anionic surfactant with sulfate, such as that used in the preparation of mesoporous sulfated tin oxide, $\text{SO}_4^{2-}/\text{SnO}_2$, has been proposed to improve the stability of the mesostructure [106]. The sulfate groups are isolated on the SnO_2 surface, which led to the stabilization of the mesostructure walls and ameliorates the stability. Additionally, $\text{SO}_4^{2-}/\text{SnO}_2$ has catalytic transesterification reaction potential because it is a strong super acid. In octanoic acid esterification at temperatures below 140 °C with methanol, $\text{SO}_4^{2-}/\text{SnO}_2$ showed superior catalytic activity than $\text{SO}_4^{2-}/\text{ZrO}_2$ [105]. Notwithstanding, the utilization of sulfated tin oxide in the biodiesel process is still very limited. The limited study carried out on sulfated tin oxide could be attributed to its complex method of preparation because it is difficult to achieve oxide gels from its salt in contrast with sulfated zirconia, which can easily be prepared [107]. Kafuku et al. [15] applied the silica-supported $\text{SO}_4^{2-}/\text{SnO}_2$ ($\text{SO}_4^{2-}/\text{SnO}_2\text{-SiO}_2$) in the production of *Moringa oleifera* biodiesel. The optimized reaction was performed with 3 wt.% catalyst and 19.5:1 MRMO at 150 °C for 2.5 h, and a maximum yield of 84% of the feed stock was obtained. Similarly, Kafuku et al. [108] used $\text{SO}_4^{2-}/\text{SnO}_2\text{-SiO}_2$ for transesterification of *Jatropha curcas*. They reported an optimum methyl ester yield of 97% for $\text{SO}_4^{2-}/\text{SnO}_2\text{-SiO}_2$ catalyst and reaction conditions of 3.0 wt% catalyst and 15:1 MRMO at 180 °C for 2 h.

Titanium dioxide (TiO_2) has attracted considerable interest in biodiesel production because of its acidic properties. Furthermore, the sulfuric group on the surface of TiO_2 would increase the catalyst strength [109]. He et al. [110] transesterified cottonseed oil with

methanol using $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{TiO}_2$ catalysts. It was found that $\text{SO}_4^{2-}/\text{TiO}_2$ could achieve a maximum biodiesel yield of >90% compared to $\text{SO}_4^{2-}/\text{ZrO}_2$ which could only achieve a yield of 85%. It was suggested that $\text{SO}_4^{2-}/\text{TiO}_2$ reactivity could be improved by adding silica SiO_2 , to obtain $\text{SO}_4^{2-}/\text{TiO}_2\text{--SiO}_2$ [111]. The catalyst surface area increased when $\text{SO}_4^{2-}/\text{TiO}_2$ was loaded onto SiO_2 (from 99 m^2/g to 258 m^2/g). Under reaction conditions of 3 wt% catalyst and 9:1 MRMO at 200 °C for 6 h, the oil conversion obtained was 92% [111]. However, when compared to homogeneous catalysts temperatures between 50 and 100 °C, the temperature of the reaction is still high. Also, Gardy et al. [112] utilized $\text{TiO}_2/\text{PrSO}_3\text{H}$ catalyst to produce WCO biodiesel and reported 98.3% biodiesel yield with 2.5 wt.% catalyst 15:1 MRMO and at 60 °C for 9 h. They reported that the catalyst was active in the production of biodiesel. They found that the catalyst maintained activity and after four cycles of reuse, there was no substantial loss in the activity. In another work, Kaur et al. [113] studied tungsten-supported $\text{TiO}_2/\text{SiO}_2$ catalyst in the transesterification of waste cottonseed oil. The sol-gel method was used to synthesize the catalyst. They reported an optimized biodiesel yield of 98% in 4 h at 5 wt.% catalyst loading and 30:1 MRMO at 65 °C reaction temperature.

Similarly, Dai et al. [114] examined the activity of Li_2TiO_3 on soybean oil treatment. Solid-state method was used to synthesize the catalyst, which involved the mixing and grinding of titanium oxide (TiO_2) and lithium carbonate (Li_2CO_3), after which a two-hour calcination at 800 °C was performed. The authors stated that optimum biodiesel conversion of 98.5% was achieved with 6 wt.% catalyst and 24:1 MRMO at 65 °C in 2 hours. To prepare a solid Li/TiO_2 -based catalyst, a wet impregnation approach was employed [115]. The authors reported that at 5.0 wt.% catalyst, 55 °C temperature, and 24:1 MRMO, they could achieve a biodiesel yield of 98% in 3 h.

Furthermore, in oil refining and shape-selective petrochemical industries, zeolites are widely used as catalyst. Zeolite's efficient catalytic activity is owing to its pore size, ion exchange, and chemical structure characteristics [33]. The zeolites framework structures contain equal-sized molecular pores and channels capable of absorbing molecules that fit within them while larger molecules are prevented. Zeolites have specific properties as a catalyst, such as shape selectivity, strong Brønsted acidity, the ability to maintain electro-neutrality, etc [32]. However, due to the small pore size of zeolites, diffusion of reactant

molecules into zeolite active sites may be a process constraint. In biodiesel production, zeolites such as H-USY, H-BETA, ZSM5, H-MOR have been discovered to have poor catalytic performance. This is because of the internal diffusion constraints of the larger reactant molecule into zeolites micropores. Thus, only the zeolite external surface catalyzes transesterification. The diffusion of bulky triglycerides molecules is severely limited, small-pores zeolites are not appropriate for transesterification [116-117]. Zeolites with large pores can be employed as a heterogeneous acid catalyst.

In the production of castor oil biodiesel, Li et al. [118] employed Li/NaY as a catalyst. The Li/NaY was synthesized using the coprecipitation method. In the coprecipitation method, LiCO_3 and NaY zeolite support are mixed for some minutes and calcined at 750 °C for 4 hours (Figure 2.6). They reported that optimized oil yield of 98.6% was achieved at 3 wt. % catalyst, 18:1 MREO, and 75 °C temperature in 2 h. Transesterification of oleic acid over zeolite Y with a Si/Al ratio of 3.1 was previously reported [119]. An optimal conversion of 85% was attained at 5 wt.% of Zeolite Y catalyst prepared from kaolin, 70 °C temperature, and 6:1 MREO in 1 h.

(A)

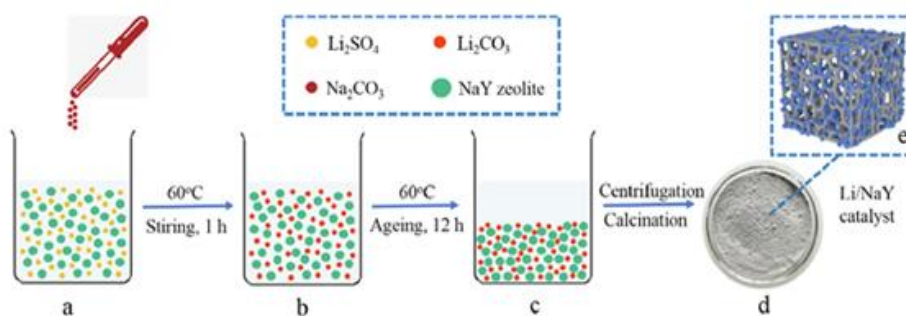




Figure 2.6 (A) Schematic diagram for (a-d) synthesis of Li/NaY zeolite catalyst and (e) structure of Li/NaY zeolite catalyst. (B) Castor oil transesterification using a Li/NaY zeolite catalyst. (Reprinted from ref. 118.)

The most widely employed heterogeneous acid catalysts in liquid phase transesterification and esterification reaction are sulfonic ion exchange resins (Nafion resins, EBD resins, and Amberlyst resins) [120-123]. Sulfonic ion exchange resin has a cross-linking polymeric component where sulfonic groups bonded protons are the active sites of the transesterification and esterification process [124]. Furthermore, the swelling properties of sulfonic ion exchange resin influence their catalytic activity because swelling capacity limits reactant access to the acid site and therefore influences their activity [125]. Nafion SAC-13, EDS-100, and Amberlytes-15 are the most prevalent types of acidic ion exchange resins and several researchers have made use of them [120-121, 126]. The performance of these catalysts was observed to be good in free fatty acid esterification but poor in transesterification [127]. The performance of Amberlyst-15 as a catalyst for biodiesel production from sunflower oil was investigated by Vicente et al [128]. It is observed that the Amberlyst-15 catalyst showed poor activity (0.7% oil conversion) with 6:1 MRMO, 1 wt% catalyst at 60 °C for 8 hours. Dos Reis et al. [129] utilized an Amberlytes-15 catalyst for biodiesel production from Babassu coconut oil. The Amberlytes-15 catalyst showed excellent transesterification performance, where oil conversion of 74% was obtained with 300:1 MRMO at 60 °C in 8 h. Therefore, if Amberlyte-15 is to be used, reaction temperature must be increased to 140 - 200 °C to achieve a faster reaction rate [123].

Amberlyte-15 and most of the ion exchange resin have poor thermal stability at a temperature above 150 °C. Therefore, this stability issue limits their applications.

Recently, biomass conversion-related reactions including transesterification and esterification have made substantial use of cellulose-derived solid acids. Among them, sulfonic ($\text{SO}_3\text{-H}$)-bearing cellulose-derived solid acids materials have drawn special attention [130]. These materials could incorporate a significant amount of hydrophobic molecules into the bulk of carbon because the density of the hydrophobic functional group bound to carbon sheets is very high. Such incorporation offers excellent accessibility to the sulfonic group and resulting in high catalytic efficiency. Hara [130] investigated the catalytic activity of $\text{SO}_3\text{-H}$ -bearing carbon material in the production of oleic acid biodiesel. With a 0.307 g catalyst and 95 °C temperature in 4 h, the optimal biodiesel yield using the $\text{SO}_3\text{-H}$ -bearing carbon material catalyst was 99.9%. The authors found that the catalyst is stable and maintains similar catalytic activity after ten reaction cycles. Another study used carbon-based solid acid catalyst for transesterification of used cooking oil [131]. Zong et al. [132] utilized sulfonated D-glucose-derived sugar for transesterification of palmitic acid and oleic acid. They found that biodiesel yield of 95% was obtained with 5 wt.% catalyst and 10:1 MRMO at 80 °C for 5 h.

To date, there are few studies on the use of sulfonated carbon-based catalyst in the transesterification of feedstock containing triglycerides, typically from used cooking oil. Lou et al [133] utilized sulfonated carbon-based catalyst produced from sucrose, cellulose, and starch in the transesterification of WCO using methanol. They claimed that the carbon-based catalyst produced from starch has higher acid sites, higher pore size, and higher pore volume which allowed reactants to access the $\text{SO}_3\text{-H}$ sites. Furthermore, the optimum used cooking oil conversion using the carbon-based catalyst produced from starch was 92% with 30:1 MRMO and 10 wt.% catalyst at 80 °C in 8 h. Also, there was an insignificant change in performance of the catalyst even after fifty cycles, proving it to be a very stable catalyst. By sulfonation of carbonized vegetable oil asphalt, Shu's group developed a carbon-based catalyst and the catalyst was made up of a flexible carbon-based framework comprising sulfonic acid groups with polycyclic aromatic hydrocarbons that are highly dispersed [131]. They found that the carbon-based catalyst exhibited improved activity for the transesterification of WCO and provided an optimum conversion of 94.8% with 0.2 wt.%

catalyst and 16.8:1 MRMO at 220 °C in 4.5 h. They explained that optimum conversion exhibited by the catalyst is due to the hydrophobicity of the carbon sheet which prevented the hydroxyl group from being hydrated and bonded $-\text{SO}_3\text{H}$ hydrophilic groups that increased the contact of methanol with the protonated carboxylic group of triglycerides. The development of an effective carbon-based acid catalyst for biodiesel production at mild reaction conditions remains a challenge. Nonetheless, carbon-based catalyst needs to be further improved including transesterification reaction conditions and improvement on catalyst synthesis.

In the field of heterogeneous acid catalysts, heteropolyacids (HPAs) also have significant potential for transesterification of waste vegetable oils. HPAs are mostly a type of solid acid with a well-defined structure that consists of early transition metal-oxygen anion clusters. HPAs are considered to be a more environmentally friendly and cost-effective alternative to traditional acid catalysts because of their high stability, high mobility of proton, strong Brønsted acidity, and non-toxicity [134]. The most widely used HPAs happens to be heteropoly tungstate ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and demonstrated outstanding performance in acid-catalyzed reaction including transesterification and esterification [135].

Cao et al. [136] evaluated the acidic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ (PW12), for the transesterification of WCO. A biodiesel conversion of 87% was attained with 4.0 wt% catalyst and 70:1 MRMO at 65 °C in 14 hours. The authors found that $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ catalyst had a high FFA tolerance and after five catalytic cycles, its catalytic activity is maintained. However, the application of this catalyst on an industrial scale can be restricted by the length of reaction time and the high alcohol/oil molar ratio. Besides, if $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ catalyst is to be used, the reaction temperature must not be more than 65 °C to achieve the stable catalytic performance [136]. They claimed that the transesterification must not be performed at a higher temperature because waste cooking oil contains a number of undesirable compounds that may induce side reactions. An attempt has been made to produce heteropolyacids with increased acidity by incorporating Lewis acid into them, resulting in heteropolyacids with Brønsted and Lewis acid sites [137].

Zhang et al. [137] transesterified used cooking oil over $\text{Zr}_{0.7}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$ (ZrHPW) catalyst. They found that $\text{Zr}_{0.7}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$ catalyst exhibited high acidity capacity compared to the original $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. The investigated $\text{Zr}_{0.7}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$ catalyst displays unique properties and yielded an optimum biodiesel conversion of 98.8% with 2.1 wt.% catalyst and 20:1 MRMO at 65 °C in 8 hours. In addition, after five catalytic cycles, a 95% yield was obtained. Elsewhere, another author used $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Nb}_2\text{O}_5$ catalyst in the transesterification process, which under optimum condition produced a methyl ester yield of 92% with 18:1 MRMO and 3 wt.% catalyst at 200 °C in 20 h [138]. Brahmkhatri et al. [139] esterified lauric acid with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported MCM-41 (Figure 2.7). They reported that butyl laurate yield efficiency reached 95% with 0.2 g of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loaded on MCM-41 supports catalyst and 1:2 oil to butanol ratio at 90 °C in 3h.

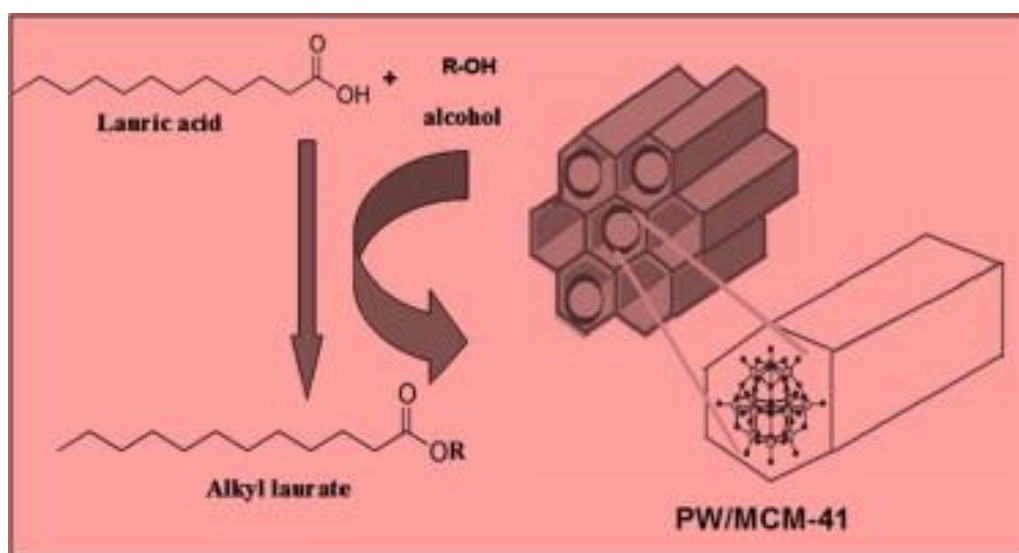


Figure 2.7. Esterification of lauric acid by $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported MCM-41 catalyst. (Reprinted from ref. 139)

Kulkarni et al. [140] utilized $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loaded on various supports (Al_2O_3 , ZrO_2 , SiO_2 , and activated carbon) in the production of canola oil biodiesel, where the biodiesel yield reached 90% with 9:1 MRMO and 3.0 wt. % catalyst ($\text{H}_3\text{PW}_{12}\text{O}_{40}$ loaded on ZrO_2 supports) at 200 °C in 10 hours. Alcañiz -Monge et al. [141] reported biodiesel production from esterification of palmitic acid using activated carbon fiber supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ($\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ACF}$) catalyst. The authors obtained a biodiesel conversion of 89% by using

97:1 MRMO at 40 °C in 6 h. Table 2.3 shows a comparison of different heterogeneous acid catalysts used by several research studies to convert different feedstock into biodiesel.

Table 2.3

Some studies on biodiesel production using heterogeneous acid catalysts

Catalyst	Feedstock	Reaction conditions (reaction time, temperature, catalyst amount, and alcohol to oil molar ratio)	Performance	Ref.
SO ₄ ²⁻ /ZrO ₂	palm kernel oil	4 h, 200 °C, 1 wt.%, 6:1	90.3%	87
	coconut oil		86.3%	
ZrO ₂ loaded on different supports (TiO ₂ , SiO ₂ , Fe ₂ O ₃ , and Al ₂ O ₃)	Waste cooking oil	3 h, 120 °C, 0.1 wt.%, 120:1	48.6%	88
WO ₃ /ZrO ₂	Waste vegetable oil	1 h, 75 °C, 4 wt.%, 9:1	93%	89
SO ₄ ²⁻ /ZrO ₂ -MCM- 41	Sunflower oil	5 h, 200 °C, 14.6 wt.%, 14:1	91.5%	93
sulfated Zr-KIT-6	Oleic acid	6 h, 120 °C, 4 wt.%, 20:1	96%	94
WO ₃ /ZrO ₂	S. Obliquus lipids	3 h, 100 °C, 15 wt.%, 12:1	94.58%	97
Zr ₂ O-supported bamboo leaf ash (Zr ₂ O/BLA)	Soybean oil	30 min, 50 °C, 12 wt.%, 15:1	89.99%	95

Zirconium-based carbonaceous	Oleic acid	2 h, 90 °C, 5 wt.%, 20:1	99.1%	96
ZrO ₂ /La ₂ O ₃	Sunflower oil	5 h, 200 °C, 5 wt.%, 30:1	84.9%	98
Na/ZnO-loaded SBA-15	Cotton seed oil	4 h, 65 °C, 12 wt.%, 24:1	98%	99
Manganese-doped ZnO	Mahua oil	50 min, 50 °C, 8 wt.%, 7:1	97%	100
Nickel-doped ZnO	Castor oil	1 h, 55 °C, 11 wt.%, 8:1	95.20%	101
Cobalt-doped ZnO	<i>Mesua ferrea</i> oil	3 h, 60 °C, 2.5 wt.%, 9:1	98.03%	102
SO ₃ H-ZnAl ₄ O ₃	Palm fatty acid	20 min, 60 °C, 1.5 wt.%, 9:1	94.59%	103
Lithium/Zinc composite supported waste chicken bone	Waste canola oil	3.5 h, 60 °C, 4.0 wt.%, 18:1	98%	104
SO ₄ ²⁻ /SnO ₂ -SiO ₂	jatropha curcas	2 h, 180 °C, 3 wt.%, 15:1	97%	108
SO ₄ ²⁻ /TiO ₂	Cottonseed oil	8 h, 230 °C, 2 wt.%, 12:1	>90%	110
SO ₄ ²⁻ /TiO ₂ -SiO ₂	Cottonseed oil	6 h, 200 °C, 3 wt.%, 9:1	92%	111
TiO ₂ /PrSO ₃ H	Waste cooking oil	9 h, 60 °C, 2.5 wt.%, 15:1	98.3%	112
20-W/TiO ₂ /SiO ₂	Waste Cottonseed oil	4 h, 65 °C, 5 wt.%, 30:1	98%	113

Li ₂ TiO ₃	Soybean oil	2 h, 65 °C, 6 wt.%, 24:1	98.5%	114
Li/NaY zeolite	Castor oil	2 h, 75 °C, 3 wt.%, 18:1	98.6%	118
Zeolite Y	Oleic acid	1 h, 70 °C, 5 wt.%, 6:1	85%	119
Amberlyst-15	Babassu coconut oil	8 h, 60 °C, 300:1	74%	129
SO ₃ -H-bearing carbon material	Oleic acid	4 h, 95 °C, 0.307 g	99.9%	130
Sulfonated vegetable asphalt	Waste cooking oil	4.5 h, 220 °C, 0.2 wt.%, 16.8:1	94.8%	131
Sulfonated D-glucose derived sugar	Palmitic acid and oleic acid	5 h, 80 °C, 5 wt.%, 10:1	95%	132
sulfonated carbon-based catalyst derived from starch	Waste cooking oil	8 h, 80 °C, 10 wt.%, 30:1	92%	133
H ₃ PW ₁₂ O ₄₀ ·6H ₂ O (PW12)	Waste cooking oil	14 h, 65 °C, 4 wt.%, 70:1	87%	136
Zr _{0.7} H _{0.2} PW ₁₂ O ₄₀	Waste cooking oil	8 h, 65 °C, 2.1 wt.%, 20:1	98.8%	137
H ₃ PW ₁₂ O ₄₀ /Nb ₂ O ₅	Used cooking oil	20 h, 200 °C, 3 wt.%, 18:1	92%	138
H ₃ PW ₁₂ O ₄₀ loaded on ZrO ₂	Canola oil	10 h, 200 °C, 3 wt.%, 9:1	90%	140

H ₃ PW ₁₂ O ₄₀ /ACF	Palmitic acid	6 h, 40 °C, 1.1 wt.%, 97:1	89%	141
H ₃ PW ₁₂ O ₄₀ supported MCM-41	Lauric acid	3 h, 90 °C. 2:1	95%	139

2.5 Biocatalyst

Catalysts derived from a living organism are known as biocatalysts and are often referred to as enzyme catalysts. Almost all biochemical reactions in living cells are initiated by these catalysts. Each enzyme has a unique three-dimensional structure that corresponds to the reactant's shape. In the study of biodiesel production, biocatalysts have lately become increasingly crucial [142]. The use of enzyme catalysts aims to address the problems posed by the use of synthetic catalysts, including a high amount of energy demands, feedstock pretreatment requirement, high costs, and complex procedures. Biocatalyst studies demonstrate an environmentally sustainable strategy for the production of biodiesel employing renewable material and polymer under moderate reaction conditions [142]. Typically, the enzyme normally utilized as biocatalyst is immobilized on inert materials that enable it to withstand the change in temperature and moisture content. Covalent bonding, cross-linking and encapsulation were among the immobilization techniques documented in the preparation of biocatalysts [143]. However, in the typical transesterification reaction, the use of polar molecules like water and methanol limits the enzyme's catalytic performance. This is alleviated via the stepwise addition of an organic solvent such as ethanol [144]. All biocatalysts do not require harsh conditions to function; however, strict hydration control is necessary since they are water-sensitive (they can be activated with small amount of water) [145]. The catalytic potential of enzymatic catalysts has been demonstrated in the transesterification process used to make biodiesel that employed an accumulation of enzymes referred to as lipases obtained from plants, microorganisms, and animals [146-147]. Lipases may be isolated from various bacterial species, including *Rhizopus oryzae*, *Rhizomucor miehei*, *Pseudomonas fluorescens*,

Expansum lipase, and *Pseudomonas cepacia* [148]. In the last few decades, the advantages associated with enzymatic transesterification, especially those using lipases, have made many researchers shift attention from chemical transesterification [148].

Several biocatalysts for transesterification have been reported in the literature over the last few decades. For instance, Shah et al. [144] examined the performance of immobilized *Pseudomonas cepacia* in the production of *jatropha curcas oil* biodiesel. It was observed that the highest biodiesel yield of 98% was obtained using the enzyme at a reaction temperature of 50 °C, 5 wt.%, 4:1 MREO in 8 h. Another study focused on the use of immobilized *Burkholderia cepacia* for the production of *jatropha curcas oil biodiesel*, which under optimal conditions achieved a maximum biodiesel yield of 100% with 10:1 MREO, 5.25 g catalyst loading, and 35 °C in 24 hours [145]. The catalytic transesterification of WCO over *Pancreatic lipase* was examined by Jayaraman et al. [149]. The optimum oil conversion using this catalyst was 88% with 3:1 MRMO, 1.5 wt.% catalyst amount, and 60 °C in 4 h. Marin-Suarez et al. [150] utilized Novozym 435 lipase as biocatalyst for transesterification of residual fish oil using ethanol. The authors reported that the Novozym 435 lipase catalyst showed excellent transesterification performance, where a maximum biodiesel yield of 82.91% was obtained for the reaction conditions of 50 wt.% catalyst and 36:1 MREO at 35 °C in 8 h. Choi et al. [151] used rice bran lipase as biocatalyst for the production of rice bran oil biodiesel. The authors found that the biocatalyst provided a yield of 83.4% with 3 wt.% catalyst and 6:1 MRMO at 40 °C in 12 days. Another research focused on the usage of Lipozyme *Thermomyces lanuginose* IM in the transesterification of *corn oil*, which under optimal process conditions gave a maximum yield of 98.95% with 6:1 MREO, 2.8 wt.% catalyst amount, and 35 °C in 12 h [152]. Arumugam et al [153] transesterified *Calophyllum inophyllum* using *Rhizopus oryzae* lipase. They found that the *Rhizopus oryzae* lipase catalyst showed excellent transesterification performance, where a biodiesel yield of 92% was obtained using the following conditions: 20 wt.% catalyst amount, 35 °C reaction temperature, and 12:1 MRMO in 72 h. Li et al. [154] also produced biodiesel from *Pistacia chinensis* bge seed oil using *Rhizopus oryzae* lipase catalyst. The authors found that the *Rhizopus oryzae* lipase catalyst shows good performance in the transesterification of *Pistacia chinensis* bge seed oil and provided maximum methyl ester yield of 94% at a temperature of 37 °C in 60 h,

5:1 MRMO and 7 wt% enzyme dosages. Caballero et al. [155] transesterified sunflower oil over immobilized *Pig pancreatic* lipase biocatalyst using ethanol under reaction conditions of temperature $T = 60\text{ }^{\circ}\text{C}$, time $t = 19\text{ h}$, 0.1 wt.% of catalyst, and 2:1 MREO, the maximum biodiesel conversion of 57.2% was obtained using this catalyst. In another study, *Rhizomucor mieher* lipase was utilized in the biodiesel production from *triolein*, which under optimal process conditions (5.0 wt.% catalyst, 3:1 MREO, and $40\text{ }^{\circ}\text{C}$ in 96 h) achieved maximum biodiesel yield of 77% [156]. Elsewhere, Kamini et al. [157] utilized *Cryptococcus* spp. S-2, as biocatalyst for transesterification of rice bran oil using methanol. The *Cryptococcus* spp. S-2 catalyst showed excellent transesterification performance, where maximum biodiesel yield of 80.2% was obtained using the following conditions: temperature $T = 30\text{ }^{\circ}\text{C}$, time $t = 120\text{ h}$, and 4:1 MRMO. Martin Mittelbach [158] examined the catalytic performance of *Pseudomonas* lipase for biodiesel production from *sunflower oil* with methanol. The authors found that the maximum biodiesel yield of 80% was achieved following the addition of oleic acid to sunflower oil using *Pseudomonas* lipase enzyme under the optimum process conditions (time $t = 5\text{ h}$, 10:1 MRMO, and temperature $T = 45\text{ }^{\circ}\text{C}$). Table 2.4 depicts a comparison of various biocatalysts utilized in several research studies, in terms of biodiesel yield, process conditions, and feedstock.

Table 2.4

Some studies on biodiesel production using biocatalysts.

Catalyst	Feedstock	Reaction conditions (reaction time, temperature, catalyst amount, and alcohol to oil molar ratio)	Performance	Ref.
Novozym 435 lipase	Residual fish oil	8 h, $35\text{ }^{\circ}\text{C}$, 50 wt.%, 36:1	82.91%	150
<i>Pseudomonas cepacian</i>	<i>Jatropha curcas</i>	8 h, $50\text{ }^{\circ}\text{C}$, 4:1	98%	144

Pancreatic lipase	Waste cooking oil	4 h, 60 °C, 1.5 wt.%, 3:1	88%	149
<i>Burkholderia cepacia</i>	<i>Jatropha curcas</i>	24 h, 35 °C, 5.25 g, 10:1	100%	145
Rice bran lipase	Rice bran oil	288 h, 40 °C, 3 wt.%, 6:1	83.4%	151
Lipozyme <i>Thermomyces lanuginose</i> IM	<i>Corn oil</i>	12 h, 35 °C, 2.8 wt.%, 6:1	98.95%	152
<i>Rhizopus oryzae</i> lipase	<i>Calophyllum inophyllum</i>	72 h, 35 °C, 20 wt.%, 12:1	92%	153
<i>Rhizopus oryzae</i> lipase	<i>Pistacia chinensis</i> seed oil	60 h, 37 °C, 7 wt.% 5:1	94%	154
<i>Pig pancreatic</i> lipase	Sunflower oil	19 h, 60 °C, 0.1 wt.%, 2:1	57.2%	155
<i>Rhizomucor mieher</i> lipase	<i>Triolein</i>	96 h, 40 °C, 5 wt.%, 3:1	77%	156
<i>Cryptococcus</i> spp. S-2	Rice bran oil	120 h, 30 °C, 4:1	80.2%	157
<i>Pseudomonas</i> lipase	Sunflower oil	5 h, 45 °C, 10:1	80%	158

2.6 Process conditions/parameters for biodiesel production

Transesterification reactions occur under various reaction process conditions, including reaction time, molar ratio of methanol to oil, reaction temperature, and catalyst amount, all of which have a significant effect on biodiesel yield. To achieve a complete reaction and high biodiesel yield that meets regulatory specifications, these conditions have to be optimized during the transesterification reaction. The effects of these reaction conditions are explained in detail in the sections that follow.

2.6.1 Effect of methanol to oil molar ratio

Methanol to oil molar ratio is vital in both transesterification and esterification reaction of triglycerides. Excess methanol is necessary to achieve high biodiesel yield during the reversible esterification of high free fatty acid triglycerides to biodiesel [159]. When triglyceride interacts with the active site of the catalyst, it is converted into fatty acid methyl ester (FAME). At the carbonyl group, triglycerides are protonated to form carbocation, that could undergo a reaction to produce an ester [160]. However, excess methanol is flooded into the active sites of the catalyst, preventing formation of protonated triglycerides. During methanolysis, excess methanol is problematic during the separation of glycerol and ester layer because of the solubility of glycerol layer in the ester layer. Methanol functions as an emulsifier due to its polar nature, aiding emulsion formation [159]. Nevertheless, it is believed that using a large amount of methanol improved the interaction between triglycerides and catalyst and enhanced biodiesel yield [159,161].

Several attempts have been made to investigate the optimum MRMO required to obtain higher biodiesel yield. Amani et al. [162] investigated the effect of process parameters on the biodiesel yield using MRMO in the range of 10:1 to 30:1. An optimal biodiesel conversion of 90% was obtained using 20:1 MRMO. Furthermore, significant decrease in biodiesel yield was observed when using MRMO from 20:1 to 30:1. Hence, for economics and ease of methanol regeneration, 20:1 MRMO was adopted. Atapour et al. [163] found that 90.8% biodiesel yield was obtained using 7:1 MRMO. The authors further observed that the biodiesel yield decreased by increasing the MRMO from 7:1 to 11:1 for the given transesterification process.

Amani et al. [164] investigated the impact of the MRMO on waste cooking palm oil biodiesel production. A biodiesel yield of 93% was obtained from the transesterification using 14:1 MRMO. Furthermore, when the MRMO was raised from 14:1 to 18:1, biodiesel yield decreased. Similarly, Hoque et al. [165] explored the impact of methanol on biodiesel yield during WCO transesterification. They reported that maximum biodiesel yield was obtained by using 6:1 MRMO in 2 h.

Birla et al. [68] utilized a heterogeneous catalyst obtained from snail shells to examine the effect of different variables on the production of biodiesel. Optimum biodiesel yield of 87.28% was obtained using 2.0 wt.% catalyst and optimal MRMO of 8.45:1 in 7 h. Furthermore, the authors observed no increase in biodiesel yield while the MRMO was increased beyond the optimum.

Phan et al. [35] studied the effect of methanol on biodiesel yield during transesterification of WCO using KOH catalyst. The authors found that methyl ester yield increased as MRMO increased from 5:1 to 8:1 and an optimum yield of 90% was obtained using 8:1 MRMO after 80 minutes. They observed that biodiesel yield decreased when MRMO was increased beyond 9:1 under the same process conditions. The authors further explained that the decrease in product yield was because separation of glycerol becomes difficult at higher MRMO and the yield of methyl ester reduced since a part of the byproduct, which is glycerol, remains in the biodiesel phase.

Patil et al. [166] investigated the effect of MRMO on biodiesel yield from WCO. They found that biodiesel yield increased as the MRMO increased. However, once the optimal MRMO of 9:1 was reached, the effect became insignificant, and the yield remained essentially unchanged. Similarly, the influence of methanol amount on biodiesel conversion from transesterification reaction of castor and linseed oils was investigated by Varma et al. [167]. They found that biodiesel yield increased as the MRMO increased and maximum biodiesel yield was obtained at an optimal MRMO of 40:1 from transesterification of each feedstock. Further, biodiesel yield remained constant when the MRMO increased from 40:1 to 70:1.

Song et al. [168] studied the effect of methanol amount on biodiesel conversion from transesterification reaction of RBD (refined, bleached, and deodorized) palm oil. The results showed that biodiesel yield increased as the MRMO increased and maximum

biodiesel yield was obtained at an optimum MRMO of 30:1 from transesterification of the feedstock. Further, it was observed that biodiesel yield remained constant when MRMO increased beyond the optimum. He et al. [169] investigated the impact of methanol oil molar ratio on biodiesel production from soybean oil. The authors claimed that biodiesel yield increased as the MRMO increased, and maximum yield was obtained with MRMO of 40:1. Moreover, the authors further reported that no substantial increase in the biodiesel yield was observed when MRMO increased beyond the optimal molar ratio (40:1).

In principle, it is generally concluded that the MRMO is one of the most important parameters that influence biodiesel yield during transesterification of oil to biodiesel. During transesterification of triglycerides to biodiesel, excess methanol is required to push the reversible reaction process to the product side in order to increase the reaction rate and biodiesel yield. However, as some studies have shown, using too much methanol slowed the formation of the biodiesel products due to dilution of the system [170]. The use of excess amounts of methanol also poses problems in processing, equipment cost, and energy consumption for methanol recovery [170-171]. Moreover, because of the increased solubility of glycerol in the ester phase, a considerable amount of methanol interferes with glycerol separation [172]. When glycerol is present in an ester solution, it aids in the shift of the reversible reaction process to the reactant's side, reducing the ester yield [172]. Therefore, for transesterification of the selected feedstock, MRMO must be optimized in order to reduce the biodiesel production cost and obtain the highest biodiesel yield possible.

2.6.2 Effect of temperature

Another important process parameter that influences biodiesel yield and reaction rate during transesterification reaction is the temperature [173-174]. In principle, the rate of reaction increases as the temperature increases. The transesterification reaction can occur at various temperatures; however, a higher temperature is favorable, as it pushes the reaction to the product side due to its endothermic nature [174]. The use of high temperature reduces oil viscosities and mass transfer problems between the phases, which in turn increases biodiesel yield, reduces reaction time, and increases the rate of reaction, [170-171].

Several experiments have been carried out to investigate the effect of temperature on biodiesel yield in order to achieve optimum temperature for the transesterification reaction. Kusdiana et al. [175] investigated the optimum reaction temperature to obtain higher biodiesel yield using supercritical methanol. They found that the conversion increases as the reaction temperature rises from 200 to 400 °C. The authors noted that after 4 min at 350 °C, rapeseed oil was completely converted to biodiesel, yielding 95.0 wt.% biodiesel. However, the rapeseed oil conversion decreased as the temperature was increased above 350 °C. This is because biodiesel thermal decomposition takes place at a temperature above 350 °C. Varma et al. [167] has reported similar findings. According to these authors, the conversion of linseed oil and castor oil to biodiesel increased with an increase in temperature, but at a temperature above 350 °C, thermal decomposition of biodiesel was observed. Besides, they also found that the conversion of palm oil and groundnut oil to biodiesel increased with temperature, and biodiesel yield reached a maximum at 350 °C after 40 min. Miao et al [176] explored the role of reaction temperature on biodiesel yield. They used methanol to transesterify soybean oil at temperatures ranging from 100 to 200 °C. A high biodiesel yield of 98.4% was recorded by the authors at 120 °C, which was considered to be the reaction's optimal temperature. In the presence of an alkaline catalyst, Phan et al. evaluated the impact of temperature on the methyl ester yield utilizing used cooking oil as a feedstock [35]. They reported that methyl ester content increased as the temperature was increased from 30 to 50 °C, and the methyl ester content slightly decreased as the temperature was increased up to 70 °C because both saponification and transesterification reactions were enhanced at high temperatures.

Lam et al. [177] evaluated the transesterification of WCO over $\text{SO}_4^{2-}/\text{SnO}_2\text{--SiO}_2$ catalyst to produce biodiesel. They found that temperature significantly influences biodiesel yield. The biodiesel yield increased with temperature, with an optimal yield of 81.4% obtained at 150 °C after 1 h. Furthermore, as stated by Saka et al. [178], at a higher temperature, typically around 400 °C, thermal decomposition of triglycerides occurred.

2.6.3 Effect of reaction time

Reaction time plays a crucial role in determining the reaction kinetics of oil conversion to biodiesel under supercritical conditions [179]. The conversion of triglycerides to biodiesel was observed to increase with time in the transesterification of triglycerides [179]. This was attributed to an increase in the reaction rate constant based on the Arrhenius equation. Also, owing to the mass transfer limitation between oil-methanol-catalyst, the conversion rate increases with reaction time. Nevertheless, exceeding the optimum reaction time can result in a decrease in biodiesel yield due to backward transesterification reaction, which in turn reduces the ester content [179–181].

The reaction time is one of the important factors that influence triglyceride conversion to biodiesel; therefore, various attempts have been made to examine the impact of reaction time on biodiesel yield and to determine the optimal time for the transesterification reaction. Rashid et al. [34] studied the influence of reaction time on biodiesel production. The authors reported gradual increases in ester yield with time, obtaining maximum biodiesel yield of 97.81% in about 70 minutes. Similarly, Lam et al. [177] investigated the influence of biodiesel yield during the transesterification of WCO in the presence of $\text{SO}_4^{2-}/\text{SnO}_2$ catalyst using a methanol-ethanol mixture. They reported that a maximum biodiesel yield of 81.40% was obtained by using MREO of 9:6:1, 6.0 wt.% catalyst, reaction temperature of 150 °C, and 60 min reaction time. Besides, the reaction temperature has a direct impact on the reaction time, where higher reaction temperature assist in the reduction of reaction time for biodiesel production and vice versa [182]. The influence of temperature on reaction time during the production of used cooking oil biodiesel was evaluated by Fu et al. [183]. The authors observed that at 65 °C, 80% biodiesel yield was obtained in 11 h reaction time, while at 120 °C, the same biodiesel yield was achieved

within just 2 h. Furthermore, the biodiesel yield increased to 95.2% when the reaction at 120 °C was continued for 5 hours. Similarly, Kapilakarn et al. [184] obtained fatty acid methyl ester (FAME) yield of 97% in 50 min at 55 °C, whereas the same FAME yield was obtained in only 20 min at 70 °C. Thus, it can be inferred that reaction time is crucial in the production of biodiesel from triglyceride transesterification reactions. Since the transesterification reaction is reversible, therefore reaction time must be enhanced to prevent backward reaction and achieve the maximum biodiesel yield for sustainable energy production.

2.6.4 Effect of catalyst loading

Catalyst is believed to increase the rate of a reaction by lowering the overall reaction activation energy. Therefore, the presence of catalysts in the conversion of triglycerides to biodiesel speeds up the reaction process by reducing the required activation energy. Typically, the reaction will be initiated with small catalyst loading, and it will be gradually increased, while other conditions are kept constant, until an optimum biodiesel yield is obtained. Bhatti et al. [185] reported a high biodiesel yield (on mutton tallow) at 40 °C with an increase in H₂SO₄ catalyst loading from 1 to 3 g. Biodiesel yield decreased when H₂SO₄ catalyst loading was increased above 3 g at the same temperature. Dependence of biodiesel yield on catalyst loading differs slightly at other temperatures. Similarly, in the presence of methanol, Amani et al. [162] evaluated the effect of catalyst loading on biodiesel yield. The authors reported a maximum biodiesel yield of 90% using 3 wt.% catalyst amount in 3 h. However, it was observed that a further increase in the catalyst loading to 4 wt.% resulted in a decrease in biodiesel yield from 90% to 83%. It must also be mentioned that low catalyst amounts can lead to methanol solubility in low-cost feedstock such as waste cooking oil [162]. The careful design of strong, effective, and reliable acid catalysts that can enhance the efficiency of biodiesel production still remains a major challenge.

CHAPTER 3

EXPERIMENTAL SECTION

This chapter include materials section, the catalysts' synthesis, characterization and evaluation for the production of biodiesel

3.1 Materials Section

In this work, WCO was obtained from staff residence at King Fahd University of Petroleum and Minerals, Saudi Arabia. Soybean oil was bought from a local store in the Eastern Province, of Saudi Arabia. All chemicals were of analytical quality and utilized just as they were received, without additional purification. Methanol (purity >99%), zinc nitrate hydrate ($\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$), tetraethylammonium hydroxide (40 wt.% TEAOH), sodium chloride (reagent grade), ammonium nitrate (NH_4NO_3), sulfuric acid, and potassium chloride (reagent grade) were purchased from Sigma-Aldrich (USA). Also, fumed silica (amorphous silicon dioxide particles produced in an oxygen-hydrogen flame), sodium hydroxide (98%), and sodium aluminate (56 wt.% Al_2O_3 , 37 wt.% Na_2O), sodium hydroxide (NaOH), n-heptane (99% pure), zirconium (IV) oxynitrate hydrate were purchased from Sigma-Aldrich (St. Louis, MO, USA). The commercial zeolite, NH_4 -ZSM-5 was purchased from Zeolyst International. Terephthalic acid (AR), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and zirconium tetrachloride (ZrCl_4), 1,3,5-benzene tricarboxylic acid (H_3 -BTC, AR) were procured from Shanghai Aladdin Industrial Inc. N,N dimethylformamide (DMF > 99%,), and ethanol were purchased from Sigma-Aldrich (USA).

3.2 Catalysts Synthesis

3.2.1 Synthesis of Beta zeolite, ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite

The hydrothermal method described by Cambor et al. was used to produce β -zeolite [23], using tetraethylammonium hydroxide as a structure-directing agent (SDA). In a typical procedure, 59.4 g of deionized water and 89.60 g of tetraethylammonium hydroxide (40%) were mixed with 0.53g of sodium chloride and 1.44 g of potassium chloride and stirred (Multi Point Magnetic Stirrer, DAIHAN Scientific Co., Ltd., Vietnam) until dissolved. Subsequently, fumed silica (30.0 g) was added to the mixture and stirred until homogenized. Then, sodium hydroxide (0.33 g) and sodium aluminate (1.79 g) were dissolved in deionized water (20.0 g) and stirred till completely dissolved. Following that, the two resulting liquids were mixed and stirred for 10 minutes. After stirring for 10 minutes, the thick gel formed was heated for 20 hours at 135 °C in hydrothermal autoclave. Following a hydrothermal reaction, the mixture was cooled in cold water and centrifuged. After centrifugation, the resulting mixture was dried at 77 °C after being washed with distilled water. The solid product that was produced after drying was calcined in a muffle furnace (Thermo Scientific F480256080, Benchtop Muffle Furnace, USA) at 550 °C for 6 hours. Sodium form of β -zeolite was thereby produced (Na- β -zeolite). Using an ion-exchange method, Na- β -zeolite obtained was transformed into H- β -zeolite. Na- β -zeolite was impregnated with 1 M ammonium nitrate solution (1.0 g sample vs 20 ml 1 M NH_4NO_3) for 4 hours at 80 °C. After two cycles of $\text{Na}^+/\text{NH}_4^+$ ion exchanged β -zeolite, the resulting product was subjected to filtration, followed by washing with distilled water before drying at 100 °C overnight. The calcination of NH_4 - β -zeolite for transformation to H- β -zeolite was carried out at 550 °C for 6 hours in a muffle furnace. H- β -zeolite is the name given to the final sample obtained (Figure 3.1).

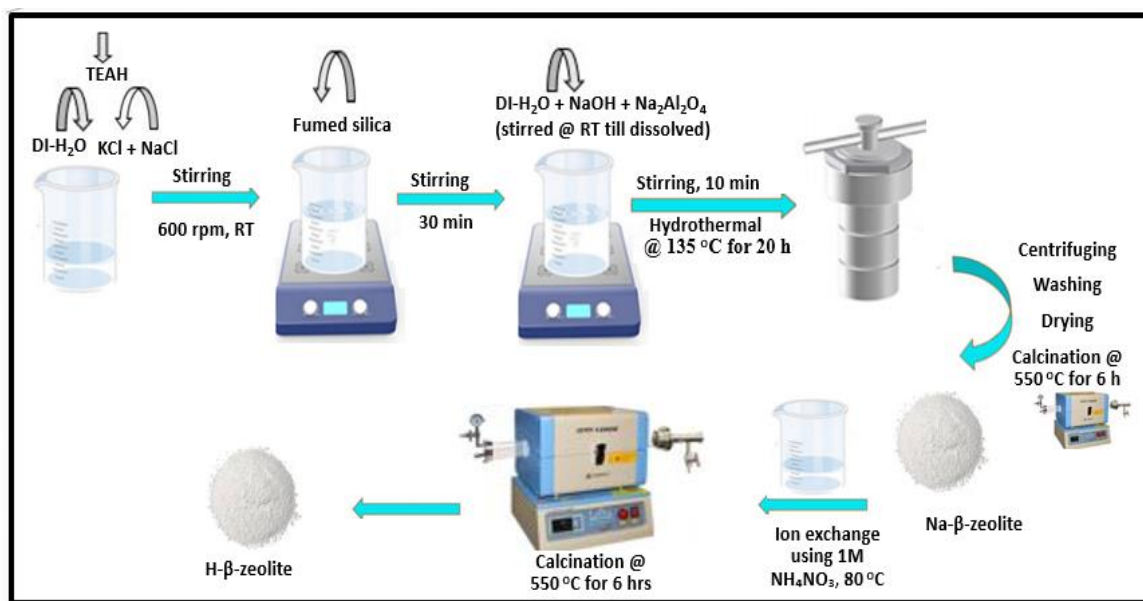


Figure 3.1: Synthesis of H-β-zeolite

In a typical synthesis, zinc oxide supported on β-zeolite (ZnO-β-zeolite) was prepared by adding a predetermined amount of zinc nitrate hydrate (equivalent to 10 wt.% of β-zeolite) and an appropriate amount of β-zeolite to 15 ml of distilled water and agitated at a temperature of 60 °C for 3 hours at 600 rpm. After stirring for 3 hours, the resulting precipitated solid was dried for 8 hours at 100 °C. Finally, the solid obtained was calcined at 550 °C for 6 hours (Figure 3.2a). SO₄²⁻/ZnO- β-zeolite was prepared by slowly adding a predefined amount of zinc nitrate hydrate and an appropriate amount of β-zeolite to 20 ml of 0.5 M sulfuric acid solutions and vigorously stirring at 60 °C for 3 hours at a speed of 600 rpm. After stirring, the resultant solid precipitate was filtered, oven-dried for 8 hours at 110 °C, and calcined for 6 hours at 550 °C in a muffle furnace (Figure 3.2b).

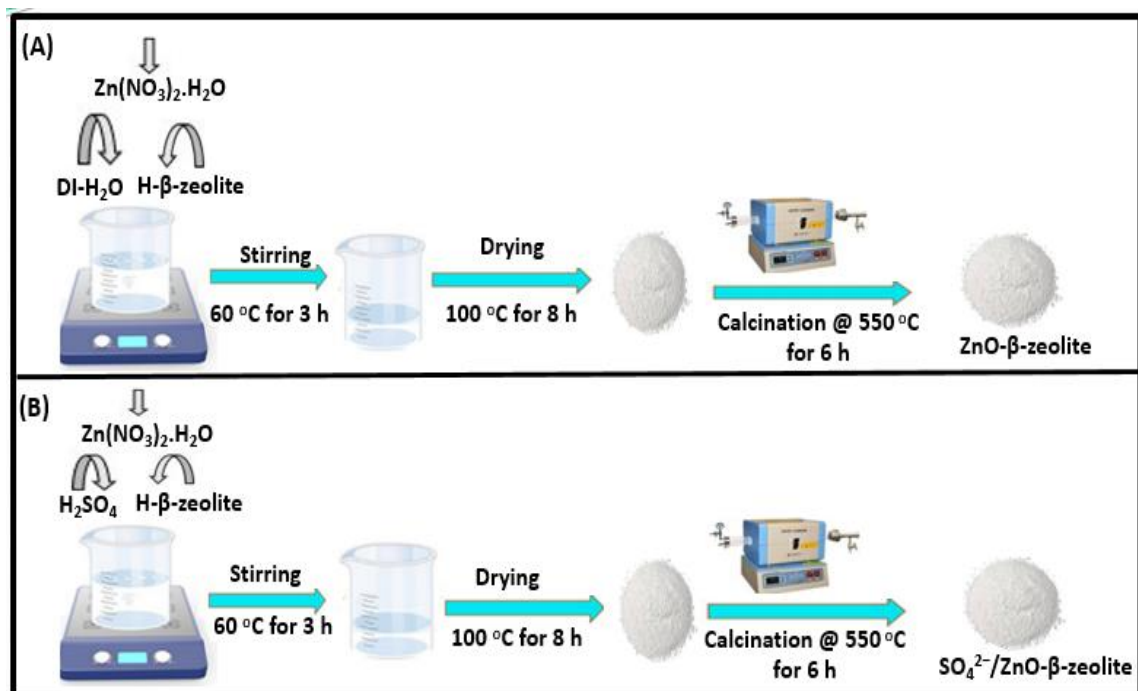


Figure 3.2: Synthesis of (a) ZnO-β-zeolite and (b) SO₄²⁻/ZnO-β-zeolite

3.2.2 Synthesis of ZrO₂/ZSM-5 and ZrO₂/ZSM-5(0.1-0.3M)

The NH₄-ZSM-5 zeolite was calcined at 550 °C under a steady flow of air for 6 hours to convert it to H-ZSM-5 as a catalyst support for the production of biodiesel. The modification of H-ZSM-5 zeolite was carried out by desilication (following zeolite synthesis, silicon is extracted from the framework using alkaline treatment) at 80 °C for 4 h with a series of NaOH concentrations (0.1- 0.3 M) under atmospheric pressure. In a reflux condenser-equipped flask, a 30-milliliter solution of NaOH was heated to 80 °C, then pre-determined amount of H-ZSM-5 zeolite (550 °C calcined) was added and agitated for 4 h at 600 rpm. After desilication with an alkaline solution, deionized water was used to wash the suspension before it was filtered, dried for 8 hours at 120 °C and Na⁺/NH₄⁺ ion exchange was then performed using 1 M NH₄NO₃ at 120 °C for 4 hours (ion exchange was carried out twice, one after the other with 1 M NH₄NO₃). The mixture was then cooled before being centrifuged at 780 rpm. The precipitate generated was purified by washing it three times with distilled water to get rid of any impurities. After drying for 10 hours at 120 °C, the reaction mixture was calcined in a muffle furnace for a total of 6 hours at 550 °C. We named the resulting desilicated zeolite sample ZSM-5(concentration), where

concentration denotes the concentration of the NaOH used in the alkaline treatment (Figure 3.3).

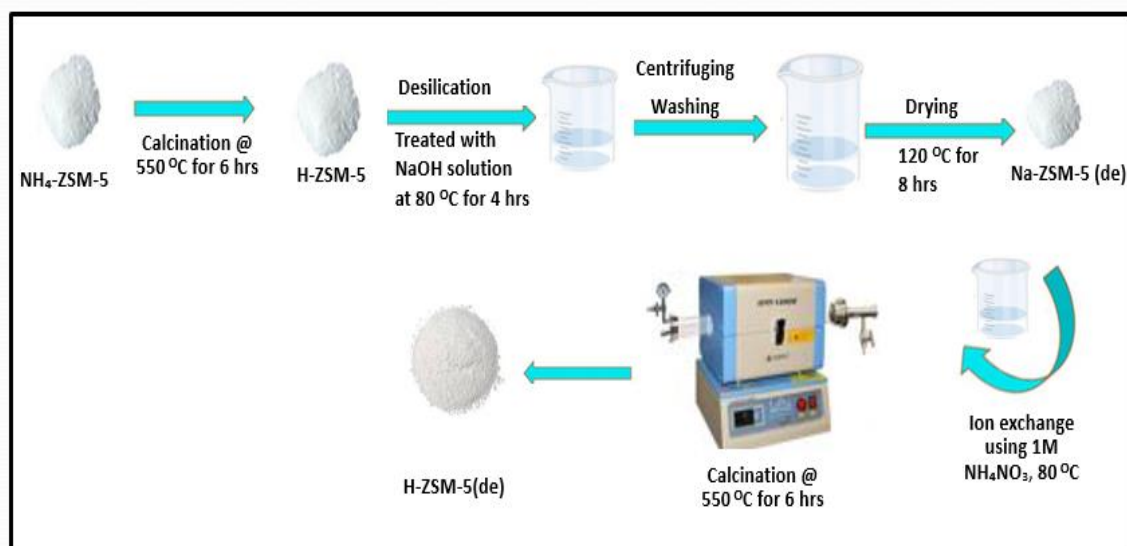


Figure 3.3: Synthesis of desilicated ZSM-5.

The wet impregnation approach was used to prepare the $\text{ZrO}_2/\text{ZSM-5}$ catalyst. The catalyst was prepared by slowly adding pre-determined amount of zirconium (IV) oxynitrate hydrate as a precursor for zirconia, and an appropriate amount of ZSM-5 to 12 ml of distilled water and agitating it at 60 °C for 3 hours. The precipitate that formed was dried for 11 hours at a temperature of 120 °C. Finally, the synthesized catalyst was calcined for 6 hours at 550 °C and was denoted as $\text{ZrO}_2/\text{ZSM-5}$ (Figure 3.4a). The $\text{ZrO}_2/\text{ZSM-5}(\text{NaOH}$ solution concentration) catalyst was also synthesized by a similar approach utilizing desilicated zeolite ZSM-5(NaOH solution concentration) as a support (Figure 3.4b).

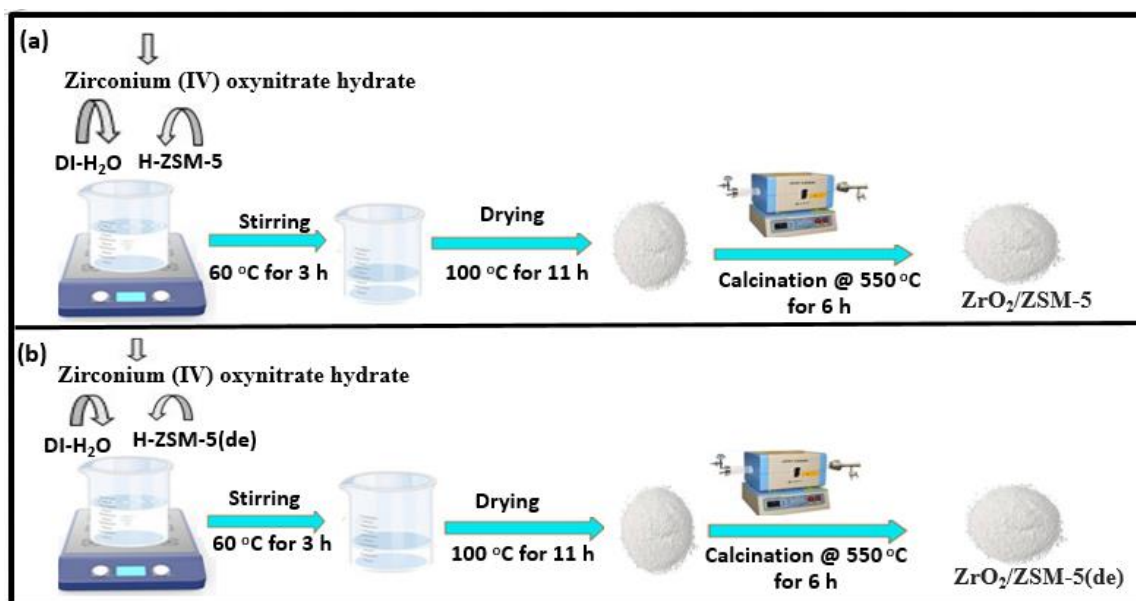


Figure 3.4: Synthesis of (a) ZrO₂/ZSM-5 and (b) ZrO₂/ZSM-5(de)

3.2.3 Synthesis of UiO-66 and Cu/UiO-66

The hydrothermal treatment method described by Zhang et al. [46] was used to synthesize UiO-66 support. Briefly, zirconium tetrachloride (0.51 g) was dissolved in 18.0 mL DMF while stirring, and then 0.3275 g of terephthalic acid was added. After 3 hours of stirring at room temperature, the mixture was hydrothermally treated (using a Teflon-lined autoclave) for 6 hours at 120 °C. Thereafter, the precipitate was obtained by centrifugation after cooling and the unreacted moieties were removed by repeatedly washing with DMF and ethanol. After that, the solid product was oven-dried at 80 °C for 12 h and this final sample is denoted as UiO-66 (Figure 3.5a).

Cu/UiO-66 catalysts were prepared via a wet impregnation approach. Briefly, a pre-determined amount of copper nitrate trihydrate as a precursor for copper (corresponding to 5%, 7%, and 10 wt.% Cu loading) was dissolved in 12 ml of distilled water. Then, an appropriate amount of UiO-66 was added and stirred for 3 h at 60 °C. The product was dried in air for 11 hours at 120 °C. Finally, the catalysts developed were calcined for 4 hours at 250 °C. Synthesized catalysts were 5%Cu/UiO-66, 7%Cu/UiO-66, and 10%Cu/UiO-66 (Figure 3.5b).

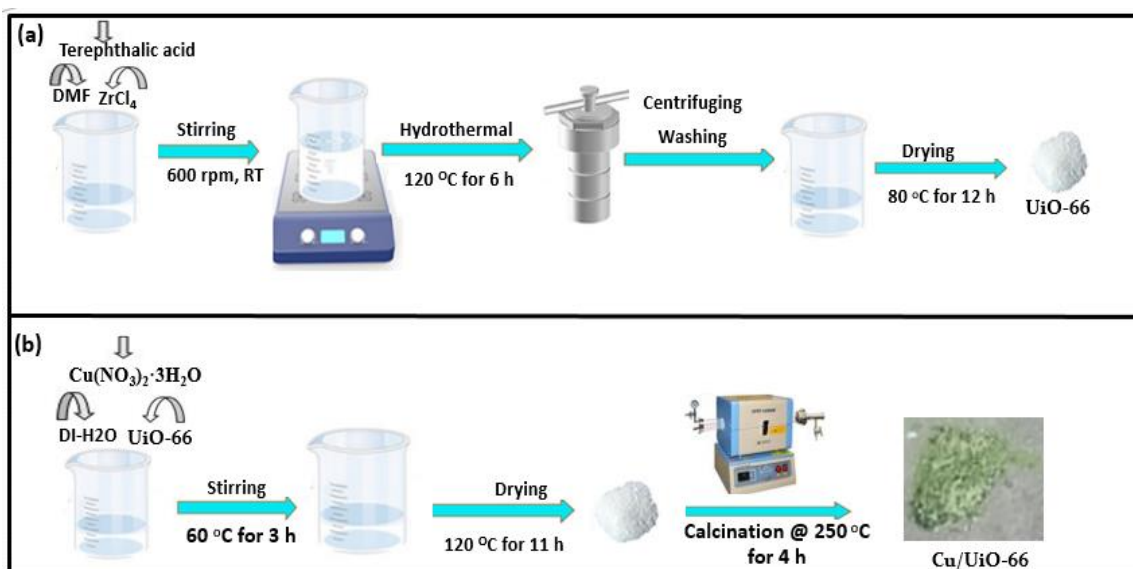


Figure 3.5: Synthesis of (a) UiO-66 and (b) Cu/UiO-66

3.2.4 Synthesis of Cu-BTC and Zn/Cu-BTC

The hydrothermal treatment method described by Zhang et al. [40] was used to synthesize Cu-BTC support. Briefly, a desired amount of copper nitrate trihydrate was dissolved in 18.0 mL of distilled water under stirring for 10 minutes. Then 0.63 g of 1,3,5-benzene tricarboxylic acid was added to the solution above with stirring for 1 hour at room temperature. After 1 hour of stirring at room temperature, the mixture was hydrothermally treated (using a Teflon-lined autoclave) for 6 hours at 120 °C, then cooled to room temperature. The precipitate was obtained by centrifugation after cooling to room temperature and washed several times with ethanol. Following that, the product was treated with hot ethanol for 3 hours many times. After that, the solid product was dried for 24 h at 120 °C and this final sample is denoted as Cu-BTC (Figure 3.6a).

Zn/Cu-BTC catalysts were prepared via a wet impregnation approach. Briefly, a pre-determined amount of zinc nitrate hydrate as a precursor for zinc (corresponding to 4%, 8%, and 10 wt.% Zn loading) was dissolved in 12 ml of distilled water. Then, an appropriate amount of Cu-BTC was added to the solution above and was stirred at 60 °C for 3 hours. The obtained mixture was dried in air for 10 hours at a temperature of 120 °C.

Finally, the catalysts developed were calcined for 2 hours at 250 °C (Figure 3.6b). Synthesized catalysts were 4%Zn/Cu-BTC, 8%Zn/Cu-BTC, and 10%Zn/Cu-BTC.

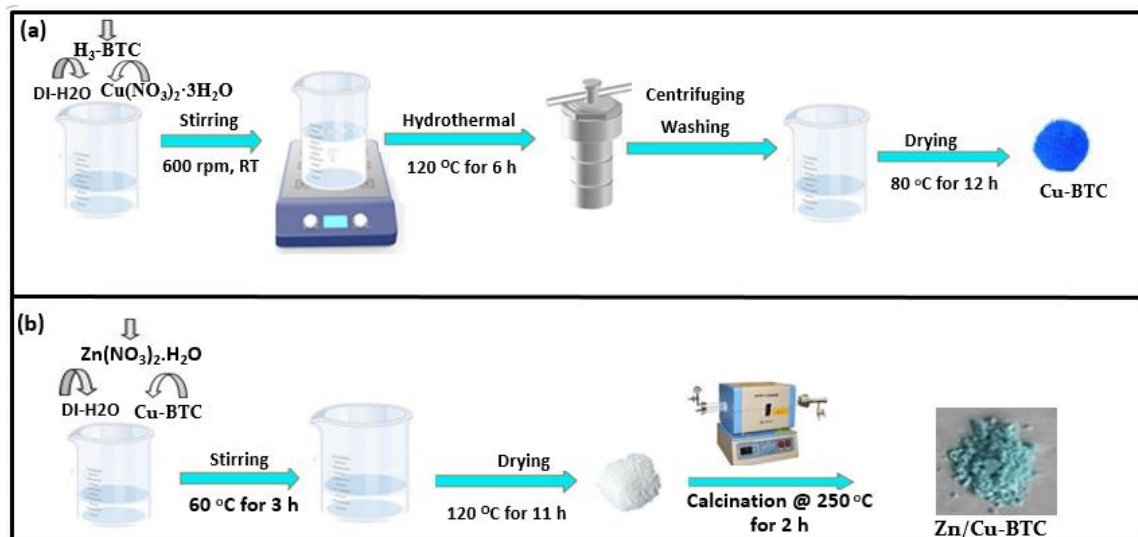


Figure 3.6: Synthesis of (a) Cu-BTC and (b) Zn/Cu-BTC.

3.3 Catalyst Characterization

3.3.1 N₂-Adsorption/Desorption Measurement

The synthesized materials were thoroughly characterized in order to determine their structural, physical and chemical characteristics. The textural properties (specific surface area, pore sizes and pore volumes) of the as-synthesized materials were measured utilizing Micrometrics ASAP 2020 instrument, (Micrometrics, USA). Pore volumes and pore sizes distribution of the catalytic materials were calculated utilizing Barrett, Joyner and Halenda (BJH) technique (Micrometrics ASAP 2020 instrument, USA). Surface area was calculated using the Brunauer, Emmett, and Teller (BET) technique. Prior to the analysis, a vacuum pretreatment process at 250 °C with nitrogen gas flow was carried out for 3 hours. After the pretreatment of the samples for 3 hours, a plastic coating is inserted on the outside of the sample holder (it helps in maintaining isothermal conditions during the reaction). Finally, the sample holder is connected to the instrument. Finally, samples were analysed at -196 °C (boiling point of liquid nitrogen).

3.3.2 X-ray Diffraction (XRD)

X-Ray diffraction (XRD) analysis was utilized to determine the crystal phase of all the samples. The XRD data were recorded on Bruker D2 Phaser 2nd Generation (Advanced diffractometer, Bruker, Karlsruhe, Germany) between $2\theta = 5-80^\circ$ with a scanning rate of $0.02^\circ\text{min}^{-1}$ utilizing a Cu-K α monochromatic radiation source ($\lambda = 1.5418 \text{ \AA}$).

3.3.3 Fourier transform infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) was utilized to determine the functional groups present in the catalysts. A Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, USA) was utilized to obtain FTIR spectra. The spectra were recorded between $400-4500 \text{ cm}^{-1}$ wavenumber range.

3.3.4 Pyridine FTIR

Pyridine-FTIR was used to measure the catalyst's acidity. In a typical procedure, the sample was put into a Specac cell and pretreated at 500°C for 1 hour under vacuum, and then the temperature (wavenumber ranging from $400-4000 \text{ cm}^{-1}$) was reduced to 150°C . Pyridine vapor was flowed for 30 minutes. Following that, the samples were degassed under vacuum conditions at 150°C in order to remove excess pyridine and then at 150°C , the FTIR spectra of the samples were recorded with a JASCO FTIR-4100 instrument, USA (wavenumber ranging from $1400-1800 \text{ cm}^{-1}$).

3.3.5 Scanning electron microscopy (SEM)

We examined the surface characteristics of the catalyst using a scanning electron microscope (SEM): Thermo Scientific™ Quattro ESEM Oxford Inc. UK, equipped with an electron gun, a secondary electron mode, and a backscattered electron mode. Before the SEM analysis, the catalysts were coated with gold films and put on carbon tape.

3.3.6 Transmission electron microscopy (TEM)

The transmission electron microscope (JEOL-JEM-2100, JOEL Ltd. USA) operated at 200 kV was utilized to measure the particle dispersion and particle size distribution. Before image analysis, samples were prepared on carbon-coated grids, placed on a sample holder, and then a high vacuum was applied.

3.3.7 Thermogravimetry Analysis (TGA)

An SDT Q600 thermogravimetric analyzer was used for the thermogravimetric analysis (TGA) (Thermal analysis instrument, USA), for which the samples were heated from 26 °C to 800 °C with an air flow rate of 10 °C/min.

3.3.8 X-Ray Fluorescence (XRF)

XRF analysis (PANalytical, Rh tube, United Kingdom) was performed in this study to determine the Si/Al ratio contents in the synthesized materials.

3.3.9 Ammonia- Temperature-Programmed Desorption (NH₃-TPD)

The acidity of the prepared samples were evaluated via temperature-programmed desorption (NH₃-TPD) method utilizing a Chemisorption analyzer, BELCAT-B, Microtrac, USA with a heating rate of 10 °C min⁻¹, the data were monitored from 100 to 420 °C.

3.4 Biodiesel synthesis

In the present study, pre-determined amounts of oil, catalyst, and methanol were introduced into a reactor (the catalytic reactions were carried out in a Parr batch reactor, Parr Instrument Company, Moline, Illinois, USA) fitted with temperature and stirring controllers. Throughout the reaction, the batch autoclave autogenous pressure was about 12 bar to ensure that all of the reactants remained in a liquid state. To ensure a uniform temperature and suspension, the reactants were stirred at a speed of 400 revolutions per minute (rpm). The mixture was cooled down after the transesterification reaction at a

specified temperature and time with continuous stirring. The insoluble catalyst was recovered using centrifugation. The insoluble catalyst was recovered using centrifugation, and the resulting sample mixture of fatty acid methyl esters (FAME)-glycerol was poured into a separatory funnel and left to settle for 24 h to allow the glycerol (lower layer) and biodiesel (upper layer) layers to separate. The bottom layer containing crude glycerol was collected. The excess methanol was removed from the biodiesel phase by heating it above the boiling point of methanol (80 °C). Finally, ^1H and ^{13}C NMR and GC-MS were used to analyze the biodiesel sample.

3.5 Biodiesel Analysis

The composition of the product was investigated using GC-MS analysis (7890A GC, Agilent Technologies, Santa Clara, USA). The measurement was carried out in split mode with an inlet temperature and helium flow rate of 220 °C and 1.2 mL/min, correspondingly. The oven was preheated at 200 °C. The solvent used was heptane. ^1H and ^{13}C nuclear magnetic resonance (NMR) analysis of the biodiesel products were carried out in a Bruker NMR (Bruker Avance III, 400 MHz NMR Spectrometer, Bruker Corporation, Mundelein, Illinois, USA). ^1H NMR was employed to determine the conversion of WCO to biodiesel. In a typical analysis, biodiesel product (0.05 g) was dissolved in 1 ml of deuterated chloroform (CDCl_3) solvent containing 0.05% tetramethylsilane (TMS). The percent conversion of biodiesel to methyl ester was calculated according to Equation 3.1:

$$C (\%) = [(2A_{\text{ME}}) / (3A_{\text{CH}_2})] \times 100 \quad (3.1)$$

where A_{CH_2} represents the integrated peak area of the methylene proton adjacent to the carbonyl group, and A_{ME} represents the integrated peak area of the methoxy proton in the methyl ester. The percentage of oil converted to biodiesel is denoted by C. [102].

3.6 Physical and chemical properties of the synthesized biodiesel

The synthesized biodiesel physicochemical properties such as dynamic viscosity, kinematic viscosity, specific gravity, density, acid value and flash point were characterized using American Society for Testing and Materials (ASTM) methods.

3.6.1 Determination of kinematic viscosity

The most crucial property of biodiesel is its viscosity, which influences the operation of fuel injection equipment, especially at low temperatures. Fuel fluidity is impacted by increasing viscosity. An automated Anton Paar instrument (model SVM3001, France ASTM D-445) was used to measure the kinematic viscosity.

3.6.2 Determination of density

One of the key properties that impact biodiesel quality is density. Specific gravity is the ratio of a substance's density to the density of a reference substance, while density is the mass per unit volume at a given temperature. The density of biodiesel was determined at 40 °C utilizing Anton Paar instrument (model SVM3001, France, ASTM D-5002) instrument.

3.6.3 Determination of specific gravity

Specific gravity is the comparison of the mass of fluid to that of water. A known-weight cylinder was filled with 10 ml of biodiesel and weighed. In order to obtain the mass of biodiesel sample, the final weight (weight of biodiesel plus weight of empty cylinder) was subtracted from the initial weight (weight of empty cylinder). The same procedure was applied to water, and data were recorded. The specific gravity of the biodiesel was calculated according to Equation 3.2:

$$\text{Specific gravity} = \frac{[\text{mass of biodiesel}]}{[\text{mass of water}]} \quad (3.2)$$

3.6.4 Determination of flash point

The flash point of a combustible material is one of the most important properties that determines its potential for fire and explosion. A flame is passed over a heated sample. The vapors of fuel will ignite with detectable flame if the temperature is at or above the flash point. Biodiesel's flash point is higher than petroleum-derived diesel's, making it safer to transport. The flash point was measured using Pensky-Martens flash point analyzer (FP93-5G2, ISL, France, ASTM D93).

3.6.5 Determination of acid value

The acid number indicates the quantity of FFAs in biodiesel. The acid value (AV) of the biodiesel was determined using the ASTM D664. According to this method, 10 g of biodiesel sample placed in a conical flask was weighed. The flask was filled with 50 mL of a solvent mixture (dehydrated ethanol and diethyl ether: 1:1) and gently agitated to dissolve the biodiesel sample. Then, the mixture was titrated against 0.1 N solution of KOH (using of phenolphthalein as indicator) with continuous stirring until a pink color persisted for 10 sec. The acid value (mg KOH/g of biodiesel) was determined according to Equation 3.3:

$$\text{Acid value (mg KOH/g of biodiesel)} = \frac{A \times N \times 56.1}{W} \quad (3.3)$$

where A represents the volume of potassium hydroxide used for titration, and N represents the normality of the potassium hydroxide (56.1 is the molecular weight of KOH). Mass of the biodiesel is denoted by W.

CHAPTER 4

RESULTS AND DISCUSSION

Biodiesel production from waste cooking oil via sulfated-metal oxide supported β -zeolite

4.1 Abstract

Biodiesel is well-known for being biodegradable, renewable, and environmentally friendly. However, the current industrial production of biodiesel from edible oil feedstocks is uneconomical due to high feedstock costs and its priority as a food resource. Readily available and cheap feedstock, like waste cooking oil in place of edible oils, can be a better option. Heterogeneous solid acid catalysts are preferred for low-cost feedstocks because the catalysts are highly insensitive to higher levels of free fatty acids in the raw materials. Therefore, in the present study, we synthesized and evaluated different solid catalysts, pure β -zeolite, ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite, for the production of biodiesel utilizing waste cooking oil (WCO) as a feedstock. The synthesized catalysts were characterized by Fourier transform infrared spectroscopy (FTIR), pyridine-FTIR, N_2 adsorption-desorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscope (SEM). The biodiesel was analyzed using Nuclear Magnetic Resonance (^1H and ^{13}C NMR) and Gas Chromatography-Mass Spectroscopy (GC-MS). The results revealed that the SO_4^{2-} /ZnO- β -zeolite catalyst showed excellent catalytic performance for simultaneous transesterification and esterification, which was higher than that of ZnO- β -zeolite and pure β -zeolite catalyst, due to the large pore size, and high acidity. The highest WCO conversion of 96.9% was achieved using SO_4^{2-} /ZnO- β -zeolite catalyst under the optimum reaction condition of 3.0 wt.% catalyst loading, 200 °C reaction temperature, and

15:1 MRMO for 8 hours Our investigation of its kinetic revealed that the reaction follows a pseudo first-order kinetic model, with an activation energy (E_a) of 38.58 kJ/mol. Moreover, the stability and reusability of the catalysts were evaluated, and it was found that the $\text{SO}_4^{2-}/\text{ZnO-}\beta\text{-zeolite}$ catalyst exhibited good stability, giving a biodiesel conversion of more than 80% after three cycles of reuse.

4.2 Introduction

For decades, fossil fuels have been major fuel sources for domestic and industrial uses. They meet the majority of the world's energy demands and are essential in the production of petrochemicals [186-187]. Nevertheless, the enormous challenges associated with this class of fuels are the reasons for the rising interest in other energy sources. Fossil fuels are linked to major environmental issues such as greenhouse gas emissions, air pollution, oil spillage, and degradation of aquatic and arable land [188-190]. Among the alternative being considered today, biofuels have a high priority because of the renewable nature of biomass resources. Biodiesel is regarded as the most promising renewable fuel among the various biofuels, presumably owing to its nontoxic, biodegradable, renewable nature, as well as its low carbon monoxide and sulfur emissions during the combustion process [191]. Biodiesel is produced by either transesterification of triglyceride or esterification of free fatty acids (FFAs) with methanol by using a suitable catalyst for the production of fatty acid methyl ester (biodiesel) and glycerol [192].

Vegetable oil-based biodiesel is yet to be extensively commercialized due to its high costs compared to fossil-based diesel [193]. Biodiesel typically costs more than 0.50 USD L⁻¹ [193-194]. Depending on the feedstock oils, the price of biodiesel is about 1.5 times that of fossil-based diesel [193]. One method for increasing the economic viability and lowering production costs of biodiesel involves the utility of cheap materials like non-edible oil and waste cooking oil (WCO) rather than fresh vegetable oils [193-194]. Another strategy for making the biodiesel production process more economically appealing is the development of highly active, cost-effective, and easily recyclable catalysts [193-194]. Moreover, producing biodiesel from WCO offers three possible solutions: environmental sustainability, waste management, and good economics. Zhang et al. [195] studied the economic feasibility of biodiesel production from waste cooking oil and canola oil. They

inferred that the process with WCO was more economically feasible because of the lowest manufacturing cost, high internal rate of return and low breakeven price. Muhammed et al. [196] investigated the economic feasibility of biodiesel production from WCO in United Arab Emirate (UAE). They reported that the process is profitable and largescale production favored reduction in selling prices and subsidies.

Owing to the high FFAs and water content in WCO, using a homogeneous base catalyst will result in saponification, which will cause significant difficulties with product separation and eventually, a significant reduction in biodiesel yield. When using feedstocks that contain a high level of FFAs, a two-step approach is typically employed [197-198]. Pre-esterification of FFAs with alcohol is the first step, in which the FFAs are catalyzed using liquid acids (liquid acid catalysis, which reduces the FFAs content in oil by more than 99%). In the second step, the products from the first step are converted into biodiesel and glycerol by base-catalyzed transesterification. Unlike base catalysts, FFAs have no effect on homogenous acid catalysts, and homogenous acid catalysts are capable of catalyzing both transesterification and esterification simultaneously [46]. Nevertheless, separation and regeneration of the catalyst, corrosion-related problems, and serious environmental issues limit the utilization of homogeneous acid catalysts. The use of heterogeneous catalysts to produce biodiesel is gaining popularity due to the fact that they are recyclable and offer a simple catalyst removal step. [199]. Heterogeneous acid catalysts may be less active but they are more stable than heterogeneous base catalysts, allowing them to be employed for feedstocks containing a high quantity of FFAs without catalyst deactivation [200].

Many scientists have made substantial progress toward producing biodiesel through solid acid catalysts [116]. Heterogeneous acid catalysts employed for triglyceride transesterification, including zeolite, Amberlyst-15, and sulfated tin oxide ($\text{SO}_4^{2-}/\text{SnO}_2$), exhibited high catalytic activity [201]. Solid acid catalysts have also been used to esterify FFAs [111]. Sulphate group incorporation into metal oxides primarily improves acidity without compromising the catalytic activity [105,116]. Sulfated titanium oxide ($\text{SO}_4^{2-}/\text{TiO}_2$), ion-exchange resin, sulfated zirconium oxide ($\text{SO}_4^{2-}/\text{ZrO}_2$) and sulfated tin oxide are some examples of typical catalysts with high catalytic activity [111,116]. When

utilized to catalyze both transesterification and esterification simultaneously, some of these heterogeneous acid catalysts, like sulfated titanium oxide, demonstrated remarkable catalytic activity and stability [116,202]. However, owing to the challenges of filtering the tiny catalyst particles and the high catalyst cost, they have not been widely used in commercial production operations. Zinc oxide and lead oxide are promising catalysts for both transesterification and esterification, but they are prone to leaching and negative reuse effects [203]. Therefore, incorporation of proper support is very important to improve the reusability of the catalyst and reduce leaching problems. Pure oxide are mostly supported by activated carbon, silica, and alumina [203]. In many cases, conventional support materials (such as activated carbon, alumina, and silica) are inefficient [203]. Zeolites, which have a significant porosity, large surface area, high acidity, and high hydrothermal stability than alumina and silica, may display improved metal-support interaction, resulting in improved stability.

β -zeolite is a form of zeolite that is rich in silica with a three-dimensional structure of intersecting 12-membered ring channel [204]. Several acid catalyzed reactions can be carried out efficiently due to the relatively large channel structure [204]. Other factors influencing reaction efficiency of β -zeolite are the high thermal stability, large surface area and tunable acidity in the protonic form [205]. It has been found that β -zeolite is an effective catalyst for transesterification, which could be utilized in the production of a vast array of products [201,205]. Transesterification occurs at the β -zeolite Bronsted acidic sites, which can be slightly altered with cation modifications, resulting in modified catalysts with appropriate acidity to fit diverse transesterifications [205-207].

In the present study, we prepared β -zeolite, zinc oxide and sulfated-zinc oxide supported on β -zeolite (ZnO- β -zeolite and $\text{SO}_4^{2-}/\text{ZnO-}\beta$ -zeolite, respectively) and investigated their catalytic performance in the production of biodiesel using WCO. The parameters that affect reactions such as reaction time, the ratio of methanol to oil, catalyst loading, and temperature were optimized. A kinetic study was also conducted at different reaction temperatures to evaluate the rate of reaction and determine the activation energy (E_a). The surface acidity (Lewis or Brønsted) and its influence on the activity of pure β -zeolite, ZnO- β -zeolite and sulfated/ZnO- β -zeolite were also investigated. sulfated/ZnO- β -zeolite

catalyst was found to exhibit a significant amount of acidity relevant to high biodiesel conversion. The superiority of $\text{SO}_4^{2-}/\text{ZnO}-\beta\text{-zeolite}$ catalyst over $\text{ZnO}-\beta\text{-zeolite}$ and pure $\beta\text{-zeolite}$ was attributed to a number of physico-chemical characteristics such as pore size, acidity, etc. that resulted from the dispersion of the active phase caused by sulfate incorporation into the catalyst matrix.

4.3 Materials and methods

Materials used in this section, catalyst synthesis procedure, characterization methods and biodiesel production procedure and biodiesel analysis were previously explained in Chapter 3, Sections 3.1, 3.2.1, 3.3, 3.4, 3.5 and 3.6.

4.4 Results and discussion

4.4.1 XRD analysis

Figure 4.1 shows the XRD patterns of the catalysts. It was observed that the synthesized H- $\beta\text{-zeolite}$ has the XRD pattern exhibiting representative Bragg reflection conforming to the $\beta\text{-zeolite}$ structure and a well-preserved crystalline structure, which is comparable to the findings that were previously reported in the literature [208-209]. The diffraction peak at $2\theta = 6-8^\circ$, ascribed to (101) reflection of $\beta\text{-zeolite}$ topology, is generally seen as an evidence of a highly distorted structure resulting from various isomorphs in the zeolite structure [210]. The narrow main distinct signal at $2\theta = 22-23^\circ$, assigned to (302) reflection of $\beta\text{-zeolite}$ indicates zeolite structure lattice expansion/contraction [211]. Following the incorporation of Zn species and sulfonate group, the typical $\beta\text{-zeolite}$ diffraction peak at $22-23^\circ$ slightly decreased, indicating a slight compression of the $\beta\text{-zeolite}$ crystalline structure in the presence of zinc species without changing in the framework [212-213]. As illustrated in Figure 4.1, the zinc oxide is well incorporated into the $\beta\text{-zeolite}$ support. The peaks position at $2\theta = 31.7^\circ, 34.4^\circ, 36.2^\circ, 56.5^\circ$ and 62.9° corresponding to (100), (002), (101), (110) and (103) lattice planes were attributed to the phase of zinc oxide, suggesting the formation of the crystals [214].

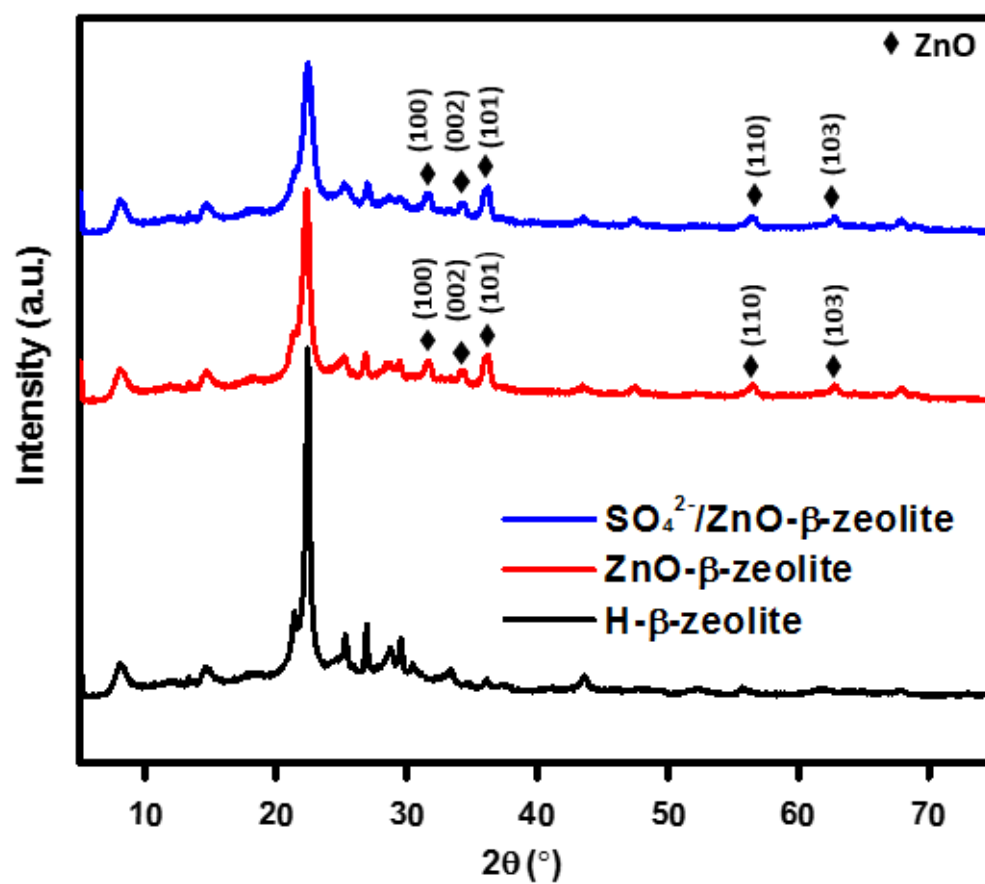


Figure 4.1. XRD patterns of the three catalysts

4.4.2 FTIR analysis

The FTIR spectra of synthesized catalysts are depicted in Figure 4.2. The band around 575 cm^{-1} is characteristic of β -zeolite since the structure contains six-membered rings [215]. The bands at about 800 cm^{-1} and 1080 cm^{-1} represent the O-T-O (T= Al or Si) symmetric and asymmetric stretching vibrations, which are susceptible to the aluminum composition of the framework [216]. Based on previous reports on different siliceous zeolites, the 950 cm^{-1} band represents the stretching vibrations of Si-O and it belongs to uncoupled SiO_4 tetrahedron [217-219]. As seen in Fig. 4.2, the structural vibration is comparable for all samples under investigation, confirming that the incorporation of metal oxide into β -zeolite support does not affect the structure. The band at 425 cm^{-1} is related to the zinc oxide stretching mode, suggesting that ZnO is incorporated into the zeolite framework and these results are consistent with the literature reports [214].

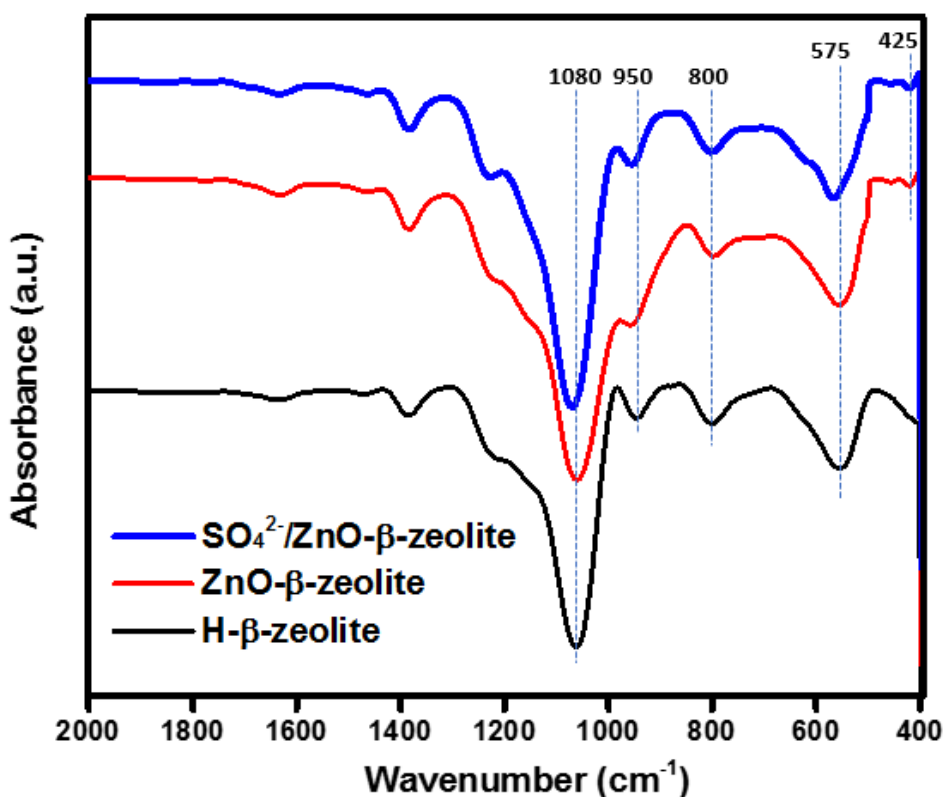


Figure 4.2. FTIR patterns of the three catalysts

4.4.3 Pyridine-FTIR analysis

Pyridine-FTIR analysis was performed on the catalysts to determine acidity, which is related to catalytic performance. Figure 4.3 shows the pyridine-adsorbed FTIR spectrum of the catalysts measured at 150 °C between 1430 and 1800 cm^{-1} . As seen in the figure, there are sharp adsorption bands resulting from the stretching of C-C bond of pyridine. Pyridine molecules interacting with Lewis (L) acid sites have sharp adsorption bands at 1456 cm^{-1} and 1630 cm^{-1} , while pyridine molecules adsorbed on Brønsted (B) acid sites have a band at 1550 cm^{-1} . A pyridine molecule interacting with both L and B acid sites was assigned to the 1490 cm^{-1} band [220]. Also, the intensity of the bands is substantially higher in $\text{SO}_4^{2-}/\text{ZnO}-\beta$ -zeolite than in H- β -zeolite and ZnO- β -zeolite, indicating an increase in total acid sites. The deposition of sulfated groups on the surface of the $\text{SO}_4^{2-}/\text{ZnO}-\beta$ -zeolite catalyst is responsible for the increase in total acid sites. Thus, the result suggests that the prepared $\text{SO}_4^{2-}/\text{ZnO}-\beta$ -zeolite has high acidity and can be utilized as a heterogeneous acid catalyst in biodiesel production.

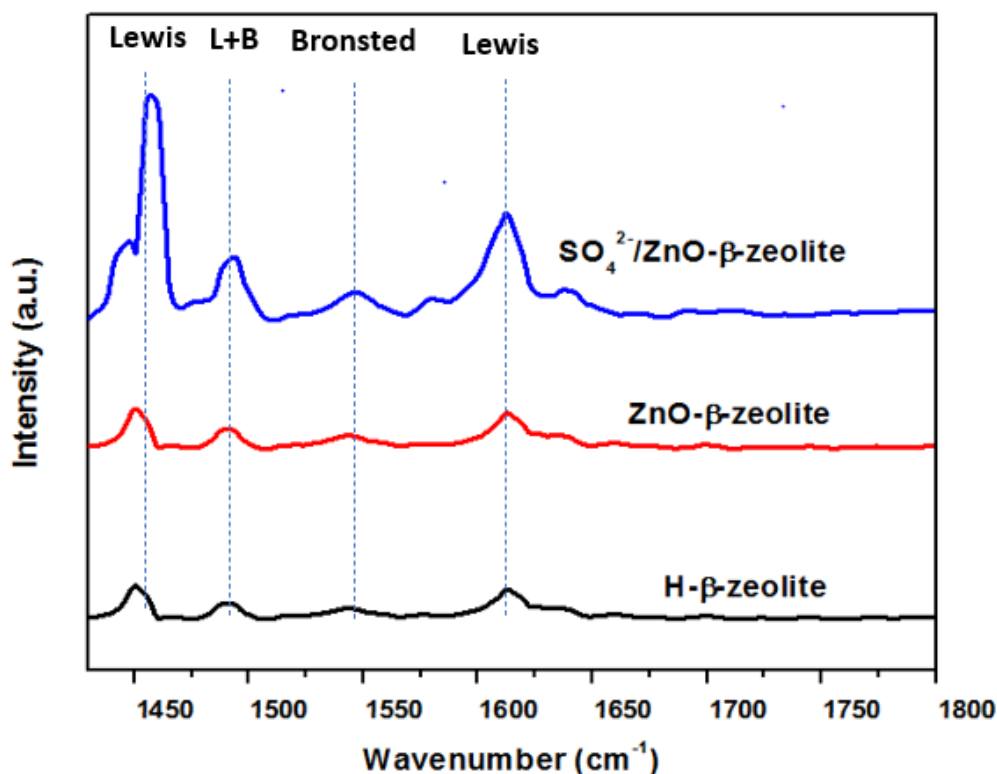


Figure 4.3. Pyridine-FTIR spectra of the three catalysts.

4.4.4 Textural properties analysis

The N₂ adsorption-desorption isotherms of the catalysts are shown in Figure 4.4. A type-1 isotherm is observed in the H- β -zeolite [221]. The type-1 isotherm pattern suggests a micro-meso hierarchical porous textural characteristics [221]. The type-1 isotherm remains the same after zinc oxide loading on the β -zeolite support. The pore size, volume and specific surface areas of the catalysts are shown in Table 4.1. The surface area of β -zeolite was 469.21 m²/g, while ZnO- β -zeolite and SO₄²⁻/ZnO- β -zeolite had surface areas of 198.01 and 250.26 m²/g, correspondingly. The reduction in surface area could be attributed to pore blockage caused by metal oxide deposition on the β -zeolite. The catalyst is mostly found on the surface of zeolite support. As a result, the decrease in support surface area is unimportant in this case because the primary role of zeolites is holding metal oxide particles together and preventing metal leaching [212]. Nevertheless, when the metal oxide is incorporated into the zeolite support, the pore size changes, and it increases upon incorporating both metal oxide and sulfate groups. The active phase dispersion caused by sulfate incorporation in the SO₄²⁻/ZnO- β -zeolite catalyst matrix was also attributed to the high surface area and pore size of SO₄²⁻/ZnO- β -zeolite compared to ZnO- β -zeolite. When producing biodiesel with a heterogeneous acid catalyst, this phenomenon is important. This could be because catalysts with larger pores reduce diffusion restrictions, particularly for long alkyl chain molecules [213].

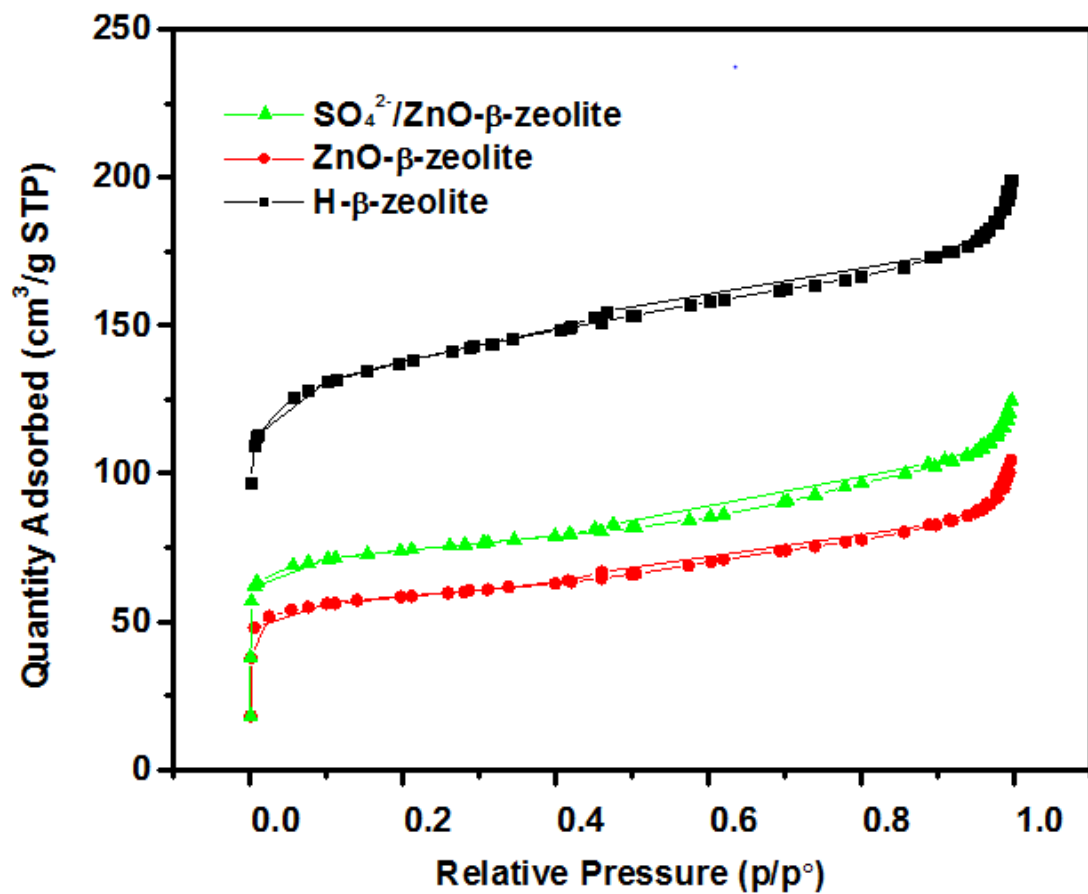


Figure 4.4. N₂ adsorption-desorption isotherms plot of H- β -zeolite support and the catalysts.

Table 4.1

Textural properties of supporting H-Beta zeolite and the catalysts

Sample	S_{BET} (m ² /g)	S_{micro} (m ² /g)	S_{meso} (m ² /g)	V_{micr} (cm ³ /g)	V_{total} (cm ³ /g)	PS (nm)
H- β -zeolite	469.21	317.72	151.48	0.14	0.28	4.52
ZnO- β -zeolite	198.01	140.72	57.27	0.06	0.13	6.46
SO ₄ ²⁻ /ZnO- β -zeolite	250.26	180.27	69.99	0.08	0.17	6.50

4.4.5 Thermogravimetric analysis

The thermal stabilities of H- β -zeolite, ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite were established with thermogravimetric analysis. In general, the TGA curve depicts the weight loss stages in the samples (Figure 4.5). According to the literature, weight loss below 350 °C can be ascribed to the removal of physically adsorbed water and the thermal degradation of noninteracting tetraethylammonium hydroxide (TEAOH) species, whereas weight loss above 350 °C can be attributed to the pyrolysis of tetraethylammonium cation (TEA^+) interacting with the framework of zeolite [207]. This effect leads to a weight loss of about 10-15%. The extra weight loss in this temperature range could be related to lower temperature decomposition residues. As seen in Fig. 4.5, the catalysts show high thermal stability as the main decomposition of the zeolite support started at high temperature, which indicates the high stability of β -zeolite. Thus, the results showed that the synthesized catalysts are thermally stable and can be utilized to produce biodiesel.

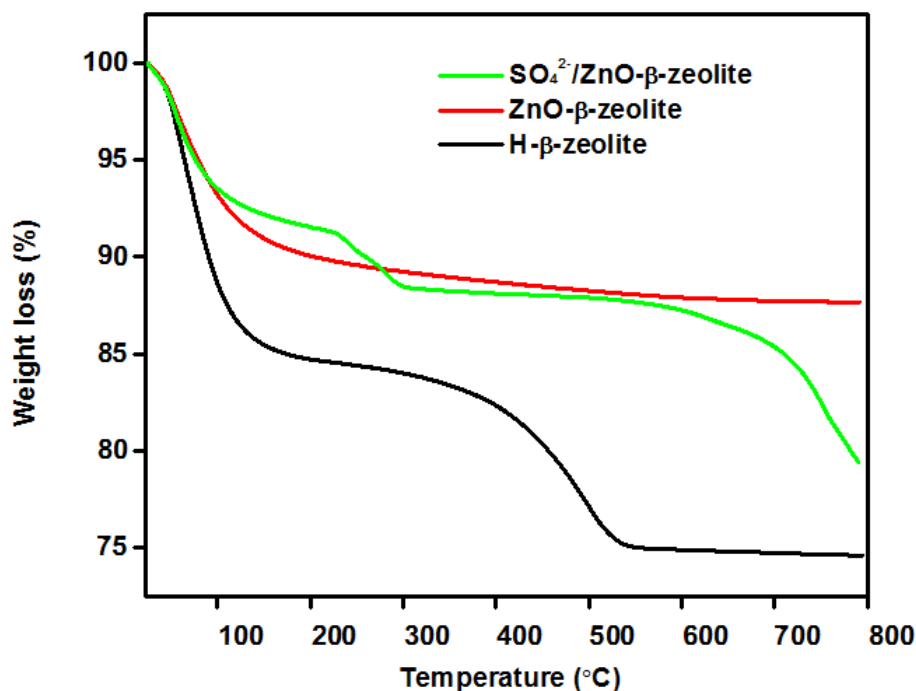


Figure 4.5. TGA analysis of the catalyst.

4.4.6 SEM analysis

Figure 4.6 shows the SEM images depicting the structures of the catalysts. The morphology of the prepared H- β -zeolite revealed uniform and spherical particles with sizes varying between 0.5-2 μm (Figure 4.6a), which is congruent with published research findings [222]. After zinc oxide had been loaded onto H- β -zeolite (ZnO- β -zeolite) and incorporation of both zinc oxide and sulfate groups in H- β -zeolite (SO_4^{2-} /ZnO- β -zeolite), there is no substantial change in the shape of the particles (Figure 4.6b-c). These results suggest that zinc oxide particles were evenly dispersed on the surface of the β -zeolite.

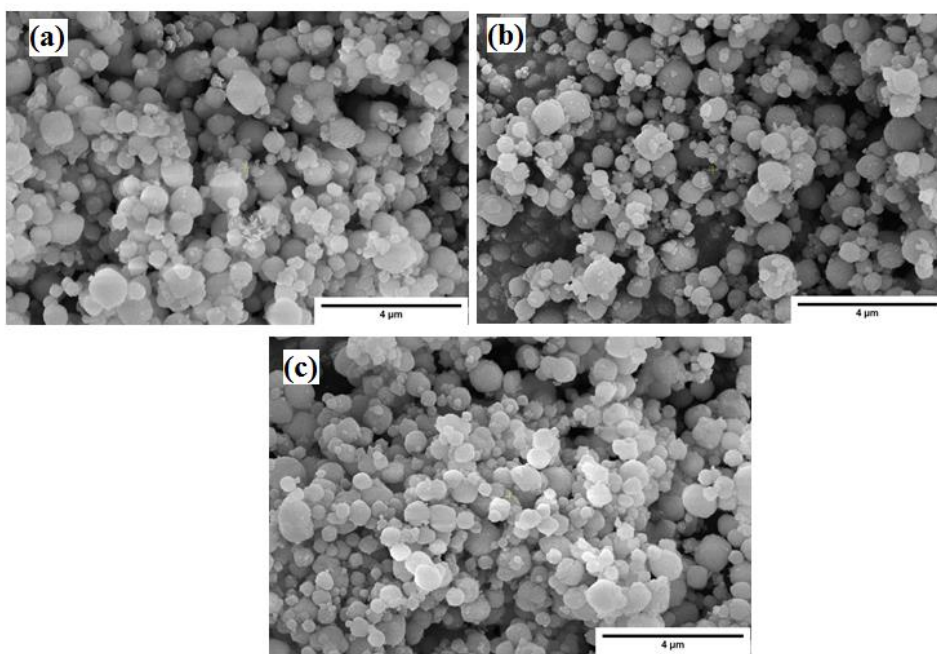


Figure 4.6. SEM images of the catalysts, a: H- β -zeolite; b: ZnO- β -zeolite; c: SO_4^{2-} /ZnO- β -zeolite

4.4.7 Biodiesel analysis

Following biodiesel synthesis as described in the experimental section, the conversion of WCO to FAME and biodiesel characterization were carried out using ^1H NMR and ^{13}C NMR spectroscopy, respectively. The ^1H NMR spectrum of the biodiesel sample obtained after WCO conversion to FAME using the SO_4^{2-} /ZnO- β -zeolite catalyst is shown in Figure A.1 (Appendix A). The presence of a triplet peak at 2.31 ppm and a single peak at 3.67

ppm corresponding to α -CH₂ protons (A_{CH2}) and methoxy protons (A_{ME}), respectively, confirms biodiesel formation [102]. These two peaks indicated oil conversion to biodiesel. Other peaks include signals at 0.88, 1.26 and 1.61 ppm for end-of-chain methyl protons, carbon methylene proton and carbonyl methylene protons, respectively. The 5.35 ppm signal is attributed to an olefinic proton [102,223-224]. Equation 3.1 describes the oil conversion into biodiesel [102]. Using Eq.3.1, the percentage conversion of WCO to equivalent FAMES was found to be 96.9 %.

Figure A.2 depicts the ¹³C NMR spectra of WCO biodiesel. The ester carbonyl carbon (-COO-) peak was observed at 174.31 ppm and the C-O carbon appears at 51.42 ppm in the biodiesel spectrum. The two signals at 127.90 and 130.19 ppm indicate the presence of unsaturated fatty acids. The 14.11 ppm signal corresponds to the end-chain methyl carbon, while the signals in the range of 22.69-34.10 ppm are related to aliphatic methylene groups (-CH₂-s) of FAMES [223-224]. The composition of the WCO biodiesel was investigated using GC-MS analysis. The GC-MS chromatogram of the biodiesel sample is shown in Figure A.3. Table A.1 lists the components of the biodiesel. The biodiesel sample comprised both saturated and unsaturated FAMES.

The performance property of the prepared biodiesel is compared with the ASTM standards. The fuel properties such as flash point, kinematic viscosity, density, specific gravity, and acid value of the WCO biodiesel are shown in Table 4.2, which conform to the recommended value specified by ASTM D6751. Therefore, as-prepared biodiesel could be utilized either as a pure fuel or blended with conventional diesel fuel.

Table 4.2**The performance properties of the WCO biodiesel in comparison with the ASTM standards.**

Fuel properties	ASTM method used	ASTM D6751 Biodiesel	WCO biodiesel
Kinematic viscosity (40 °C, mm ² /s)	D445	1.9-6.0	5.04
Density (40 °C, g/cm ³)	D5002	0.86-0.90	0.871
Specific gravity (40 °C, g/cm ³)	D287	0.88	0.876
Flash point (°C)	D93	100-170	132
Acid value (mg KOH/g)	D664	0.5	0.15

4.4.8 Catalytic performance of the catalysts

The performance of the synthesized catalysts was investigated for the methanolysis of WCO for biodiesel production. The catalytic activities of H- β -zeolite, ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite were investigated at fixed process parameters such as reaction temperature of 200 °C, WCO/methanol molar ratio of 1:12, and catalyst loading of 2.0 wt.% for 4 hours. Figure 4.7 shows the biodiesel conversion trend when the catalysts were used. The highest WCO conversion was achieved by using ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite. This increase in catalytic activity is most likely due to the appropriate particle size. It should be emphasized that triglyceride access to β -zeolite internal sites may be limited due to their sizes; consequently, catalytic activity originates primarily from sites on the β -zeolite external surfaces. Due to the large size of zinc species, Zn ion exchange is expected to occur on the β -zeolite external surface, which can significantly increase the number of sites on the β -zeolite exterior surfaces. Thus, it can be inferred that the ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite has a greater number of external active sites available for the reactant. As depicted in Figure 4.7, ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite catalysts were more appropriate in terms of external accessibility to promote WCO conversion, which appears to be guided primarily by the improvement of characteristics of the β -zeolite external surface. Therefore, ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite catalysts were further compared for biodiesel production, and the process parameters (such as: methanol to WCO molar ratio, catalyst loading, time, and temperature) were optimized.

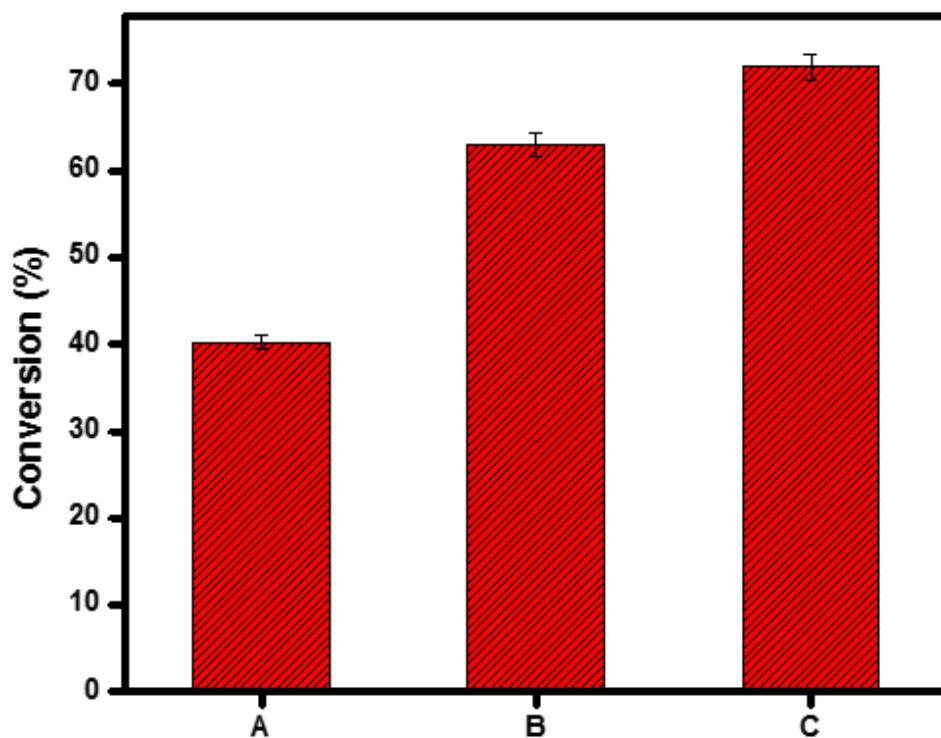


Figure 4.7 Catalytic performance of H-β-zeolite, ZnO-β-zeolite and SO₄²⁻/ZnO-β-zeolite catalysts related to conversion of WCO [A = H-β-zeolite, B = ZnO-β-zeolite and C = SO₄²⁻/ZnO-β-zeolite].

4.4.9 Effect of different reaction parameters

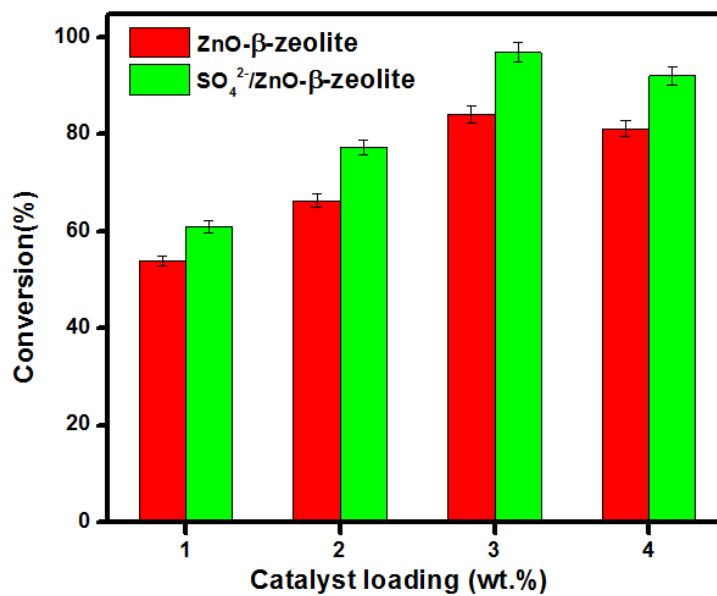
To investigate the activity of the catalyst in biodiesel's production, WCO was reacted with methanol over ZnO-β-zeolite and SO₄²⁻/ZnO-β-zeolite catalysts. Thus, different parameters affecting methyl ester conversion were examined here. The effect of experimental parameters such as the molar ratio of methanol to oil (MRMO), catalyst loading, time, and temperature were investigated. Figures 4.8 and 4.9 depict the results of the parametric investigation for biodiesel production while varying the experimental conditions.

A. Effect of catalyst loading and methanol/oil ratio

In order to investigate the impact that catalyst loading has on biodiesel conversion, the amount of catalyst used was varied from 1.0 wt.% to 4.0 wt.% (Figure 4.8a). At a constant MRMO of 15:1, the reaction was run for 8 hours at 200 °C. As displayed in Fig 4.8a, increasing the loading of the catalyst from 1.0 wt.% to 3.0 wt.% steadily enhanced biodiesel conversion, reaching a maximum of 84.1 % for ZnO- β -zeolite and 96.9 % for SO_4^{2-} /ZnO- β -zeolite. Increased catalyst loading above 3.0 wt.% reduces biodiesel conversion due to mixing problem that involves solid catalyst, reactant and product [24,40]. Moreover, if catalyst loading exceeds the optimum amount, biodiesel products can adsorb on the catalyst, reducing conversion [102,226]. Therefore, in the present study, the optimum catalyst loading for biodiesel production using WCO was capped at 3.0 wt.%. Therefore, other reaction parameters were optimized with a 3.0 wt.% catalyst loading.

Another factor that affects biodiesel conversion is the molar ratio of methanol to oil (MRMO). Transesterification reaction requires one mole of oil and three moles of methanol to produce one mole of glycerol and three moles of FAMES. Since the reaction is reversible, it is preferable to use excess methanol to favor the forward reaction. The MRMO was varied from 9:1 to 18:1 to see what influence it had on biodiesel conversion (Figure 4.8b). The reaction was run for 8 hours at 200 °C with 3.0 wt.% catalyst loading. We found that increasing the MRMO increases biodiesel conversion. When the MRMO rose to 15:1, the biodiesel conversion increased to 84.1% and 96.8% for ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite catalyst, respectively. However, when the MRMO exceeds 15:1, biodiesel conversion begins to decrease. Increasing the molar ratio might lead to incomplete transesterification and mass transfer limitation caused by dilution [227]. Therefore, optimum methanol to oil molar ratio for biodiesel production was kept at 15:1 in this study.

(a)



(b)

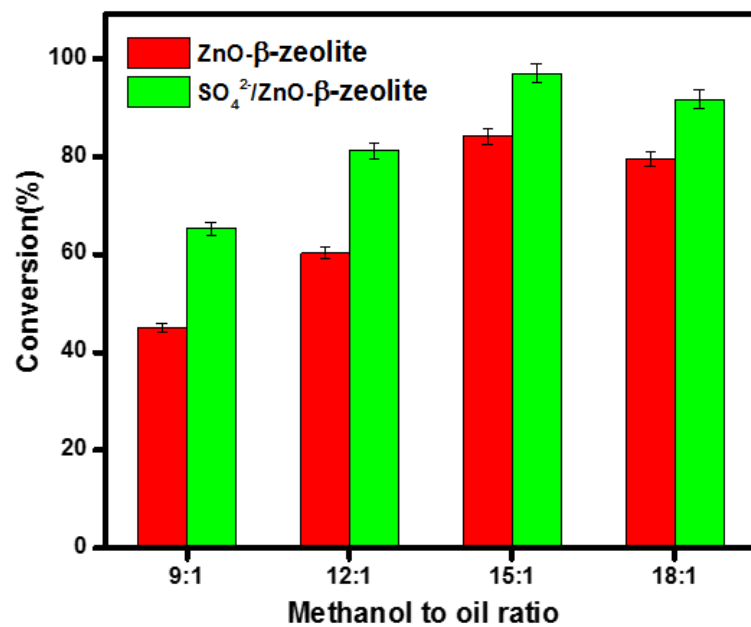


Figure 4.8 (a) Effect of catalyst loading and (b) Effect of molar ratio of methanol to oil.

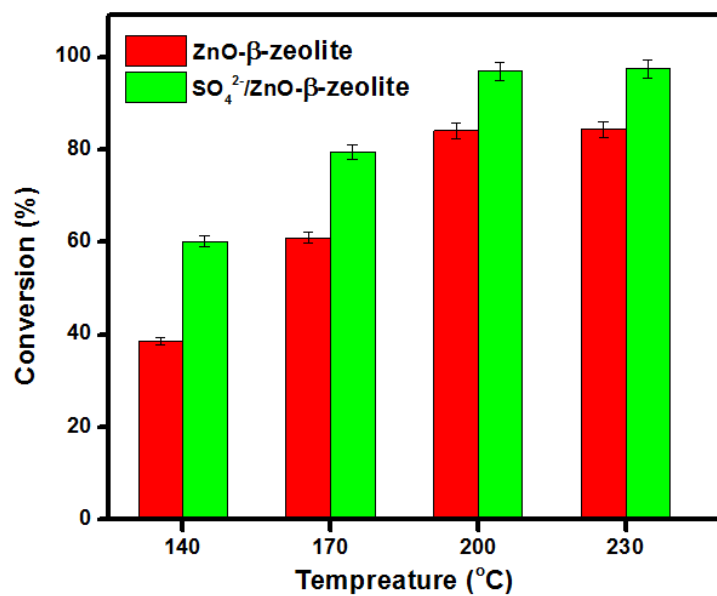
B. Effect of reaction temperature and time

Due to the fact that temperature has a significant impact on reaction rate, one of the most important parameters to optimize is the reaction temperature. Furthermore, the formation of three immiscible phases consisting of oil, methanol, and solid acid catalyst at the beginning of the reaction, which limits mass transfer, increases the temperature of the reaction when a heterogenous catalyst is employed [13]. Thus, in order to increase the system's mass transfer rate, one needs to maintain a high reaction temperature, allowing for higher biodiesel conversion in less time. Most studies reported that high temperature favor biodiesel conversion from low-grade material/WCO feedstock [111,116]. Figure 4.9a depicts biodiesel conversion as reaction temperature changes. The reaction temperature was varied from 140 °C to 230 °C. The reaction was conducted for 8 hours with a fixed MRMO of 15:1 and 3 wt.% catalyst loading. It can be easily noticed that at the lower reaction temperature, the biodiesel conversion was very low (Figure 4.9a). However, the reactants acquired sufficient kinetic energy at higher temperatures to enhance the system's mass transfer rate, resulting in the optimum conversion of 84.1% and 96.9% for ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite catalyst, respectively, at 200 °C. When the temperature rose beyond 200 °C, the biodiesel conversion began to increase marginally. Hence, 200 °C is considered as the optimal reaction temperature.

The impact of reaction time on biodiesel conversion was also investigated by varying the reaction time from 2 to 10 hours at 2-hour intervals with a catalyst loading of 3.0 wt.% and a 15:1 MRMO. (Figure 4.9b). The result showed that the heterogeneous catalyst had not yet been fully activated in the first two hours, resulting in a slow reaction rate and low biodiesel conversion. However, increasing the reaction time to 8 hours increases biodiesel conversion to 84.2 % and 96.9 % for the ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite catalysts, respectively, and these are the maxima. Notably, after 8 hours, there was a decrease in biodiesel conversion. This behavior could be attributed to reverse transesterification between fatty acid methyl esters and glycerol as reaction time increases [228-229]. The optimal reaction time for biodiesel production was thus taken to be 8 hours. Interestingly, the activity of SO_4^{2-} /ZnO- β -zeolite catalyst was substantially higher than ZnO- β -zeolite

catalyst activity, and these behaviour may be attributed to the highly acidic nature of $\text{SO}_4^{2-}/\text{ZnO-}\beta\text{-zeolite}$ catalyst.

(a)



(b)

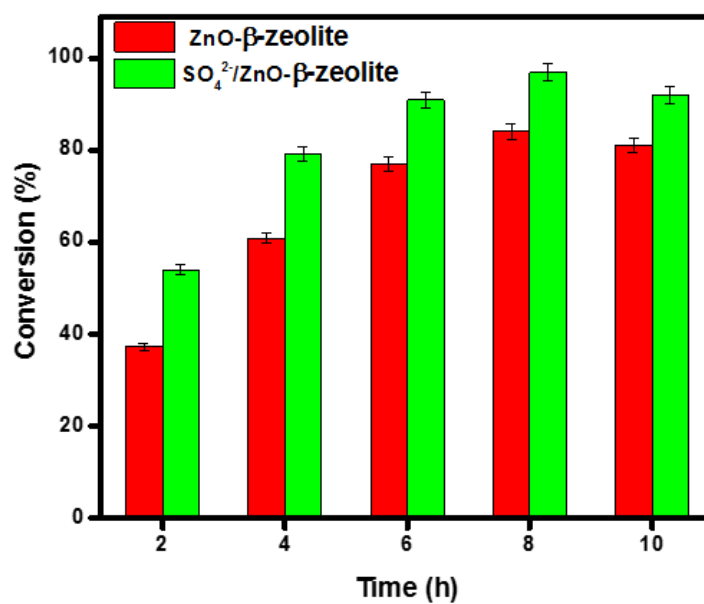


Figure 4.9. (a) Effect of reaction temperature and (b) Effect of reaction time

4.4.10 Kinetic studies of biodiesel production

The kinetics of WCO biodiesel production was studied utilizing $\text{SO}_4^{2-}/\text{ZnO-}\beta\text{-zeolite}$ catalyst at varying temperatures (140 to 230 °C) under optimum reaction conditions, and the reaction activation energy (E_a) was thereby computed. The reverse reaction can be ignored since an excess amount of methanol was employed, and the pseudo-first-order model is assumed to govern the reaction [230-231]. Therefore, equation (4.1) fits the reaction rate constant, the activation energy (E_a) of the process is computed using the Arrhenius equation (4.2) [232]

$$k = -\ln \frac{1-X}{t} \quad (4.1)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4.2)$$

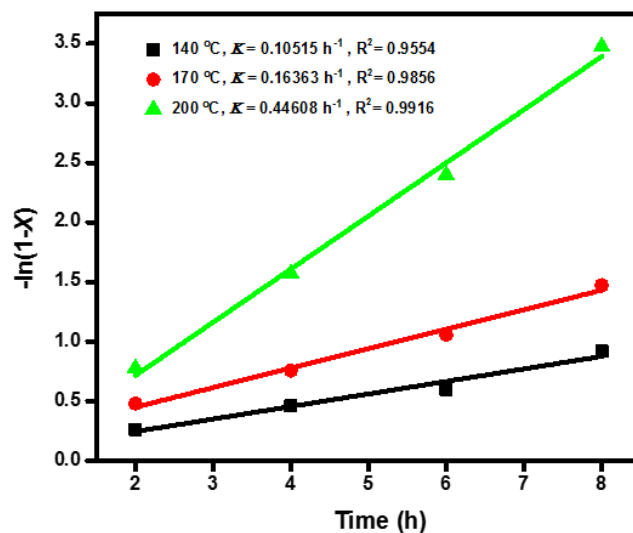
where R = universal gas constant; A = Arrhenius constant; T = reaction temperature;

X = conversion of WCO at time t ; k = reaction rate constant;

According to equation (4.1), a plot of $-\ln (1- X)$ versus time is linear, as depicted in Figure 4.10a. The plots show that the model is acceptable for pseudo-first order kinetics due to its good linearity and high regression coefficients. A linear plot of $\ln k$ against $1/T$ that shows a high regression coefficient is depicted in Figure 4.10b. According to the Arrhenius plot, the activation energy (E_a) of the reaction was 38.58 kJ/mol using the $\text{SO}_4^{2-}/\text{ZnO-}\beta\text{-zeolite}$ catalyst. The activation energy obtained from the WCO is consistent with the literature and is comparable to the activation energy achieved for soybean oil transesterification (i.e.

33.6-84kJ/mol) [233,44]. Moreover, a value of E_a greater than 15 kJ/mol indicates that the reaction is controlled chemically [233].

(a)



(b)

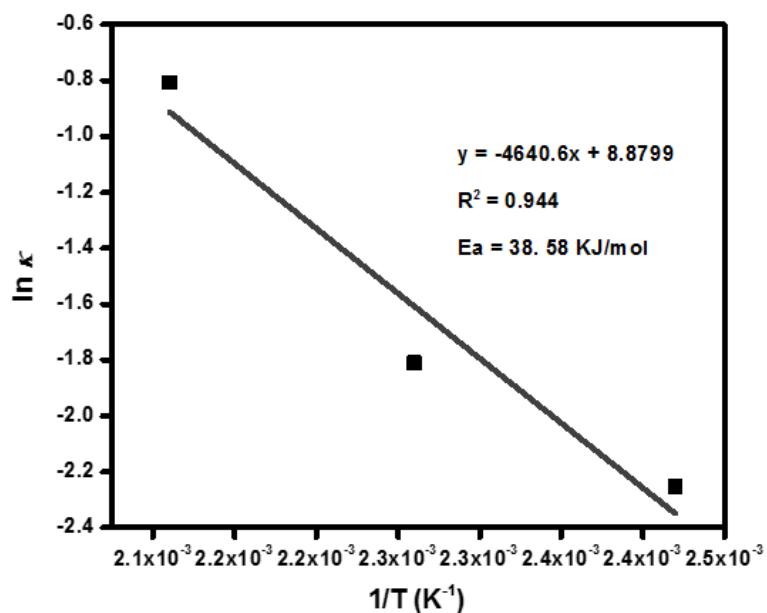


Figure 4.10 (a) A graph depicting the relationship between $-\ln(1-X)$ and time and (b) An Arrhenius graph showing the relationship between k and $1/T$.

4.4.11 Plausible mechanism

Figure 4.11 shows a plausible mechanism for simultaneous transesterification and esterification of WCO. Carbonyl group of fatty acid/triglyceride is typically adsorbed on $\text{SO}_4^{2-}/\text{ZnO}-\beta$ -zeolite catalyst to produce the protonated carbonyl group, which is then attacked by the nucleophilic oxygen atom from methanol hydroxyl group to form a tetrahedral intermediate. Finally, in the esterification reaction, the tetrahedral intermediate removes water to produce methyl ester. This intermediate removes glycerol during the transesterification reaction to produce a new methyl ester.

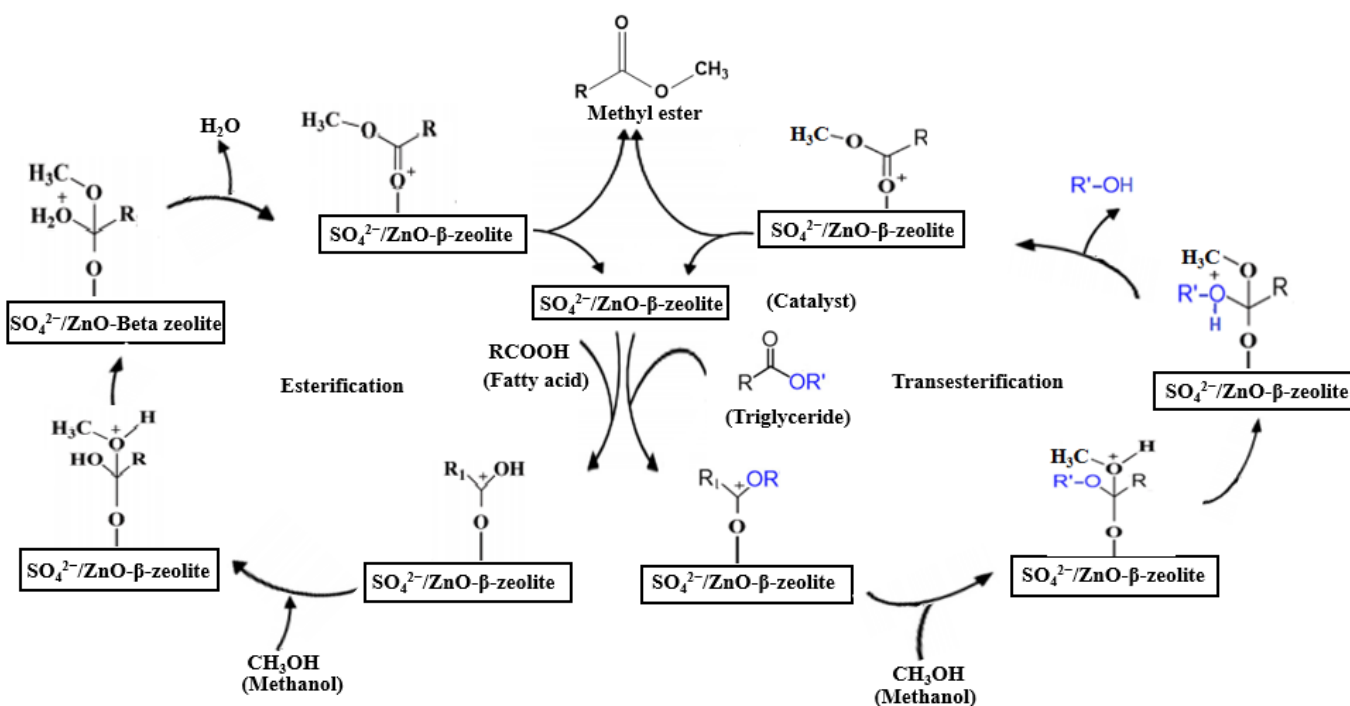


Figure 4.11. Plausible mechanism for concurrent esterification and transesterification reactions.

4.4.12 Reusability of catalysts

Solid catalysts have the primary advantage of being reusable. The reusability of the catalyst was examined in this work (Figure 4.12). To evaluate catalyst reusability, both ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite catalysts were centrifuged from the reaction mixture, rinsed with methanol, oven-dried at 100 °C for 12 hours, and then utilized for next cycle. Both transesterification and esterification reaction of WCO were carried out five times under the optimal conditions of 3.0 wt.% catalyst loading at 200 °C and 15:1 MRMO for 8 hours, and the results are shown in Fig. 4.12. We found that the catalysts maintained fairly good stability even after three experiments retaining 67.49% and 80.89% conversion for ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite catalysts, respectively. Furthermore, XRD analyses was conducted to determine the stability of the catalyst (see Fig. A.4). According to Figure A.4, the XRD spectra of the five-recovery catalyst was nearly identical to that of the fresh one, except for a slight decrease in peak intensity, indicating the better recyclability of the two catalysts. The partial loss in activity was most likely due to the leaching part of the active component into the reaction media during repeated reactions. Therefore, these findings clearly show that the catalysts are highly recyclable.

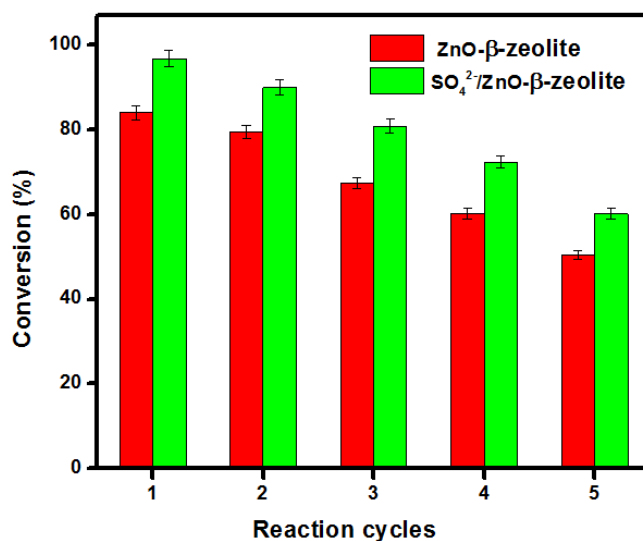


Figure 4.12. Reusability potential of the ZnO-treated catalysts.

Table 4.3 compares the performance of different heterogeneous catalysts in simultaneous transesterification and esterification reaction using low-grade/waste oils as feedstock. Our catalysts' performance is comparable to other studies.

Table 4.3. Different solid catalysts' performance in biodiesel production utilizing low grade material/waste oils as feedstock.

Catalyst	Operating conditions ^a	Performance	Reference
Mg–Al–CO ₃ hydrotalcite	3 h, 200 °C, 1 wt.%, 6:1	99% oil conversion	[44]
SO ₄ ⁻² /TiO ₂ –SiO ₂	6 h, 200 °C, 3 wt.%, 16:1	92% oil conversion	[111]
Zn ₃ La ₁	3 h, 200 °C, 2.3wt.%, 36:1	96% oil conversion	[234]
Zinc stearate immobilized on silica gel	10 h, 200 °C, 3 wt.%, 18:1	98% oil conversion	[235]
12-Tungstophosphoric acid supported on zirconia	10 h, 200 °C, 3 wt.%, 9:1	90% oil conversion	[236]
H-ZSM-5	4 h, 100 °C, 10 wt.%, 45:1	55% oil conversion	[132]

H-ZSM-5 (1.0 M citric acid modified)	4 h, 100 °C, 10 wt.%, 45:1	84% oil conversion	[237]
La ₂ O ₃ /Na-Y-800	1 h, 70 °C, 10 wt.%, 15:1	80% oil conversion	[238]
S-La ₂ O ₃ /Na-Y-800 (S = surfactant modified)	1 h, 70 °C, 10 wt.%, 15:1	84% oil conversion	[238]
CaO/Zeolite	1.25 h, 8 wt.%, 30:1	90.85% oil conversion	[239]
ZnO-β-zeolite	8 h, 200 °C, 3.0 wt.%, 15:1	84.1% conversion	This work
SO ₄ ²⁻ /ZnO-β-zeolite	8 h, 200 °C, 3.0 wt.%, 15:1	96.9% conversion	This work

^aThe operating conditions (reaction time, temperature, catalyst loading, and molar ratio oil/alcohol)

4.5 Conclusion

H-β-zeolite, ZnO-β-zeolite and SO₄²⁻/ZnO-β-zeolite catalysts prepared proved to be effective catalysts for simultaneous transesterification and esterification of WCO. The SO₄²⁻/ZnO-β-zeolite catalyst exhibited remarkable catalytic activity in contrast to H-β-zeolite and ZnO-β-zeolite. Characterization analyses show that when the sulfonate group is incorporated to the surface of the catalyst, Lewis/Brønsted acid sites are formed. These acid sites contribute to the large surface area, high acidity, and high dispersion of the active phase of the SO₄²⁻/ZnO-β-zeolite. The highest WCO conversion of 96.9% was achieved using SO₄²⁻/ZnO-β-zeolite catalyst under the optimum reaction condition of 3.0 wt.% catalyst loading, 200 °C reaction temperature, and 15:1 MRMO for 8 hours. Kinetic studies show that simultaneous transesterification and esterification exhibit a pseudo-first order kinetic model, with an apparent activation energy of 38.58 kJ/mol. This result suggests that

the reaction is chemically controlled and not by mass transfer and diffusion constraints. Furthermore, the $\text{SO}_4^{2-}/\text{ZnO}-\beta$ -zeolite showed good stability, and after three cycles of use, biodiesel conversion was about 81% (indicating no significant activity loss). Overall, this catalyst system has the potential to be used in industrial biodiesel production since it is capable of converting waste oil, low-grade oil, and inexpensive oil with a high FFA content into biodiesel.

CHAPTER 5

Zr-modified desilicated ZSM-5 catalysts as highly active and regenerable catalysts for production of biofuel from soybean oil: Insight into improved catalyst properties, acidity and dispersion through desilication

5.1 Abstract

Bio-based fuels, such as biodiesel, have recently gained attention due to concern about ever-increasing energy consumption and global warming. Solid catalysts are key materials in the production of green biodiesel. The use of solid catalysts in the production of biodiesel can lower the cost of the separation and thus reduce biodiesel costs. In the present study, zeolite-supported ZrO_2 catalyst ($\text{ZrO}_2/\text{ZSM-5}$) and a series of desilicated zeolite-supported ZrO_2 catalyst [$\text{ZrO}_2/\text{ZSM-5}(0.1\text{-}0.3\text{M})$] were successfully synthesized by impregnation method and used as new catalysts for the production of soybean oil biodiesel through transesterification. Desilication at various sodium hydroxide concentrations enhances the external surface area and mesoporous volume, without jeopardizing crystallinity or microporosity of the catalysts. The synthesized catalysts were characterized via X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), pyridine-FTIR, scanning electron microscopy, TEM, XRF, TGA and nitrogen adsorption-desorption. Nuclear magnetic resonance (NMR) and gas chromatography-mass spectrometry (GC-MS) were used to characterize the biodiesel that was produced. The as-prepared $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalyst exhibited better catalytic activity in the transesterification of soybean oil with methanol, compared to $\text{ZrO}_2/\text{ZSM-5}$ catalyst, due to large pore volume, high surface area, and high dispersion of ZrO_2 on the desilicated zeolite support with improved acidity and

high number of active sites. A biodiesel conversion of 90.1% and 97.84% were obtained for zeolite-supported ZrO_2 catalyst and desilicated zeolite-supported ZrO_2 catalyst, respectively, under optimum reaction conditions of 1.0 wt% catalyst loading, 1:16 soybean oil/methanol molar ratio at 200 °C in 4 hours reaction time. Moreover, the desilicated zeolite-supported ZrO_2 catalyst exhibited excellent stability and re-usability giving a biodiesel conversion of 93.8% after three cycles of reuse.

5.2 Introduction

Due to the increased fossil fuel resource demand, constant population rise, the present rise in fuel prices, and environmental issues such as pollution and global warming, alternative energy sources such as biofuels have been proposed [240-241]. Biodiesel is regarded as the most promising sustainable fuel among the various biofuels, presumably due to its lower emission of carbon dioxide, non-toxicity, higher cetane index, and biodegradable properties [192]. Biodiesel is made via transesterification of triglycerides or esterification of free fatty acids (FFAs) with alcohol in the presence of a heterogeneous, homogeneous or enzymatic catalyst [242]. Bio-enzyme catalytic advancement is still challenging because of the enzyme's poor stability and high price [243]. For homogeneous base/acid catalysts, for example, NaOH, KOH, H_3PO_4 , H_2SO_4 , or HCl are often used in industrial biodiesel production, but they have several disadvantages including non-reusability, toxicity, and high corrosiveness [244-245]. Therefore, in an extensive effort to circumvent the constraints of homogenous catalysts, the application of heterogeneous solid catalysts are now being researched, owing to their reusability, non-corrosiveness, and easy product separation [225,246-248]. Heterogeneous base catalysts (for example: MgO, SrO, CaO, MgZnO, and NaOH/ Al_2O_3) often provide better conversion at lower temperatures, although leaching of metal in the product mixture is an issue [225,249]. However, heterogeneous base catalysts are not appropriate for low-cost feedstocks containing a huge amount of FFAs because these catalysts will react with the FFAs to produce soaps, resulting in low biodiesel yields and poor product quality [250]. In these instances, a heterogeneous acid catalyst is more desirable since it is insensitive to free fatty acid (can avoid saponification).

A heterogeneous acid catalyst, such as acid-functionalized metal oxides, zeolite, and ion exchange resins are among catalysts with extremely high catalytic activity [251]. However, the major problems associated with heterogeneously acid catalyzed biodiesel production is their inability to withstand high water content in the feedstocks and obstruction of the catalyst active site by product species or adsorbed intermediates, which in turn leads to catalysts deactivation after a few runs [172]. In addition, a high reaction temperature is required for transesterification of raw materials to ensure reasonable activity, while oil/alcohol molar ratio is very high, energy consumption is very high, and the processing time is very long. These drawbacks have rendered heterogeneous acid catalysts impractical for industrial use [53]. Although ZnO, ZnO/Al₂O₃, PbO, and ZrO₂ are promising transesterification and esterification catalysts, but they are prone to leaching [203]. Among the heterogeneous acid catalysts mentioned above, the most well-studied solid acid catalyst for different chemical processes is sulfated zirconia [252]. It has high thermal stability and a considerable number of acid sites generated from the modification of sulfur ions. However, due to rapid SO₄²⁻ leaching, traditional sulfated zirconia produced with sulfuric acid has poor reusability and limited acidity [102]. Therefore, incorporation of proper support is very important to reduce leaching problems.

Metal oxides are mostly supported by activated carbon, silica, and alumina [253]. In many cases, conventional support materials (such as activated carbon, alumina, and silica) are inefficient [253]. Zeolites, which have a higher acidity than alumina and silica, may display improved metal-support interaction, resulting in improved stability. Nevertheless, since zeolites have small pores, slow diffusion of reactant molecules within zeolites could be a process limitation.

The zeolite's diffusional constraint can be reduced by forming an intracrystalline mesopore structure under controlled conditions [254]. Desilication is one of the most well-known efficient methods for introducing mesoporosity into various zeolite systems [254-255]. We believe that there is little or no scientific investigation available on catalytic transesterification of triglycerides in which desilicated zeolites have been harnessed as a catalyst support in biodiesel production to investigate their long-term stability and commercial viability. In this study, we designed new catalysts using parent zeolite and a

series of desilicated zeolite as supports and investigated their efficiency in biodiesel production from soybean oil. The structure-performance characteristics of the catalysts were probed via nitrogen adsorption-desorption, XRD, XRF, FTIR, pyridine-FTIR, TGA, TEM, SEM, GC-MS, and NMR. The high performance of desilicated ZSM-5/ZrO₂ catalyst is attributed to better textural properties, high surface acidity and dispersion, which resulted in a high number of active sites necessary for efficient transesterification reaction.

5.3 Materials and methods

Materials used for this section, catalyst synthesis procedure, characterization methods, transesterification procedure and biodiesel analysis were previously explained in Chapter 3.

5.4 Results and discussion

5.4.1 XRD analysis

Figure 5.1 depicts the XRD pattern of parent ZSM-5 and hierarchical ZrO₂/ZSM-5 catalysts. The results obtained show that all the synthesized catalysts exhibited the characteristic peaks of a parent ZSM-5 at $2\theta = 8.01^\circ$, 8.94° , 23.17° , 24.05° , and 45.59° . The diffraction peaks correspond quite well to those reported in the literature [256]. We also observed that the parent ZSM-5 zeolite structure is preserved after desilication and ZrO₂ deposition. This implies that the ZSM-5 crystalline structure remained stable following the sample treatment (desilication) with alkaline and loading of ZrO₂. Nevertheless, a closer examination of the peaks at 8° - 10° reveals a significant reduction in the peak intensity upon desilication treatment with NaOH. This suggests that the ZSM-5 framework has partially disintegrated, coupled with a decrease in crystallinity [256-257]. The findings are consistent with those of Sadowska et al., who showed that the crystallinity of ZSM-5 is unaffected by mild desilication [254]. Nevertheless, higher NaOH concentration has a substantial impact on crystallinity. Moreover, no relevant peak position corresponds to ZrO₂ in the zeolite-supported catalysts' XRD patterns. This suggests that when ZrO₂ is supported by zeolites, its crystallinity decreases drastically. This is due to the great dispersion of ZrO₂ crystallites of small size, which prevents agglomeration, which

may have resulted in crystalline peaks of ZrO_2 . This claim is supported by the TEM analysis. The average particle size of Zr, as determined by TEM analysis was 3.85 nm, which confirms the good dispersion of the metals. Also, the absence of crystalline ZrO_2 peaks in the XRD pattern of $\text{ZrO}_2/\text{ZSM-5}$ catalysts indicates that Zr crystallites were below the XRD detection limit (<4 nm) [258]. Moreover, during the treatment, we believe that some metal oxides might be either dispersed over the zeolite crystals' surface or permeated into zeolite's interstices.

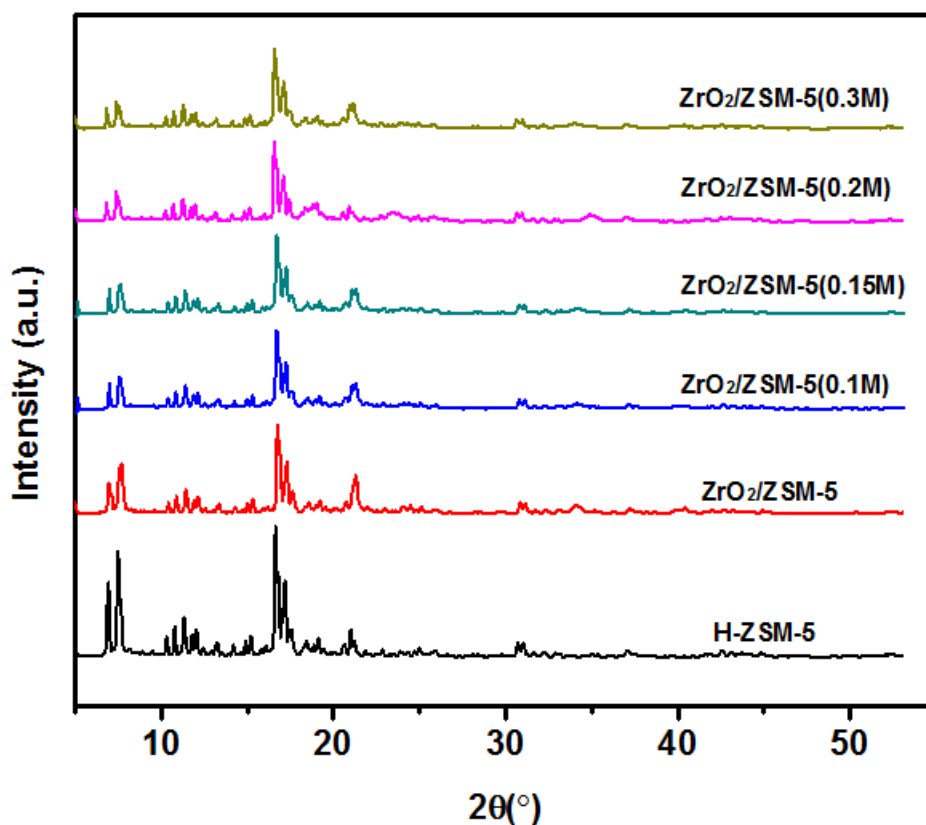


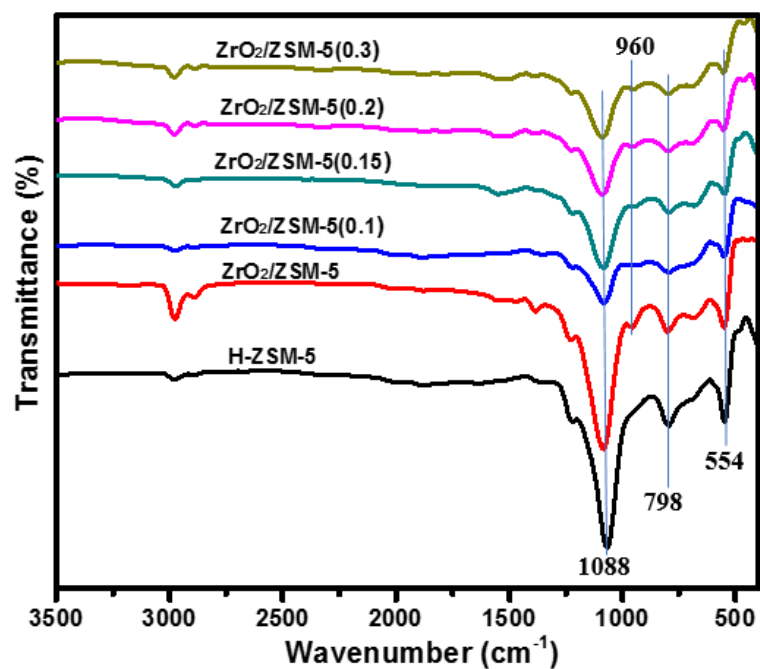
Figure 5.1 XRD patterns of H-ZSM-5 and hierarchical $\text{ZrO}_2/\text{ZSM-5}$ catalysts

5.4.2 FTIR analysis

The FTIR spectra of parent ZSM-5 and hierarchical $\text{ZrO}_2/\text{ZSM-5}$ catalysts are depicted in Figure 5.2a. The 549 cm^{-1} intensity band, which shows the parent ZSM-5 structure's five-membered ring pentasil as well as the crystallinity of zeolite, is apparent in all the synthesized catalysts [259]. This indicated that the ZSM-5 crystalline structure remained stable following the desilication treatment and loading of ZrO_2 . The band at 780 cm^{-1} represents the symmetric Si-O-Si stretching in the H-ZSM-5 framework. The external asymmetric stretching (T-O-T bridge, where T is Al or Si) is shown by the intensity bands at 1098 cm^{-1} , which provides more evidence for ZSM-5. It is the ZSM-5 zeolite's structure-sensitive IR band [260-261]. Furthermore, the band at 960 cm^{-1} is related to the Si-O-Zr (stretching mode of the SiO_4 with Zr ions) antisymmetric stretching mode, suggesting that Zr species is incorporated into the zeolite framework [262].

In order to gain an insight into the acid sites of the catalyst, we carried out pyridine-adsorbed FTIR analysis of H-ZSM-5, $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalysts at $150\text{ }^\circ\text{C}$. The catalyst's acid sites aid in metal dispersion [263]. According to the literature, the 1582 cm^{-1} intensity band is often associated with free pyridine, and a Lewis acid site is indicated by a shift to $1590\text{-}1630\text{ cm}^{-1}$ [263-264]. At a frequency of 1540 cm^{-1} , Brønsted acid site due to pyridine is observed [264]. Figure 5.2b shows the pyridine-FTIR spectra of H-ZSM-5, $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalysts. The intensity of the band at 1450 and 1630 cm^{-1} are characteristic peaks attributed to the pyridine ions coordinated to Lewis acid site (L) and the adsorption band at 1540 cm^{-1} can be attributed to pyridine interaction with Brønsted acid sites (B). The band at 1630 cm^{-1} suggests pyridine ion adsorbed on both L and B (Fig. 5.2b), which is consistent with the work performed by Abdulkadir et al [265]. After desilication, the amount of Lewis acid sites increases, while the Brønsted acid site is essentially unaffected by the desilication process. Due to the protrusion of some Si-OH-Al groups into mesopores, Brønsted acid sites cannot be identified with Si-OH-Al groups, according to reported studies [266-268]. Moreover, all aluminum atoms in desilicated zeolites can form protonic sites, but during the activation process, some of them dehydroxylated, which results in the formation of Lewis acid sites: one protonic site was turned into one Lewis site [267-268].

(a)



(b)

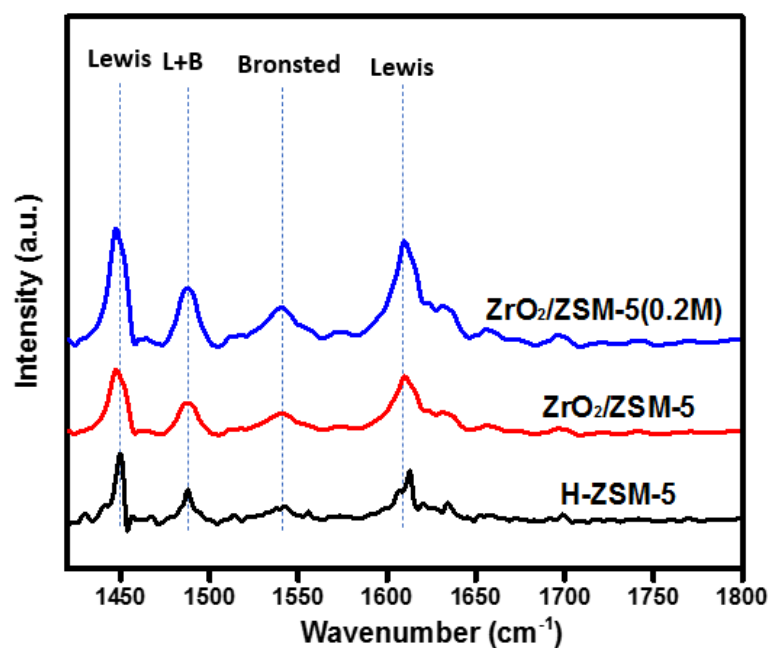


Figure 5.2 FTIR spectra of (a) the H-ZSM-5 and hierarchical ZrO₂/ZSM-5 catalysts and pyridine-FTIR spectra; and (b) the H-ZSM-5, ZrO₂/ZSM-5 and ZrO₂/ZSM-5(0.2M).

5.4.3 Nitrogen adsorption-desorption isotherms studies

Nitrogen adsorption-desorption isotherms of parent ZSM-5 and hierarchical $\text{ZrO}_2/\text{ZSM-5}$ catalysts are presented in Figure 5.3. The textual properties of the materials are depicted in Table 5.1. The parent ZSM-5 zeolite support displayed type-IV isotherm characteristics (Fig. 5.3), which are often produced by mesoporous materials according to IUPAC classification [269]. A Type I isotherm was produced after loading the catalyst onto the parent ZSM-5 ($\text{ZrO}_2/\text{ZSM-5}$). This means that $\text{ZrO}_2/\text{ZSM-5}$ catalyst has low proportion of mesopores and extremely fine micropores, based on the IUPAC classification (Table 5.1). However, following the loading of the catalyst on the desilicated zeolite support (desilication using different NaOH concentrations), the type-IV isotherm nature remained unchanged. The desilication involves the extraction of silicon atoms from the zeolite framework, which incorporates mesoporosity [270]. The desilication process increased the mesopore surface area compared to the parent zeolite, as shown in the Table 5.1. The formation of the mesopore system in zeolite grains increases the mesopore surface area (S_{meso}), which reaches a high value of $275.02 \text{ m}^2/\text{g}$ compared to $197.49 \text{ m}^2/\text{g}$ for the parent ZSM-5. It is notable that the S_{meso} increased when the concentrations of NaOH increased up to 0.2 M NaOH, but thereafter decreased. This is probably due to collapse in the mesopore walls (due to framework rearrangement), which increases mesoporosity [271]. The desilication process has an impact on the micropore volume as well. As previously stated, the desilicated zeolites' structure was retained, however, the crystallinity has decreased marginally. As a result, the observed decrease in micropore volume is most likely caused by the existence of extra framework material within the channels of zeolite and a decrease in crystallinity. The decrease in the pore volume and specific surface area (decreased by 10.34%, 11.33%, 0.59%, and 28.53% relative to parent ZSM-5 following desilication using NaOH concentrations of 0.1 M, 0.15 M, 0.2 M, and 0.3 M, respectively, and ZrO_2 loading of 10 wt.%) of the desilicated zeolite-supported catalysts may be attributed to the decrease in catalysts zeolite content (reduction to 90%). The reduction could also be attributed to pore blockage caused by metal oxide loading on the zeolite support. In the case of the $\text{ZrO}_2/\text{ZSM-5}$ catalyst, a similar drop in pore volume and specific surface area (decreased by 11.12% after the ZrO_2 loading) was found. The catalyst can be found on the zeolite supports external surface. As a result, the decrease in the zeolite

support surface area is irrelevant here because the primary function of the zeolite is to prevent ZrO_2 particles from leaching by holding the ZrO_2 particles. The catalysts and zeolite support pore sizes are essentially unchanged. Table 5.1 further illustrates that desilication changed the elemental composition when compared with parent ZSM-5 zeolite. The Si/Al ratio of parent ZSM-5 decreased upon treatment with different concentrations of sodium hydroxide solution (Table 5.1).

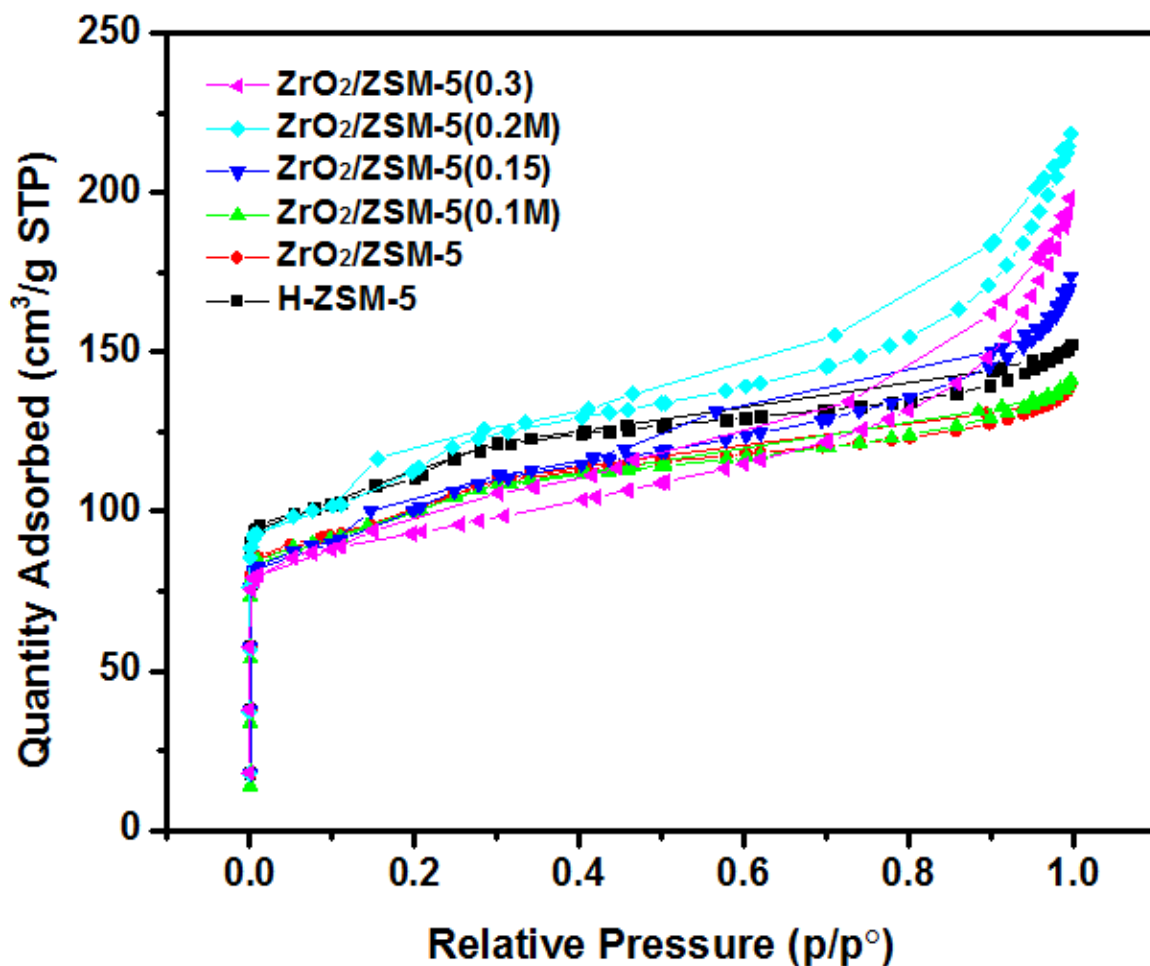


Figure 5.3 N_2 adsorption/desorption isotherms of H-ZSM-5 and hierarchical $\text{ZrO}_2/\text{ZSM-5}$ catalysts

Table 5.1. Textural properties of parent ZSM-5 and hierarchical ZrO₂/ZSM-5 catalysts

Sample	S _{BET} (m ² /g)	S _{micro} (m ² /g)	S _{meso} (m ² /g)	V _{micro} (cm ³ /g)	V _{total} (cm ³ /g)	PS (nm)	Si/A I ^a	Zr ^a (wt. %)
H-ZSM-5	389.63	192.14	197.49	0.09	0.22	3.2 2	72	-
ZrO ₂ /ZSM-5	346.07	185.87	160.20	0.08	0.20	3.29	68	9.45
ZrO ₂ /ZSM-5 (0.1M)	345.35	153.13	192.22	0.07	0.23	3.86	62	9.24
ZrO ₂ /ZSM-5(0.15M)	349.50	110.27	239.23	0.05	0.23	4.00	58	9.32
ZrO ₂ /ZSM-5(0.2M)	387.32	112.30	275.02	0.04	0.29	4.63	55	9.41
ZrO ₂ /ZSM-5(0.3M)	278.46	109.48	168.97	0.09	0.21	5.03	51	9.82

^aXRF analysis

5.4.4 Thermogravimetric analysis

The thermal stabilities of the parent ZSM-5, $\text{ZrO}_2/\text{ZSM-5}$, and $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ samples were determined by thermogravimetric analysis (Figure 5.4). The parent and modified ZSM-5 samples displayed no decomposition and about 1.5% weight loss was observed at 100 °C. The desorption of physically adsorbed water molecules is responsible for this weight loss. The result also indicated that the thermal stability of parent ZSM-5 remains intact following the desilication by alkaline treatment and loading of ZrO_2 .

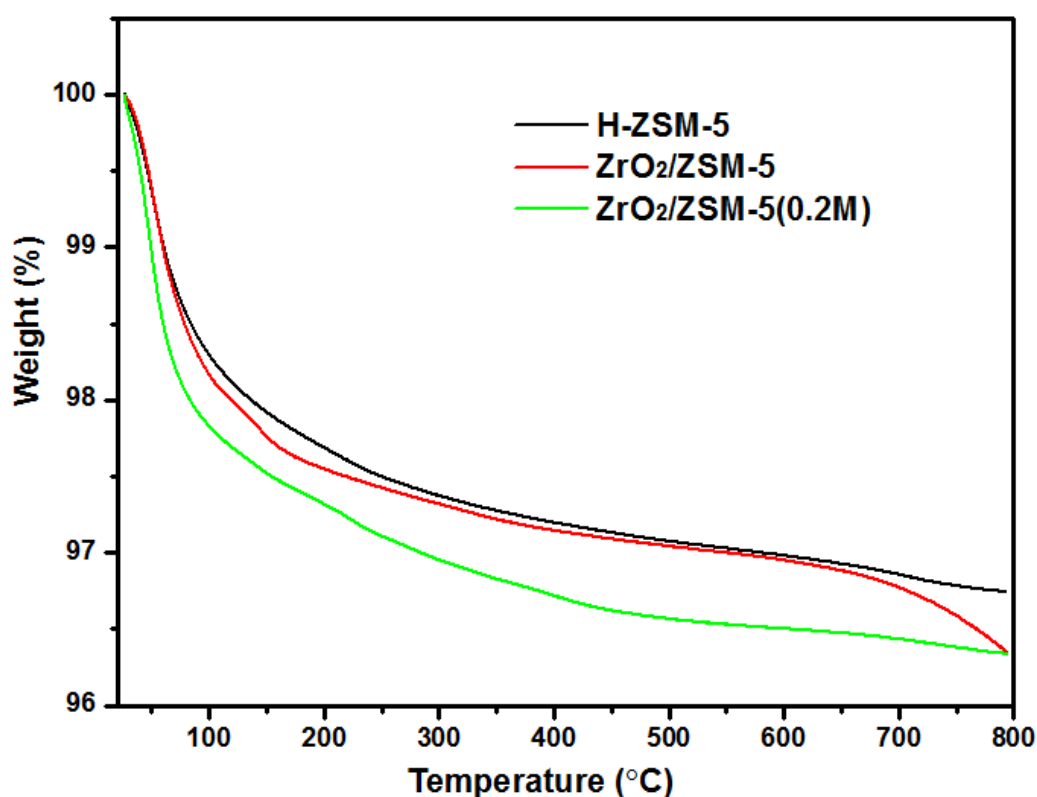


Figure 5.4 TGA curves of H-ZSM-5, $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ samples.

5.4.5 SEM and TEM studies

The surface morphology of the materials was determined by scanning electron microscope. The SEM images of zeolite supports (ZSM-5) and the synthesized catalysts $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}$ (0.2 M) were depicted in Figure 5.5a,b,c, respectively. The SEM study revealed that the zeolite particles had no uniform morphologies, and the distribution of the particle sizes was large. These results show that there are no substantial changes in the form or size of the grains after desilication process and loading of ZrO_2 (Fig.5.5b,c).

The TEM analysis of the synthesized catalysts $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}$ (0.2 M) are shown in Figure 5.5d,e, correspondingly. The catalyst morphology, metal dispersion, and particle size of Zr on the zeolite support were studied using TEM. The TEM image of $\text{ZrO}_2/\text{ZSM-5}$ is depicted in Fig. 5.5d. The ZrO_2 was consistently dispersed on the zeolites' surfaces. High magnification of the calculated particle size dispersion of Zr on ZSM-5 (Fig. 5.5d) reveals that the average particle size is 4.19 nm (Fig. 5.5d inset). The average pore size of zeolite (3.22 nm, according to BET analyses Table 5.1) was smaller than the ZrO_2 particles; therefore, the majority of ZrO_2 was deposited on the zeolite's surface. In the case of $\text{ZrO}_2/\text{ZSM-5}$ (0.2 M), a comparable dispersion of ZrO_2 over desilicated zeolite was found (Fig. 5.5e). The particle size of ZrO_2 was 1.91 – 7.85 nm, with particle size of 3.85 nm on average, as shown by the histogram in Fig. 5.5e inset. Moreover, the arrangement of Zr on the desilicated zeolite support without particle agglomeration demonstrated that high specific surface area and porosity were retained following Zr integration, as indicated by N_2 -sorption studies.

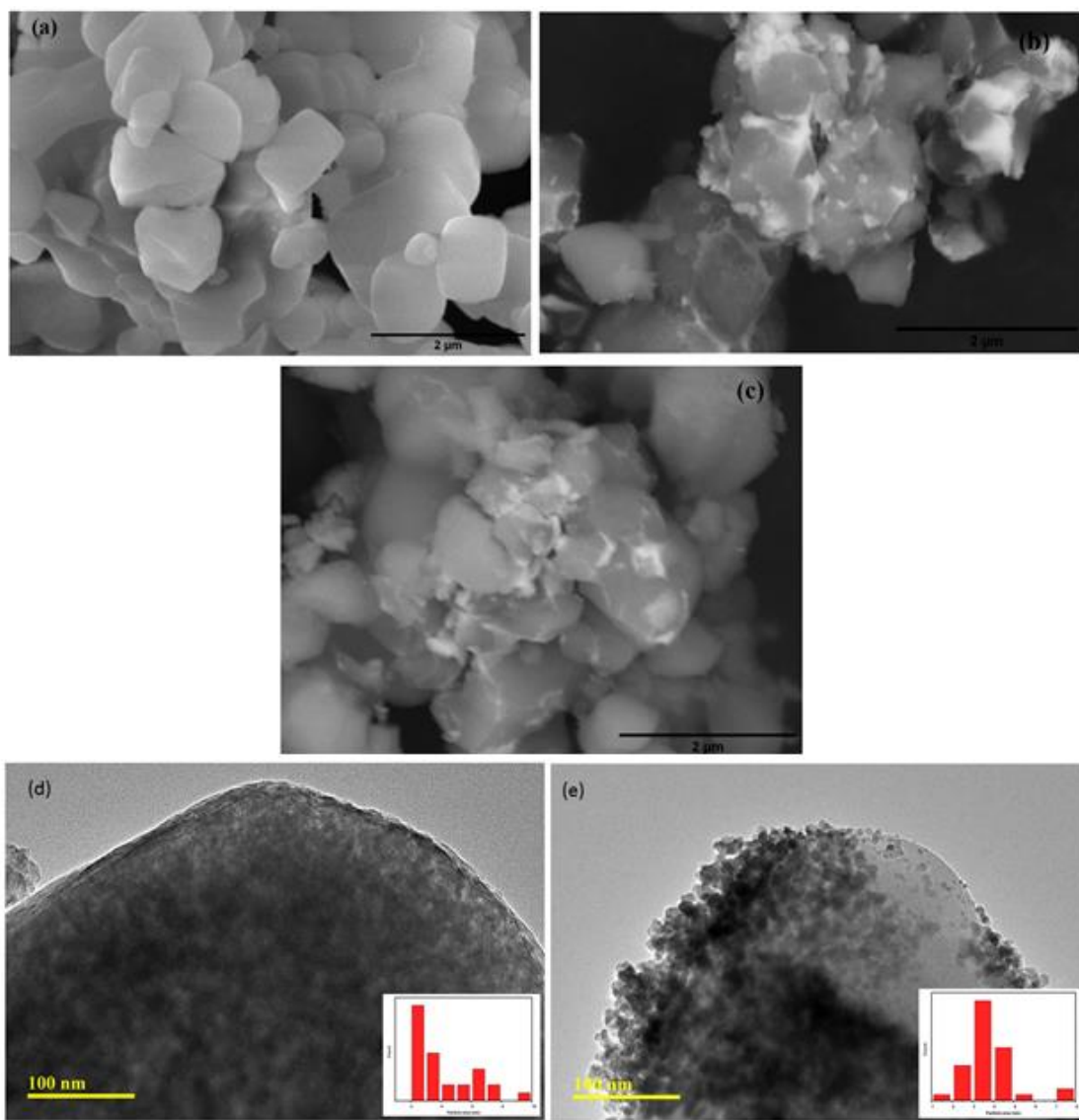


Figure 5.5. SEM images (a-c) represent the H-ZSM-5, ZrO₂/ZSM-5, and ZrO₂/ZSM-5(0.2M) and TEM (d-e) images of ZrO₂/ZSM-5, and ZrO₂/ZSM-5(0.2M)

5.4.6 Catalytic investigation

The performance of the synthesized catalysts was investigated for the methanolysis of soybean oil for biodiesel production. A series of desilicated zeolite-supported ZrO_2 catalysts were evaluated at fixed process parameters such as reaction time of 2 hours, catalyst loading of 0.75 wt%, and oil/methanol molar ratio of 1:8 at 200 °C. Figure 5.6 depicts the trend of biodiesel conversion when employing various synthesized catalysts. When the concentration of NaOH solution was increased (alkaline treatment), it was found that the conversion of biodiesel increased; however, from the textural properties, it was found that the pore volume and surface area increased, allowing for facile adsorption of reactant molecules to the catalyst. Notwithstanding, as shown in Figure 5.6, increasing the concentration of NaOH solution beyond a certain limit reduces biodiesel conversion. This may be due to the poor mass transfer of reactants and products. Mild desilication of ZSM-5 has been reported to have no noticeable impact on crystallinity (using 0.10 and 0.20 M NaOH) [256,368]. Nevertheless, the catalyst activity increases from 0.10 and 0.2 M NaOH (60 to 72%) but reduces at 0.3 M NaOH concentration to 70%. The improved active site could be ascribed to the specific surface area and mesopore surface area enhancements (Table 1). The increase in surface area from 345.35 to 387.32 m^2/g and the increase in mesoporous external surface area of these materials from 192.22 to 275.02 m^2/g (Table 5.1) show that active site has been improved, which enhances the product's transport outside of their channels and accelerate the reaction. It can also be concluded that the high activity of $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ is due to the fact that it provides an optimum number of active sites for transesterification. Therefore, $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalyst was further examined for biodiesel production, and the process was optimized for process conditions. The process variable selected for optimization includes methanol to oil molar ratio, catalyst loading, time, and temperature. The $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalyst was further compared with the parent zeolite supported ZrO_2 catalyst.

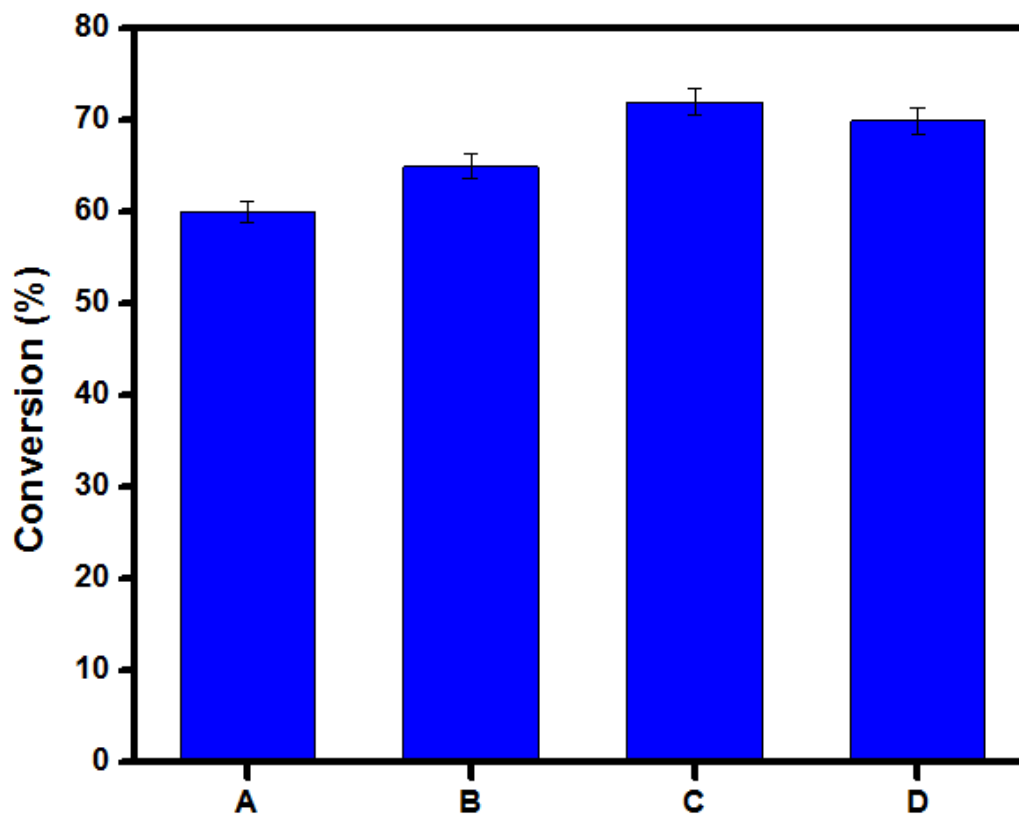


Figure 5.6 Catalyst evaluation for the production of biodiesel through transesterification of soybean oil in the presence of desilicated zeolite supported ZrO_2 catalysts [A = $\text{ZrO}_2/\text{ZSM-5}(0.1\text{M})$, B = $\text{ZrO}_2/\text{ZSM-5}(0.15\text{M})$, C = $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ and D = $\text{ZrO}_2/\text{ZSM-5}(0.3\text{M})$]

5.4.7 Characterization of fatty acid methyl esters

Soybean oil was transesterified with methanol in the presence of $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalyst to examine the catalytic activity in the production of biodiesel. The composition of the biodiesel obtained from the transesterification of soybean oil with methanol was determined using gas chromatography. Figure A.5 depicts a GC-MS measurement of soybean oil biodiesel using $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalyst. Table A.2 describes the FAME profile of the sample (validated using the National Institute of Standards and Technology mass spectral library). ^1H and ^{13}C NMR spectroscopic methods were used to analyze the products to estimate the conversion of soybean oil with $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalysts. The ^{13}C and ^1H NMR spectra of the sample obtained after transesterifying soybean oil with $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalyst are shown in Figure A.6a,b. The presence of FAME was confirmed using the NMR spectrum. Using the results of ^1H NMR analysis, the conversion of soybean oil to FAME was estimated to be 97.84% (according to equation 3.1). The peak areas of methylene group (A_{CH_2}) and the methoxy group (A_{ME}) of the FAME were explicit in the ^1H NMR spectrum, with signals at 2.28 ppm and 3.64 ppm, respectively. Furthermore, these signals correspond to methyl ester in the biodiesel product. In addition to the signals used to calculate the fatty acid methyl ester %conversion, there were other signals such as 0.87 ppm for end of chain aliphatic methyl group ($-\text{CH}_3$). The presence of methylene group ($-\text{CH}_2-$) adjacent to the double bond and olefinic group ($-\text{CH}=\text{CH}-$) were indicated by signals at 2.02 and 5.34 ppm, correspondingly [272–276]. The ^{13}C NMR spectra confirmed the presence of methyl ester carbon ($\text{CH}_3\text{-O-}$) and ester carbonyl ($-\text{COO-}$) at 51.3 and 174.2 ppm, respectively. The signals for the unsaturated fatty acid appear at 129.6 ppm and 127.8 ppm. The presence of aliphatic methylene ($-\text{CH}_2-$) carbons is supported by the signal in the region of 27.15–34.05 ppm. Aside from these signals, the end of chain methyl ($-\text{CH}_3$) carbon signal is at 14.05 ppm [272,276–277].

Table 5.2 shows the fuel properties of the biodiesel that was produced along with a comparison to the ASTM D6751 standard. These properties conform to the quality requirements recommended by ASTM D6751, which suggests that the as-produced biodiesel could be used as either a neat fuel or blended with petroleum diesel.

Table 5.2**The properties of the biodiesel in comparison with the ASTM standards**

Fuel properties	ASTM method used	ASTM D6751 Biodiesel	Prepared biodiesel
Kinematic viscosity (40 °C, mm ² /s)	D445	1.9-6.0	5.02
Density (40 °C, g/cm ³)	D5002	0.86-0.90	0.872
Specific gravity (40 °C, g/cm ³)	D287	0.88	0.878
Flash point (°C)	D93	100-170	130
Acid value (mg KOH/g)	D664	0.5	0.06

5.4.8 Effect of transesterification conditions

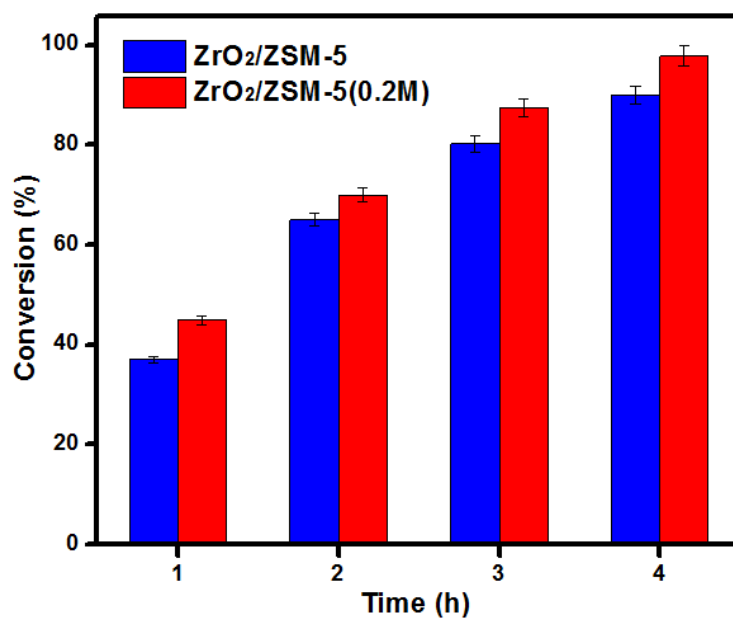
The effect of different reaction conditions on soybean oil conversion was investigated using ZrO₂/ZSM-5 and ZrO₂/ZSM-5(0.2M) catalysts. Temperature, soybean oil/methanol molar ratio, time, and catalyst loading were the reaction conditions. The optimal conditions for the transesterification reaction were determined, and the findings are depicted in Figures 5.7 and 5.8.

A. Influence of time and temperature on transesterification reaction

The effect of reaction time as an operating condition for methyl esters production was examined at 200 °C with soybean oil/methanol molar ratio of 1:16, and catalyst loading of 1.0 wt%. Figure 5.7a illustrates biodiesel production over time. Soybean oil methyl ester conversion was investigated from 1 to 4 hours. As illustrated in Figure 5.7a, the conversion of soybean oil increases with time. When the time was raised to 4 hours, the conversion of soybean oil increased to 90% for $\text{ZrO}_2/\text{ZSM-5}$ and 97.84% for $\text{ZrO}_2/\text{ZSM-5(0.2M)}$, correspondingly, and attained its optimum reaction time. In a study that was quite similar to this one, which was conducted by Wang et al, the best reaction time was shown to be 4 hours [278]. The activity of $\text{ZrO}_2/\text{ZSM-5(0.2M)}$ catalyst was significantly higher than $\text{ZrO}_2/\text{ZSM-5}$ catalyst, and these remarkable results could be attributed to the fact that the desilicated zeolite support offers the active species with increased pores and mesoporous external surface area in which they could attach and react with bulky triglycerides. Therefore, it is suggested that the reaction time of 4 hours is sufficient (optimal condition) for the production of soybean oil biodiesel and was employed for further investigations in this study.

The effect of reaction temperature as a process parameter on the conversion of biodiesel was investigated using $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5(0.2M)}$ catalysts (Figure 5.7b). The transesterification conversion process was conducted at 180, 200, and 220 °C for 4 hours with a molar ratio of 1:16 and a catalyst loading of 1.0 wt%. Figure 5.7b showed that the transesterification conversion is accelerated as the temperature rises, with an optimal conversion of 97.8% for the $\text{ZrO}_2/\text{ZSM-5(0.2M)}$ catalyst at 200 °C. The soybean oil conversion is lower at 180 °C compared to 200 °C, but the conversion is unchanged on further temperature increases to 220 °C. Therefore, the optimum reaction temperature in the present study for biodiesel production is 200 °C.

(a)



(b)

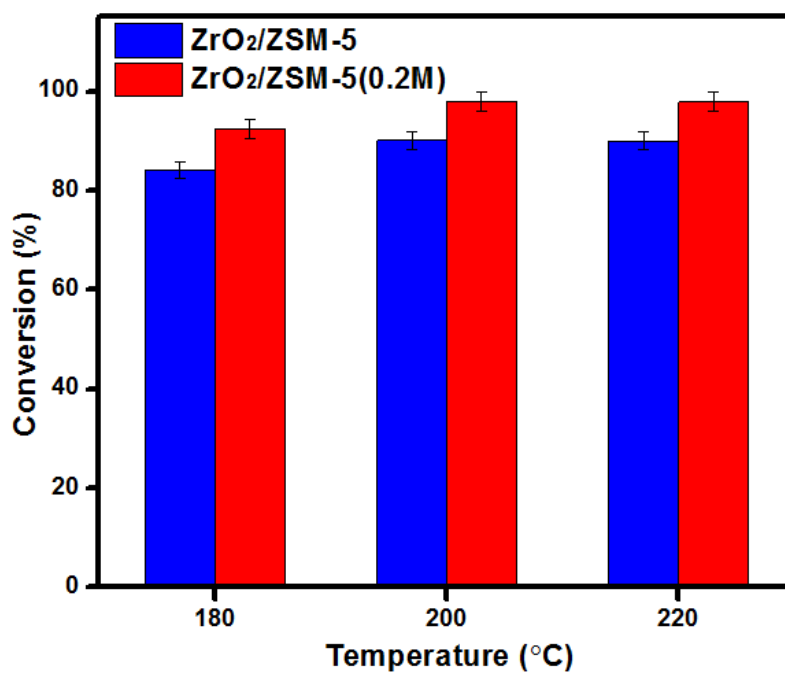


Figure 5.7 (a) Influence of reaction time (b) Influence of reaction temperature

B. Influence of molar ratio and catalyst loading on transesterification reaction

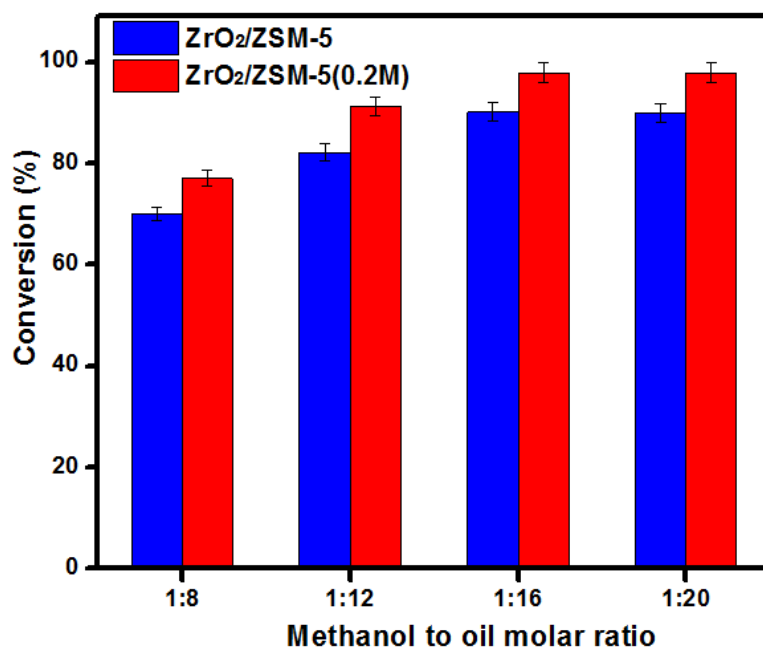
One of the crucial parameters influencing methyl ester conversion is the oil to methanol molar ratio. The influence of soybean oil/ methanol molar ratio was examined by using $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalysts (with a catalyst loading of 1.0 wt% at 200 °C for 4 h). The molar ratio was varied between 1:8 to 1:20. The conversion of soybean oil is low when the molar ratio is 1:8 (70.1% and 77.0% for $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$, respectively). However, the conversion of soybean oil increases due to an increase in the oil/methanol molar ratio from 1:8 to 1:16 (Figure 5.8a). This suggests that the equilibrium will shift to the product side due to the excess methanol. Aside from the excess reactant shifting the equilibrium, the active site's availability may be responsible for the increased conversion rate. When the soybean oil/methanol molar ratio rose to 1:16, soybean oil conversion increased to 90.1% and 97.8% for $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$, respectively. Subsequently, when the molar ratio is raised to 1:20, the soybean oil conversion remains nearly constant. Therefore, the ratio 1:16 was chosen as the optimal soybean oil/methanol molar ratio. Increase in the molar ratio beyond their optimum conditions has no effect on the conversion and may incur additional costs and energy requirements of the process. Also, a large excess of methanol can enhance the solubility of glycerol in the FAME-rich phase, which could adversely affect the purity final biodiesel product [114].

Another important factor that influences methyl ester yield is catalyst loading. The influence of catalyst loading on soybean oil transesterification was evaluated under optimal reaction conditions of 1:16 soybean oil/methanol molar ratio at 200 °C and 4 h. Figure 5.8b illustrates the influence of catalyst loading. When the catalyst loading is increased from 0.75 wt% to 1.25 wt%, the conversion increases from 82.2% to 90.02% for $\text{ZrO}_2/\text{ZSM-5}$ catalyst, and the conversion increases from 90.09% to 97.84% for $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$. There may be insufficient active sites for the reaction at low catalyst loading, necessitating the use of more catalysts. However, when the catalyst loading was increased from 1.0 wt% to 1.25 wt%, there was no improvement in conversion, perhaps due to the mixing problem involving catalyst, products, and reactants [114]. Biodiesel conversion decreased as catalyst loading increased to 1.25 wt% because of the formation of thick slurries that

inhibited the reaction. These thick slurries decreased the biodiesel conversion because of the difficulty in adequate mixing of the methanol, oil, and catalyst. Finally, in this study we conclude that 1.0 wt% catalyst loading is sufficient for the production of soybean oil biodiesel.

A blank experiment (catalyst-free) was carried out and the conversion is very low (<20%), which is not appreciable and cost-effective. Also, when ZSM-5 was used only, the conversion was 45%, and this shows that zeolite desilication and incorporation of ZrO₂, which improves the acidity and characteristics properties exhibited high catalytic performance.

(a)



(b)

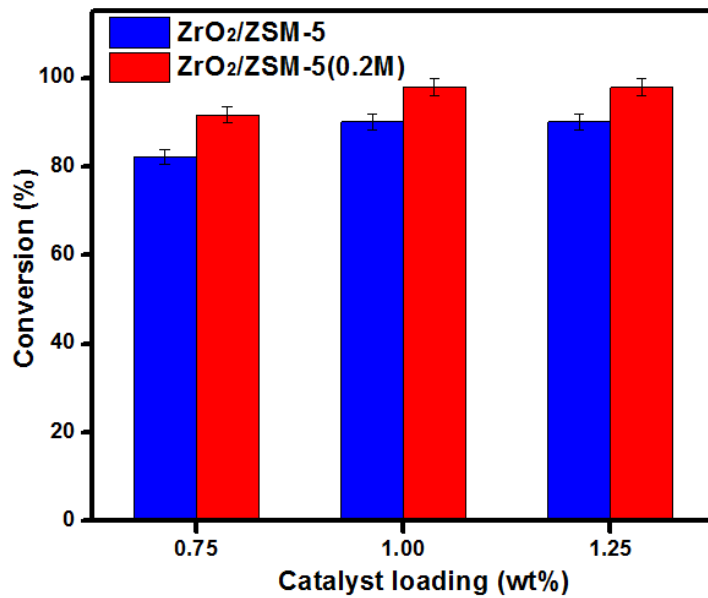


Figure 5.8 (a) Influence of soybean oil-to-methanol molar ratio (b) Influence of catalyst loading

5.4.9 Plausible mechanism for transesterification

A plausible mechanism for transesterification reactions is depicted in Figure 5.9. Generally, the carbonyl oxygen of the vegetable oils is adsorbed on the acid site of the catalyst to form the protonated carbonyl group. This protonated carbonyl group is subsequently attacked by the nucleophilic oxygen atom from methanol hydroxyl group, generating a new C-O bond (tetrahedral intermediate). The tetrahedral intermediate then rearranges, and the glycerol molecule (by-product of transesterification reaction) was eliminated to produce a fatty acid methyl ester. Finally, the produced fatty acid methyl ester detached from the surface of the catalyst via electron delocalization at the oxygen atom, where fatty acid methyl esters are collected as the main product. After the catalytic process was completed, the active species of the deprotonated catalyst is regenerated for another catalytic cycle.

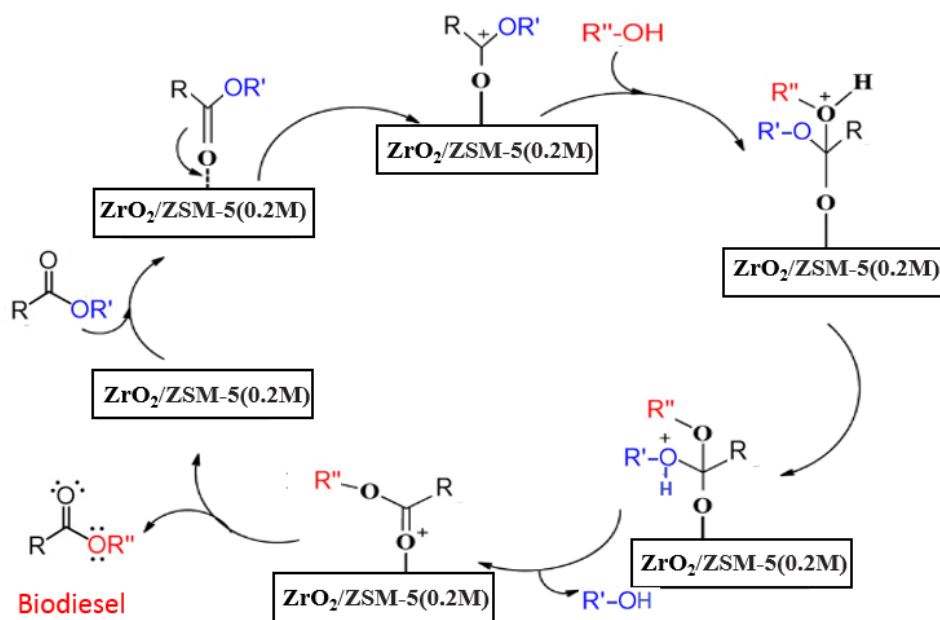


Figure 5.9 Plausible mechanism of transesterification.

5.4.10 Catalyst reusability

The reusability nature of heterogeneous solid catalysts is one of their most important features. In the present work, the $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5(0.2M)}$ catalysts were immediately recovered after the reaction has completed by centrifugation, methanol-washing, oven drying, and finally utilized following every cycle. The catalysts ($\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5(0.2M)}$) were tested for four cycles continuously at 1.0 wt% catalyst loading, 1:16 soybean oil/methanol molar ratio at 200 °C for 4 h. Figure 5.10 illustrates the plot of soybean oil conversion in each cycle the catalysts were reused. According to these results, the catalysts remained active after three cycles of the transesterification process. Beyond that, the catalytic activity reduced drastically so that in the sixth cycle the soybean oil conversion was 65.25% and 78.3% for $\text{ZrO}_2/\text{ZSM-5}$ and $\text{ZrO}_2/\text{ZSM-5(0.2M)}$ catalysts, correspondingly. To evaluate the activity of mild deactivation, XRD analysis was utilized to determine the catalyst stability. The XRD pattern of the spent catalyst after the six cycles was almost similar to the fresh catalyst (Figure A.7). This shows that the material structure remained stable after repeated uses. However, soybean oil conversion decreased slightly with each reuse of the catalysts, which could be attributed to the fact that part of the active component is being leached as a result of multiple reactions and surface poisoning by the triglyceride. The Zr contents were determined using XRF. The result (XRF analysis) indicates that the Zr contents of the fresh catalyst $\text{ZrO}_2/\text{ZSM-5(0.2M)}$ and the used catalyst after the four cycles were 9.41 wt.% and 5.8 wt.%, respectively. Thus, this confirms that part of the active component is being leached in the course of multiple catalytic runs.

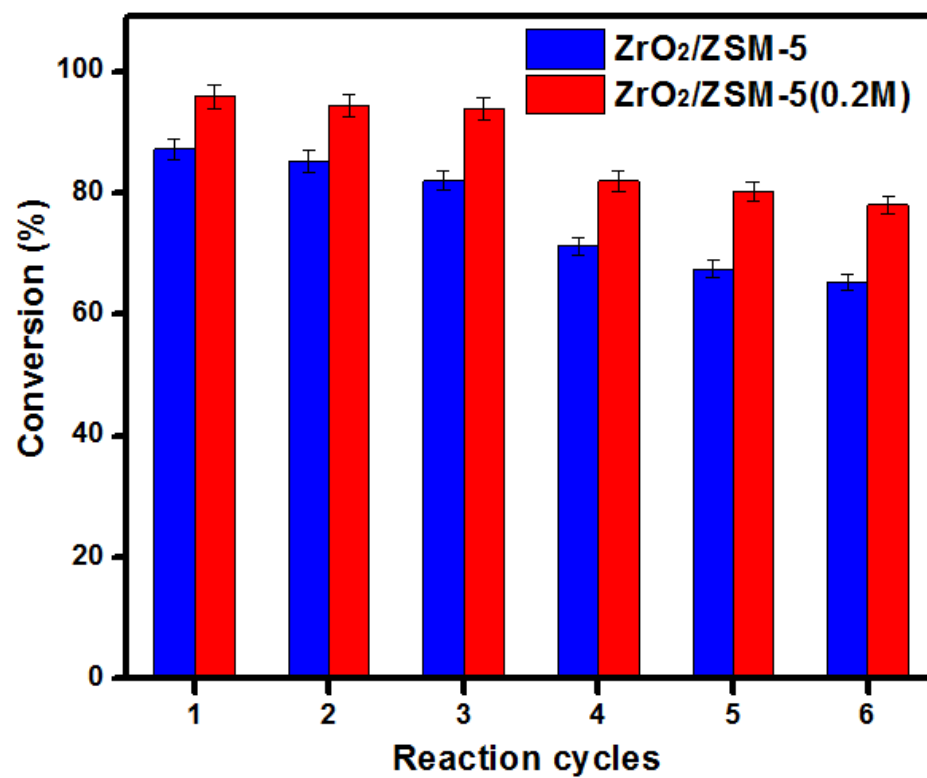


Figure 5.10 Reusability of the ZrO₂/ZSM-5 and ZrO₂/ZSM-5(0.2M) catalysts for four cycles under optimal transesterification conditions (T = 200 °C, t = 4 hours, 0.4 g catalyst loading, and 1:16 molar ratio).

5.4.11 Comparison with other heterogeneous catalysts for soybean oil biodiesel

The performance of our catalyst is compared to those of previously published heterogeneous catalysts for soybean oil biodiesel in terms of the optimum achievable conversion capacity as highlighted in Table 5.3. It follows that when soybean oil was utilized as a feedstock, our catalyst's activity is comparable to many catalysts reported in the literature and thus these zeolite-supported catalysts possess great potential in biodiesel production.

Table 5.3. Activity of different heterogeneous catalysts used to produce soybean oil biodiesel

Catalyst	Operating conditions ^a	Performance	Reference
Li ₂ TiO ₃	2 h, 65 °C, 6 wt.%, 24:1	98.5% oil conversion	[114]
La/zeolite beta	4 h, 160 °C, 14.5:1	48.9% oil conversion	[278]
Reduced graphene oxide	3 h, 80 °C, 3 wt.%, 20:1	99% FAME yield	[279]
PbO	2 h, 215 °C, 7:1	89% FAME yield	[203]
Fe ₃ O ₄ /SiO ₂	6 h, 120 °C, 9 wt.%, 35:1	93.3% oil conversion	[225]
basic ETS-10	3h, 100 °C, 10 wt.%, 6:1	92% oil conversion	[280]
tungstated zirconia-alumina	20 h, 250-300 °C, 40:1	>90% conversion	[281]
KF/ZnO	9 h, 65 °C, 10:1	87% oil conversion	[227]

ZrO ₂ /ZSM-5(0.2M)	4 h, 200 °C, 1.0 wt.%, 16:1	97.84% conversion	This work
ZrO ₂ /ZSM-5	4 h, 200 °C, 1.0 wt.%, 16:1	90.1% conversion	This work

^aThe operating conditions include reaction time, temperature, catalyst loading (in some cases), and alcohol to oil molar ratio.

5.5 Conclusion

Desilication of parent ZSM-5 zeolite at various sodium hydroxide concentrations increased the mesoporous external surface area, mesoporous volume, acidity, and degree of dispersion of ZrO₂ while preserving the crystallinity and microporous volume. Biodiesel conversion was better over Zr-impregnated desilicated ZSM-5 zeolites when compared to Zr-impregnated parent zeolite catalyst. The improved textural properties of the desilicated ZrO₂/ZSM-5(0.2M) catalyst resulted in better performance. The prepared catalysts are suitable for the catalytic transesterification of soybean oil with methanol. A high conversion of 97.84% was achieved using the ZrO₂/ZSM-5(0.2M) catalyst under the optimum transesterification reaction conditions of 1.0 wt% catalyst loading, 1:16 soybean oil/methanol molar ratio, 4 h and 200 °C. Furthermore, the ZrO₂/ZSM-5(0.2M) catalyst can be recovered and recycled for three consecutive runs with no significant loss in catalytic activity. So, the Zr-impregnated desilicated ZSM-5 zeolites catalyst presents enhanced activity and higher biodiesel conversion than the Zr-impregnated parent zeolite catalyst, and they can still be efficiently regenerated. We conclude that desilicated ZSM-5 zeolite is a better catalyst support for the conversion of soybean oil to biodiesel. The potential of these catalysts is comparable to many catalysts previously reported in the literature and may add to the economic advantages of biodiesel production.

CHAPTER 6

Synthesis and evaluation of Cu/UiO-66 metal-organic frameworks as a solid catalyst for biodiesel production from waste cooking oil

6.1 Abstract

Metal-organic frameworks (MOFs) are excellent options for immobilizing guest active species due to their high surface area, diversified structures, and porosity. In the present study, copper oxide supported on UiO-66 (Cu/UiO-66) has been successfully synthesized by wet impregnation method and was utilized as a solid acid catalyst in the production of biodiesel from waste cooking oil (WCO). The as-synthesized catalysts were characterized utilizing N₂ adsorption-desorption, X-ray diffraction (XRD), temperature-programmed desorption (NH₃-TPD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) analysis to reveal their physical and chemical features. The biodiesel produced was characterized using NMR and GC-MS. The result showed that Cu/UiO-66 displayed high catalytic activity in biodiesel production from WCO due to the appropriate pore size, large specific surface area and the synergistic effect between UiO-66 and copper oxide in the composite. With 7%Cu/UiO-66 catalyst which included a suitable amount of copper oxide (7 wt. %) incorporated into the UiO-66 structure, a high conversion of 90.1% was achieved under optimum conditions of 6 wt% catalyst loading, 20:1 methanol/WCO molar ratio at 160 °C for 4 hours. Moreover, 7%Cu/UiO-66 catalyst displayed good stability and reusability giving a biodiesel conversion of 81.06% after three reuses. Our kinetic investigation showed that the reaction follows a pseudo-first order kinetic, with an activation energy (E_a) of 32.26 kJ/mol, which suggests that the reaction is chemically controlled and not by mass transfer and diffusion constraints.

6.2 Introduction

The depletion of oil reserves, different environmental concerns and the increasing need for energy have prompted the quest for sustainable, environmentally benign alternative energy resources [282]. Biodiesel is considered an alternate fuel among several renewable energy sources that could effectively alleviate the environmental concerns about fossil fuel [283]. Furthermore, biodiesel has numerous benefits over fossil diesel fuel owing to its clean combustion, higher lubricity, biodegradability, nontoxicity, and renewability [283]. Biodiesel is produced by either esterification of free fatty acids (FFAs) or transesterification of triglycerides with methanol by using a suitable catalyst [284]. Biodiesel can be easily obtained from microalgae, animal fats, waste cooking oil (WCO) and vegetable oil [285]. For instance, edible oils like soybean, coconut, and sunflower have been extensively applied as biodiesel feedstock [286]. However, the high cost of these raw materials, as well as its use for food, hinders biodiesel production from them. Therefore, non-edible oils and WCO are favored as raw materials for biodiesel production due to their availability and low-cost [287–289]. Furthermore, using WCO will enhance economic benefits and solve the issues associated with its disposal. Biodiesel is typically formed utilizing homogenous catalysts dissolved in alcohol [46,290-291]. Generally, homogeneous catalysts have the disadvantages of not being reusable and difficulty in separating the catalyst from products after the reaction. In addition, washing of biodiesel to remove dissolved impurities and catalyst residues generates huge amounts of wastewater [291]. These constraints with homogeneous catalysts can be circumvented using heterogeneous catalysts, which can be regenerated and recycled without losing activity [292]. Among the reported heterogeneous catalysts are carbon-based, sulfated zirconia, ion exchange resins, mixed metal oxides, transition metal oxides, heteropolyacids, zeolite, waste material based, Fe_3O_4 @HKUST-1-ABILs and alkaline metal oxides catalysts [64,73,131,236,293-301]. However, in the instance of WCO having a significant amount of FFAs, solid base catalysts react with FFAs to generate soaps, resulting in poor product quality [302]. In such instances, solid acid catalysts are preferred since they prevent saponification. However, the disadvantages of solid acid catalysts include lower conversion, low acidity, high cost, low thermal stability, and poor mass transfer. Previous

studies showed that heteropolyacids could be used as Brønsted solid acid catalysts to produce biodiesel with high conversions [303-304]. Nevertheless, owing to their solubility in polar solvents, pure heteropolyacids are challenging to recover [305]. Heteropolyacids immobilization could be an effective catalytic reaction strategy to circumvent these limitations because the proton exchange of heteropolyacids with different cations leads to insoluble salts. Recently, heteropolyacids-immobilized catalysts for organic reaction were developed using various supports, such as MCM-41, mesoporous polymer of PDVB-VBC, montmorillonite K10 or SiO₂ [306–308]. However, high cost of synthesis, heteropolyacids solubility in polar media and weak heteropolyacids-support interaction make immobilization on the above materials challenging. Thus, developing highly effective immobilized heteropolyacids catalysts for biodiesel production is important.

MOFs have recently emerged as a novel class of materials with high surface area, controllable pore size, tunable composition, easy separation, and flexibility [309-310]. Several features of MOFs have been employed in various sectors, including electronic, separations, optic, and catalysis [311]. Several relatively stable MOFs, such as MIL-101, ZIF-8 and UiO-66 have recently been produced [311–317]. However, some MOFs, such as ZIF-8, quickly decompose in acidic environments, indicating that they are not resistant to acid medium [318]. In contrast, UiO-66 has shown excellent acid resistance (pH 2), high water resistance, relatively high chemical stability and high decomposition temperature due to the Zr's +4 oxidation state, allowing for 12 coordination and stabilizing the framework [314]. UiO-66 metal-organic framework has been employed to support photocatalysts for organic wastewater degrading applications [317,319]. UiO-66's porous crystalline network has an imperfect framework with missing linkers, which induces active defects that aid substrate adsorption and reactant interactions [45]. Due to its reusability, thermal stability, and increased activity, UiO-66 is widely studied as a host matrix [319].

Some research has focused on the production of biodiesel utilizing UiO-66 catalyst [320]. The activity of HSiW-UiO-66 catalysts in the production of biodiesel has also been investigated, whereby an optimum biodiesel conversion of 80.5% was obtained. Bravo Fuchineco et al. [317] synthesized UiO-66(Zr) and UiO-66(Zr)-NH₂ and made use as catalysts for the esterification of levulinic acid for obtaining biodiesel. To the best of our

knowledge, we believe that there is no study on catalytic transesterification of triglycerides for biodiesel production from WCO utilizing Cu-impregnated Zr-based UiO-66 as catalysts. In this work, we prepared a series of Cu supported on a UiO-66 (5-10%Cu/UiO-66) catalysts and utilized those catalysts to produce biodiesel from WCO with methanol. Nitrogen adsorption-desorption, TGA, TEM, NH₃-TPD SEM, XRD, and FTIR were utilized to characterize the synthesized catalysts' textural properties, structural and chemical properties, and to correlate with their performance. Furthermore, the effect of various process parameters, including temperature, reaction time, molar ratio of methanol/WCO, and catalyst loading were studied to optimize the reaction. Finally, the catalyst reusability and reaction kinetic parameters were investigated.

6.3 Materials and methods

Materials used for this section, catalyst preparation procedure, characterization methods, biodiesel production procedure and biodiesel analysis were previously explained in Chapter 3 (sections 3.1, 3.2.3, 3.3, 3.4, 3.5 and 3.6)

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6.4 Results and discussion

6.4.1 XRD analysis

Figure 6.1 depicts the XRD patterns of the UiO-66 support and the catalysts. It is clear that the UiO-66 is highly crystalline. The XRD pattern of the prepared materials coincides with those reported in the literature [320-322]. The typical UiO-66 diffraction peaks at 6–8° are apparent following the copper loading (5%, 7%, and 10%, correspondingly) via impregnation, indicating that the catalyst preparation does not significantly influence support crystallinity. Nevertheless, when the Cu loading increases, the pertinent peak of UiO-66 decreases. The characteristic diffraction peak of copper oxide phase was detected on all Cu/UiO-66 catalysts, which appeared at $2\theta = 38.7^\circ$ and 68.1° represent (111) and (220) planes, correspondingly [310], and its intensity increases with increasing Cu. This indicates successful formation of the crystals.

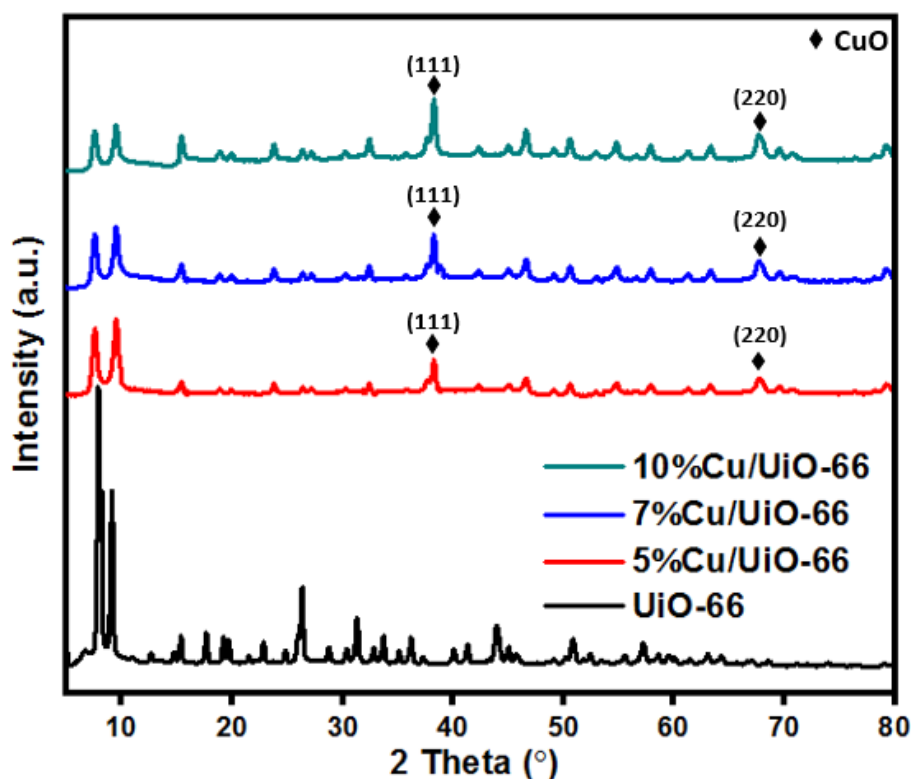


Figure 6.1. XRD patterns of the as-synthesized UiO-66 and Cu-modified UiO-66.

6.4.2 Nitrogen adsorption-desorption isotherms studies

Figure 6.2 depicts the N₂-adsorption/desorption isotherms of the materials. The profile of the UiO-66 exhibits type I adsorption isotherm, indicating the presence of micropores. Despite the different loading of Cu, the profile of all the Cu/UiO-66 catalysts display the type 1 isotherm, suggesting that the structure of UiO-66 support was preserved after the modification. Table 6.1 shows the textual features of the prepared materials. The BET surface area of 1190 m²/g and a pore volume of 0.52 cm³/g of UiO-66 coincides with the literature [323]. The surface area of UiO-66 decreases after Cu loading due to pore blockage caused by Cu deposition on the UiO-66 support. As the Cu loading increases from 5% to 10%, the surface areas of Cu/UiO-66 catalysts drop (Table 6.1). Also, the pore volume of the catalysts decreases compared to the UiO-66 support, showing that the impregnation-reaction approach successfully introduces Cu metal into UiO-66. The pore size of UiO-66 was 4.07 nm. The pore size of Cu/UiO-66 increased with more Cu doping. This may be due to the fracture pores accumulated by Cu, during the Cu self-assembly coating onto the surface of the UiO-66.

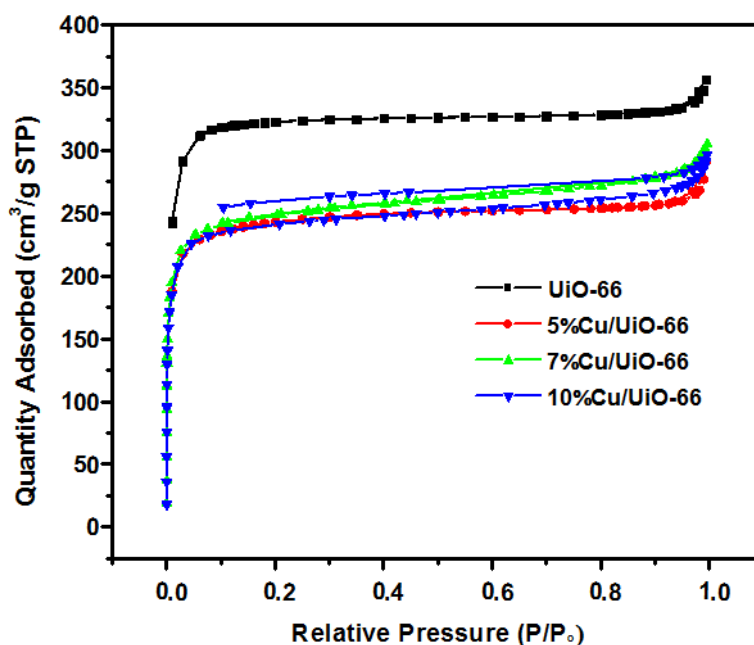


Figure 6.2. N₂ adsorption-desorption analysis of the as-synthesized UiO-66 and Cu-modified UiO-66.

Table 6.1. Textural features of the materials.

Samples	S_{BET} (m^2/g)	V_{total} (cm^3/g)	PS (nm)	Acidity ^a (mmol/g)
UiO-66	1190	0.52	4.07	0.181
5%Cu/UiO-66	878	0.41	5.46	0.185
7%Cu/UiO-66	827	0.43	7.25	0.196
10%Cu/UiO-66	789	0.42	7.20	0.206

^aThe acidity was measured by NH_3 -TPD

6.4.3 FTIR analyses

FTIR spectra of the materials are depicted in Figure 6.3. For UiO-66 support, the BDC ligand's O–C–O symmetric and asymmetric stretching are indicated by the peak intensity at 1395 and 1581 cm^{-1} , correspondingly. The asymmetrical Zr-(OC) asymmetric stretch is attributed to the band at 544 cm^{-1} . The peak intensity around 741 and 660 cm^{-1} are associated with the O-H and C-H vibrations in the BDC ligand. These results coincides with the previous findings [324]. The FTIR spectra of catalysts are comparable to the spectra of the support, confirming that impregnation of Cu species into UiO-66 support has no effect on the framework of the support. Comparatively, the stretching vibration peak at 1660 cm^{-1} was detected on all Cu-UiO-66 catalysts, corresponding to the Cu-O phase [51]. This demonstrates that Cu-impregnated Zr-based UiO-66 catalysts are formed through the covalent bonding of Cu to UiO-66's empty sites [325].

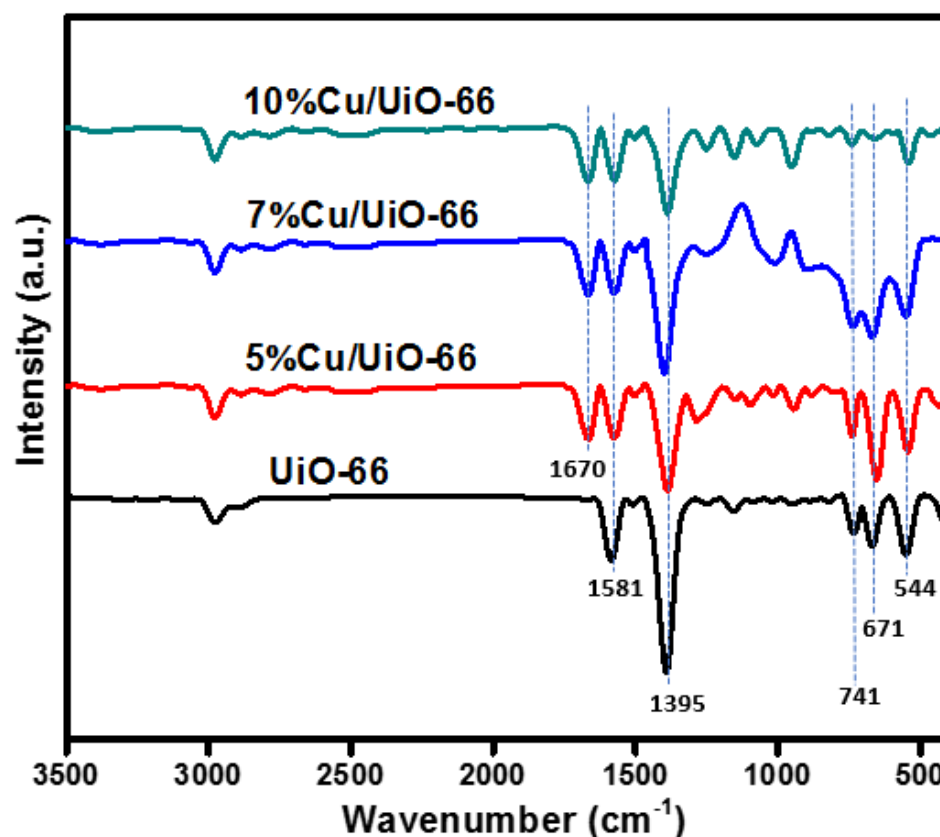


Figure 6.3. FTIR spectra of the as-synthesized UiO-66 and Cu-modified UiO-66.

6.4.4 Thermogravimetric analysis

The thermal stabilities of the 7%Cu/UiO-66 catalyst and UiO-66 support were determined from 50 to 700 °C by thermogravimetric analysis (Figure 6.4). At first, the loss of solvent molecules and physically adsorbed water caused the mass loss up to 300 °C. The mass loss at 300-550 °C is mostly due to the thermal decomposition of organic ligand [228,325]. As depicted in Fig. 6.4, the catalyst exhibits high thermal stability as the main decomposition of the UiO-66 support started at a high temperature, which indicates improved thermal stability of the UiO-66 support. Therefore, the findings show that the synthesized catalyst is thermally stable and can be employed to produce biodiesel.

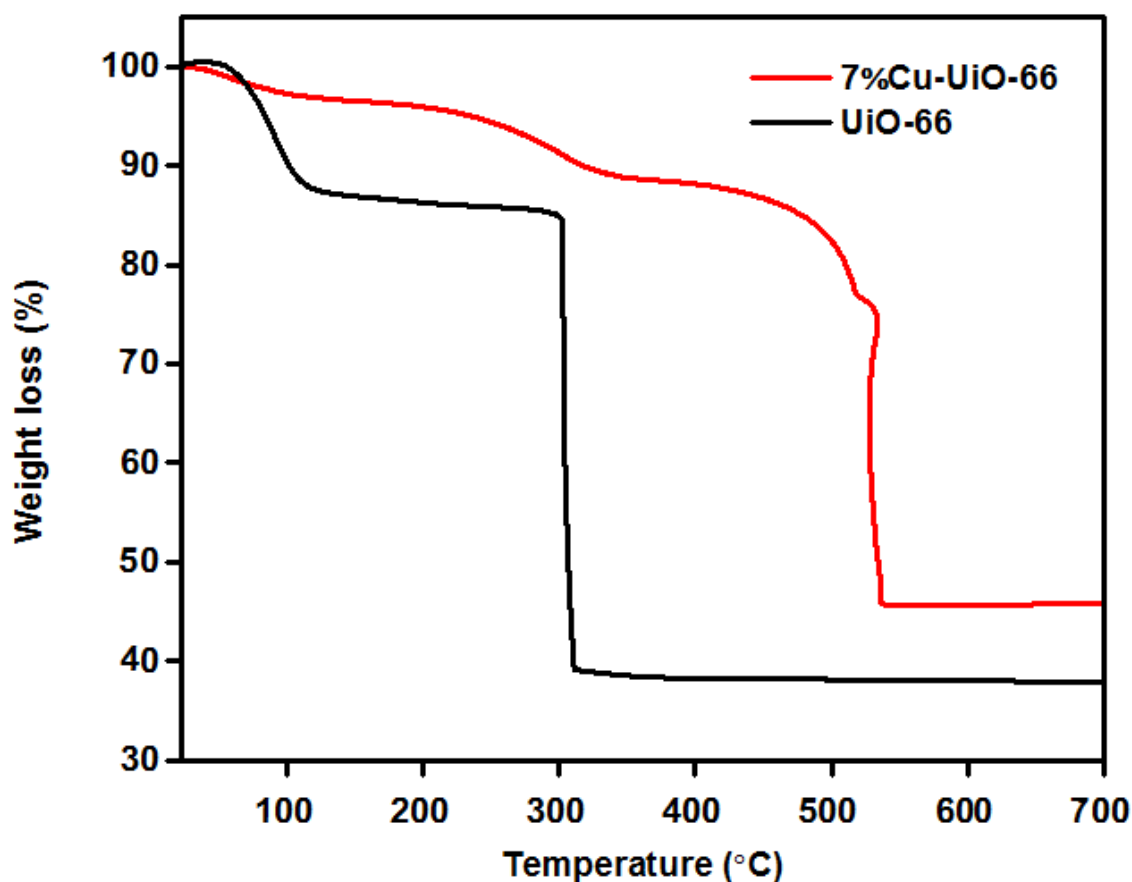


Figure 6.4. TG curve of the as-synthesized UiO-66 and 7%Cu/UiO-66 catalyst.

6.4.5 SEM and TEM studies

SEM images of UiO-66 support and the catalysts are shown in Fig. 6.5. SEM analysis revealed that UiO-66 exhibits uniform octahedral morphology (Figure 6.5a). The morphology is comparable to the findings that were previously reported in the literature [229]. The crystals are uniformly dispersed, and the aggregated crystals are 100-200 nm in size (Fig. 6.5a). After copper oxide had been loaded onto UiO-66 (Cu/UiO-66), there is no substantial change in the shape of the particles (Fig. 6.5b-d). These results suggest that copper oxide particles were uniformly distributed on the surface of the MOF.

TEM was utilized to determine the particle dispersion and particle size distribution of the catalysts. TEM images of the synthesized Cu/Uio-66 catalysts are depicted in Fig. 6.5e-g. As shown, the images indicate that the Cu particles are evenly distributed on the surface of Uio-66. Selected area electron diffraction of the TEM images (Figure 6.5e-g inset) supported the uniform distribution of Cu over Uio-66. The histogram in the Fig. 6.5e-g inset depicts that the estimated particle size of Cu was in the range of 2.5-16 nm, and the average particle size for 5%Cu/Uio-66, 7%Cu/Uio-66 and 10%Cu/Uio-66 were 7.69 nm, 6.44 nm and 6.89 nm, respectively. The Cu particles were larger than the average pore size of Uio-66 (4.07 nm according to BET analyses); thus, a substantial amount of Cu was deposited on the external surface of Uio-66. Moreover, the arrangement of Cu on the Uio-66 without particle agglomeration suggests adequate dispersion of Cu over Uio-66.

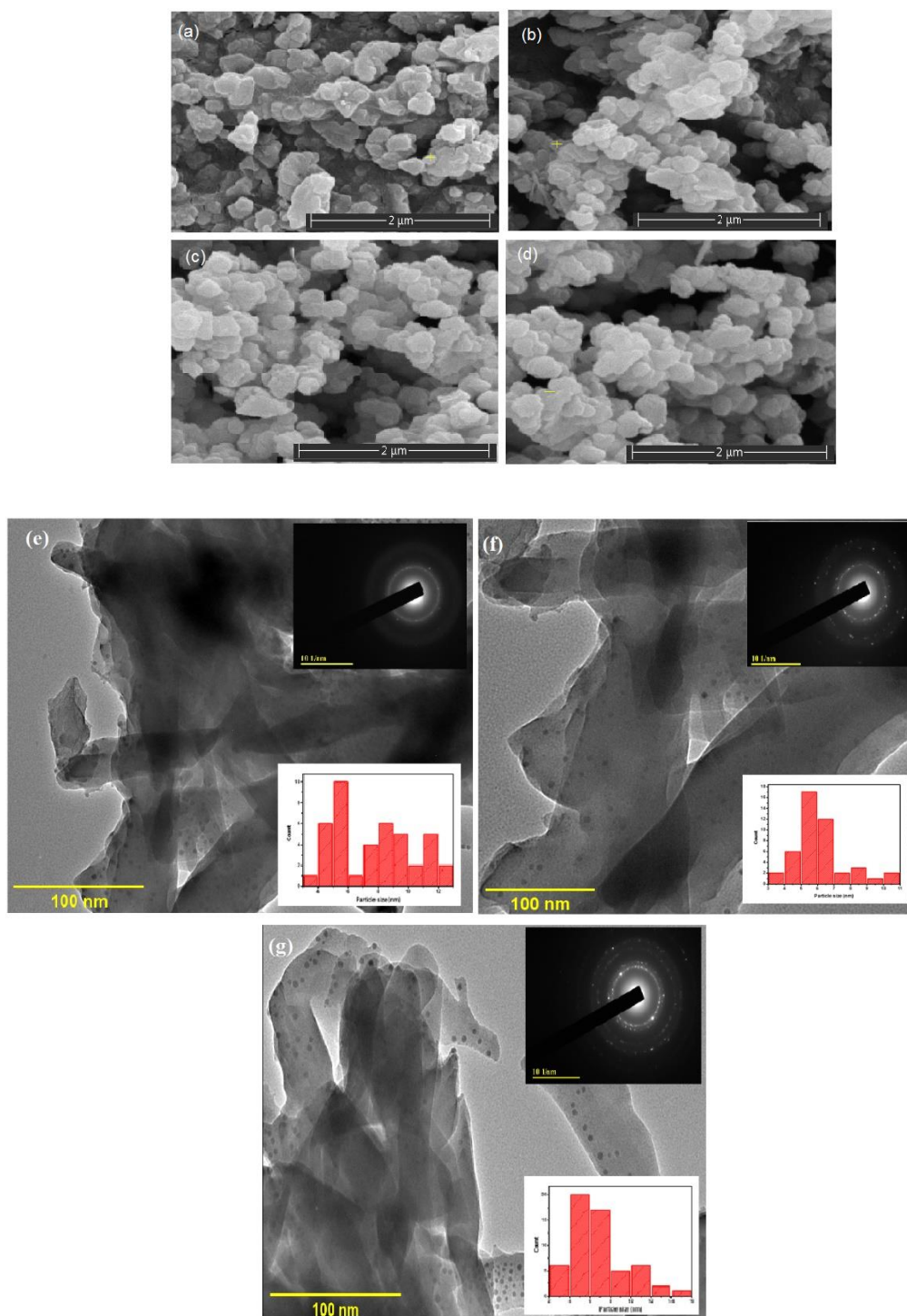


Figure 6.5. SEM images of the UiO-66 and Cu-modified UiO-66 [a: UiO-66, b: 5% Cu/UiO-66, c: 7% Cu/UiO-66, and d: 10% Cu/UiO-66]. TEM (e-g) images of 5% Cu/UiO-66, 7% Cu/UiO-66 and 10% Cu/UiO-66.

6.4.6 NH₃-TPD analysis

NH₃-TPD was utilized to determine the acidity of the samples, and the results are shown in Figure 6.6 and Table 6.1. According to Figure 6.6, NH₃-TPD measurement shows that all samples exhibit a pronounced desorption peak between 110 and 420°C, indicating the desorption of ammonia from acid sites. UiO-66 acidity originates from Lewis acidic Zr sites (Zr-OH) and defect generation in Zr₆ clusters due to missing organic linkers [326-328]. The acidity of Cu/UiO-66 increases following Cu loading compared to UiO-66 because of the missing linker and the presence of a coordinated free carboxylate group. As shown in Table 6.1, the acid sites gradually increased with the catalyst loaded.

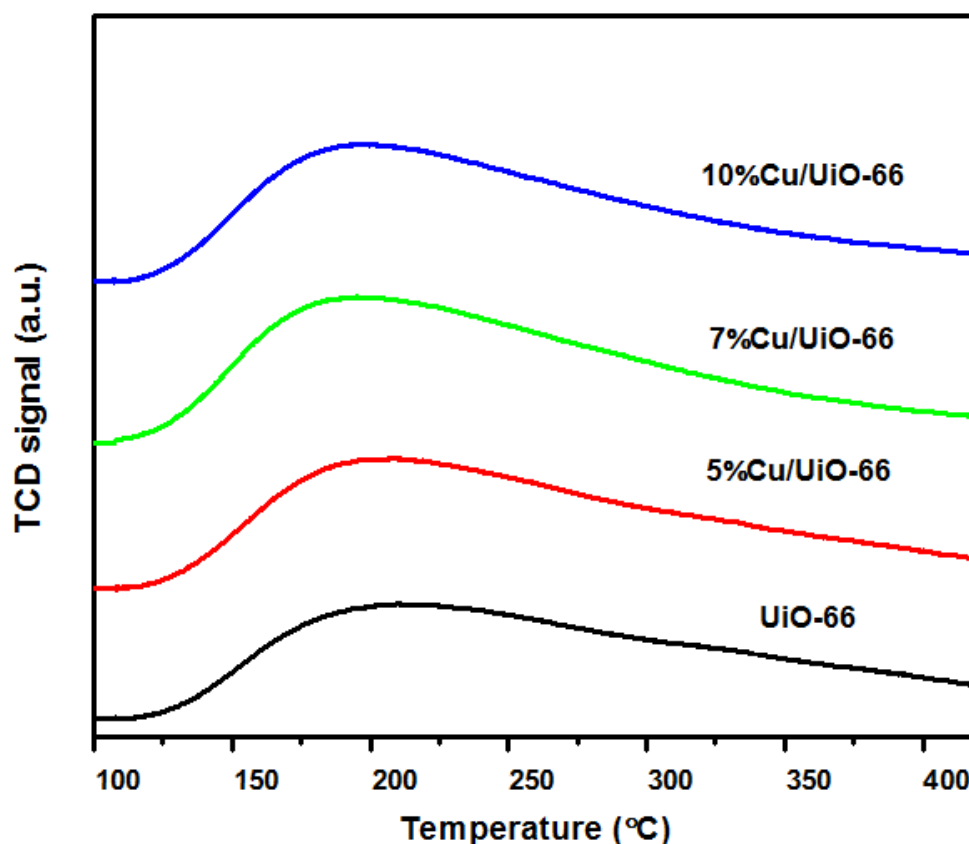


Figure 6.6. NH₃-TPD profiles of UiO-66 and Cu-modified UiO-66

6.4.7 Catalytic investigation

The performance of the prepared materials for WCO methanolysis for biodiesel production was investigated. The catalytic activities of the samples were evaluated at fixed process parameters (catalyst loading of 4 wt% and 16:1 methanol/WCO ratio for 2 hours at 150 °C). Figure 6.7 depicts the biodiesel conversion using several synthesized catalysts. As shown, the biodiesel conversion of Cu/UiO-66 catalysts were significantly increased in comparison with that of the UiO-66. This increase in activity may be ascribed to the large pore and the synergistic effect between UiO-66 and copper oxide composite. These pores trap the substrate and move it closer to the catalytic system's active site since they are considerably larger than triglyceride molecules. Also, the synergistic effect between UiO-66 and copper oxide composite enhanced the adsorption of bulky triglycerides to reach the active sites and provide sufficient active sites for transesterification reaction, which favored the conversion of bulky triglycerides molecules into biodiesel molecules. Further increasing the Cu loading in the UiO-66 support increases the active Cu sites, which results in improved WCO biodiesel conversion of 7%Cu/UiO-66 than 5%Cu/UiO-66 (Fig. 6.7). While if more Cu were incorporated to UiO-66 framework, it may block the pore and lead to the increase of the diffusion resistance during the mass transfer reactions, which can reduce the number of accessible active site, and thus, the 10%Cu/UiO-66 shows a lower biodiesel conversion than that with lower Cu loading (7%Cu/UiO-66). In addition, at a higher loading of Cu particles into the UiO-66 framework, the agglomeration induced molecular hindrance between the reactants methanol and triglycerides, resulting in a decrease in biodiesel conversion. Among all the samples, 7%Cu/UiO-66 shows the highest biodiesel conversion. Therefore, it is possible to conclude that this reaction's optimum Cu loading amount is 7%. Also, in order to avoid Cu agglomeration on the UiO-66 support surface and to conserve raw materials, we utilized this 7%Cu/UiO-66 as the solid acid catalyst for further investigation.

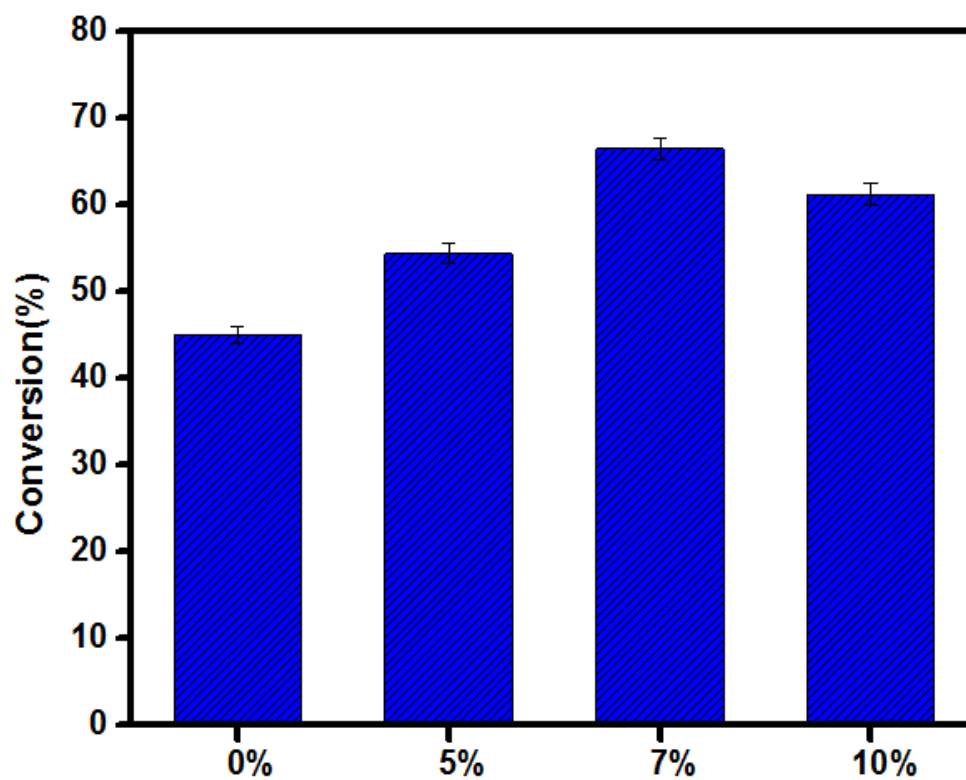


Figure 6.7. Catalysts evaluation for the production of biodiesel

6.4.8 Biodiesel Characterization

Figure A.8 (a & b) shows the ^1H NMR of WCO and biodiesel, correspondingly. As depicted in Fig. S1 (a), the ^1H NMR of WCO revealed triglyceride peaks with olefinic protons at 5.37 ppm and glycerol signals at 4.17- 4.32 ppm. The disappearance of glyceridic backbone signals between 4.17- 4.32 ppm and the appearance of a triplet signal related to $\alpha\text{-CH}_2$ protons at 2.31 ppm and a single peak corresponding to methoxy protons at 3.67 ppm confirm biodiesel production [Fig. A.8 (b)]. Other signals observed include signals at 1.60, 1.25, and 0.89 ppm for beta-carbonyl methylene protons, carbon methylene protons and terminal methyl protons, respectively [230, 223,329]. The signals at 5.36 ppm are related to olefinic hydrogens [223-224,329].

The ^{13}C NMR of WCO and biodiesel is depicted in Figure A.9 (a & b). The signals at 68.88 and 62.09 ppm are attributed to -O-CH- and $\text{-O-CH}_2\text{-}$ functional groups information for WCO, respectively [Fig. A.9 (a)]. These signals disappear with the formation of methyl esters, and a new signal associated with -OCH_3 carbon appears at around 51.42 ppm [Figure A.9 (b)]. The carbonyl of ester in WCO produces a peak at 173.24 ppm. Unsaturated fatty acids can be seen at 127.90 and 130.19 ppm in ^{13}C NMR spectra of biodiesel, and ester carbonyl is shown at 174.31 ppm. Signals between 22 and 34 ppm are attributed to the $\text{-CH}_2\text{-CH}_2\text{-}$, while another peak at 14.11 ppm is due to the methyl group's end-chain carbon of FAME [223,226].

The composition of WCO biodiesel was further examined using the GC-MS technique to identify the various esters that comprised the sample. Table A3 lists the biodiesel sample identified components. The sample of biodiesel contained both saturated and unsaturated FAMEs. Figure A.10 depicts the GC-MS chromatogram.

Table 6.2 shows the fuel properties of the biodiesel that was produced along with a comparison to the ASTM D6751 standard. These properties conform to the quality requirements recommended by ASTM D6751, which suggests that the as-produced biodiesel could be used as either a neat fuel or blended with petroleum diesel.

Table 6.2

The properties of the biodiesel in comparison with the ASTM standards

Fuel properties	ASTM method used	ASTM D6751 Biodiesel	Prepared biodiesel
Kinematic viscosity (40 °C, mm ² /s)	D445	1.9-6.0	5.2
Density (40 °C, g/cm ³)	D5002	0.86-0.90	0.872
Specific gravity (40 °C, g/cm ³)	D287	0.88	0.878
Flash point (°C)	D93	100-170	140
Acid value (mg KOH/g)	D664	0.5	0.13

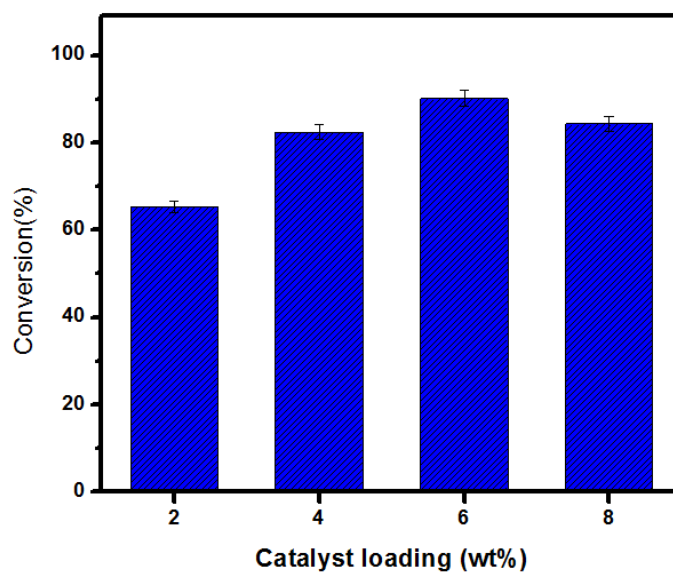
6.4.9 Effect of transesterification conditions

A. Effect of catalyst loading and methanol to oil molar ratio

The influence of catalyst loading as a process parameter on biodiesel conversion was examined by varying the catalyst loading from 2 to 8 wt% with molar ratio of methanol/WCO of 20:1 at 150 °C for 4 hours (Figure 6.8a). As shown in Figure 6.8a, when the amount of catalyst increased from 2 to 6 wt%, biodiesel conversion steadily increased and reached a maximum of 90.08%. When the catalyst loading is increased beyond 6 wt%, the biodiesel conversion declines, presumably due to a mixing issue that involves the solid catalyst, reactants, and products (increase in viscosity of the reaction mixture) [330-331]. Also, biodiesel conversion may drop because of the higher adsorption of biodiesel products onto the catalyst as the amount of catalyst increases above the optimal level [226]. Therefore, 6 wt% catalyst loading was used to optimize other reaction parameters.

Figure 6.8b depicts the influence of methanol loading on WCO biodiesel production using 7%Cu/UiO-66 (catalyst loading of 6 wt%) at 150 °C for 4 hours. We observed that increasing the methanol/WCO ratio increases biodiesel conversion. When the molar ratio rose to 20:1, the biodiesel conversion increased to 90.10%. Nevertheless, beyond the ratio of 20:1, biodiesel conversion decreased. The higher molar ratio might lead to an incomplete reaction, with the presence of monoglycerides and diglycerides as byproducts [332-333]. Finally, in this study, we conclude that the 20:1 methanol/WCO ratio is sufficient to produce WCO biodiesel.

(a)



(b)

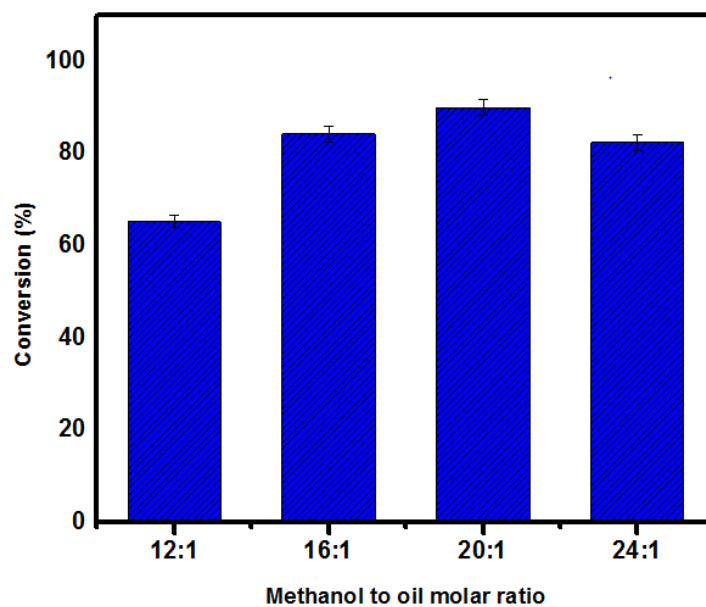


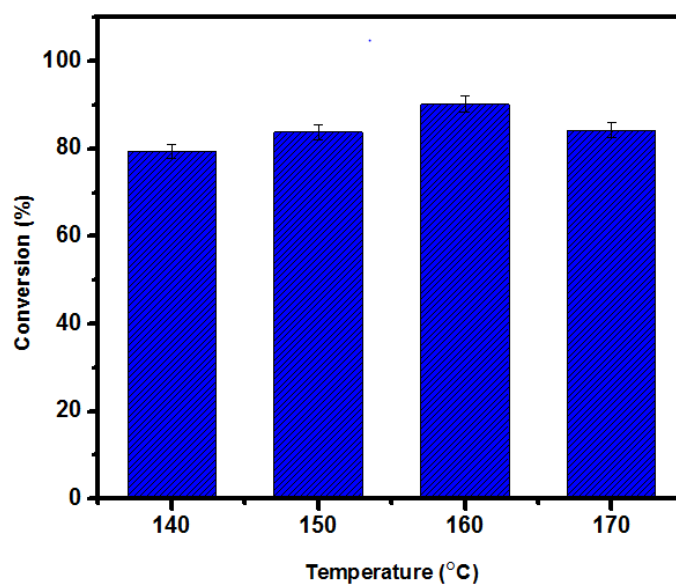
Figure 6.8. (a) effect of catalyst loading and (b) effect of methanol to oil molar ratio.

B. Effect of temperature and reaction time

One of the most crucial parameters to optimize is the reaction temperature because it profoundly influences the reaction rate. To investigate how the reaction temperature influences the biodiesel conversion, some experiments were carried out using of 7%Cu/UiO-66 catalyst at 140, 150, 160, and 170 °C with a catalyst loading of 6 wt% and molar ratio of 20:1 at 4 hours (Figure 6.9a). The results revealed that at higher temperatures, biodiesel conversion increases, with an optimal conversion of 90.10% for the 7%Cu/UiO-66 catalyst at 160 °C. Since the reactants acquired enough kinetic energy at higher reaction temperatures, the mass transfer rate between the catalyst, oil, and methanol increased, resulting in maximum biodiesel conversion. At the temperature higher than 160 °C, the WCO conversion started to decrease marginally. The optimal temperature for the process was 160 °C.

The effect of reaction time on biodiesel conversion was also investigated with a 6 wt% catalyst loading and molar ratio of 20:1 at 160 °C (Figure 6.9b). Figure 6.9b shows that the catalyst was partially activated during the first hour, which resulted in a low reaction rate and low biodiesel conversion. Nevertheless, the conversion increased progressively as the reaction time increased and reached 90.09% at 4 hours. After 4 hours, biodiesel conversion reduced. This behavior could be explained by reverse transesterification that occurs between glycerol and FAME as reaction time increases [226,334]. Therefore, 4 hours is considered as the optimal reaction time.

(a)



(b)

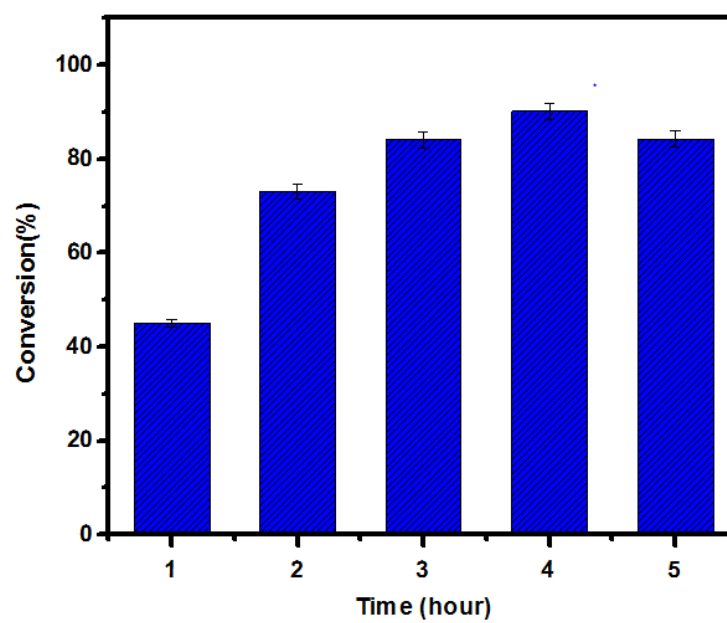


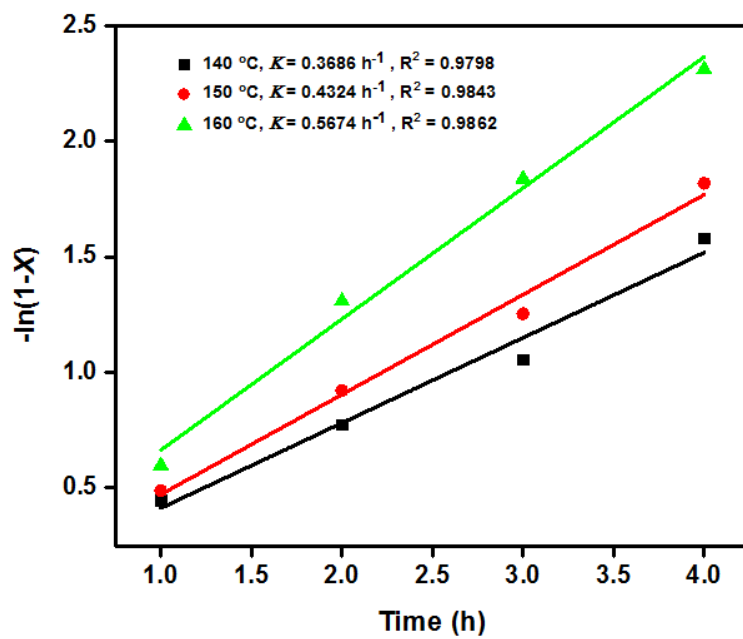
Figure 6.9. (a) effect of reaction temperature and (b) effect of reaction time

6.4.10 Kinetic studies of biodiesel production

Independent experiments were conducted under the optimum WCO conversion conditions for the kinetic study: methanol/WCO ratio of 20:1, 6 wt% catalyst loading, and reaction temperature was varied in each experiment (140 °C, 150 °C, 106 °C). Since methanol was utilized in excess, the reverse reaction may be ignored, and the reaction is believed to be governed by the pseudo-first-order model [231,233]. Thus, equation (4.1) fits the reaction rate constant, and the activation energy (E_a) needed for the reaction is computed utilizing the Arrhenius equation (4.2).

Figure 6.10a depicts a plot of $-\ln(1-X)$ vs. *time*. The linear regression was used to obtain the k at different temperatures, and it was discovered that k increases with increasing reaction temperature. Due to the improved mass transfer effect, raising the temperature increases the reaction process. The E_a of the reaction was calculated to be 32.26 kJ/mol using the Arrhenius plot ($\ln k$ against $1/T$) [Figure 6.10b]. It has been reported that chemically controlled reactions typically have E_a higher than 25.0 kJ/mol, while diffusion-limited reactions have a lower E_a (10 to 15 kJ/mol) [335-338]. Therefore, these findings show that the reaction is chemically controlled in the present study due to the high E_a (32.26 kJ/mol).

(a)



(b)

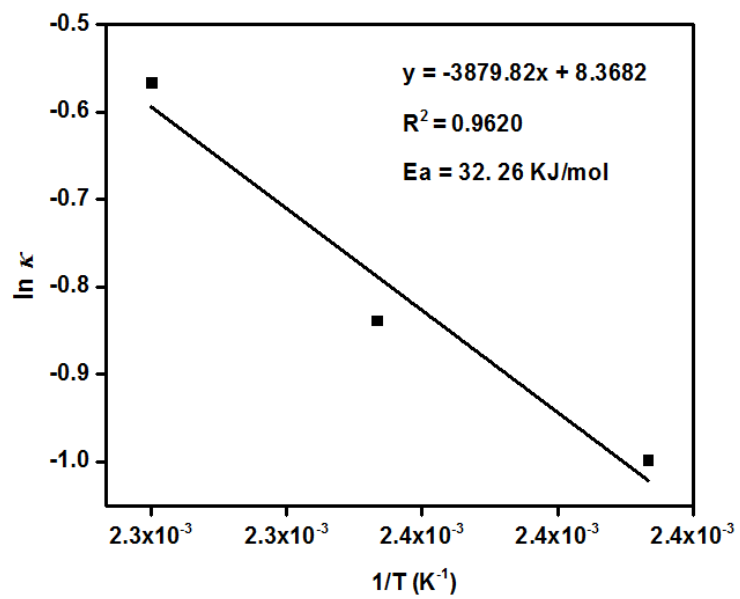


Figure 6.10. (a) A plot of $-\ln(1-X)$ vs. time and (b) An Arrhenius graph showing the relationship between k and $1/T$

6.4.11 Plausible mechanism

Figure 6.11 illustrates a plausible mechanism for WCO's simultaneous transesterification and esterification. Typically, the methanol molecule binds to the Zr metal site of the catalyst. The fatty acid and triglyceride species that are present in the WCO bind to the Cu atom of the Cu/UIO-66 via their carbonyl oxygen atom. Methanol and fatty acid/triglyceride are in close proximity to one another, allowing for easy interaction. Then, the two neighboring molecules undergo a nucleophilic attack. Glycerol is a byproduct produced in the transesterification pathway in FAME production. Meanwhile, water molecule is formed as a byproduct in the esterification pathway in FAME production. FAMES are desorbed from the catalyst through electron delocalization at the oxygen atom. After regeneration, the catalyst can be utilized for another catalytic cycle.

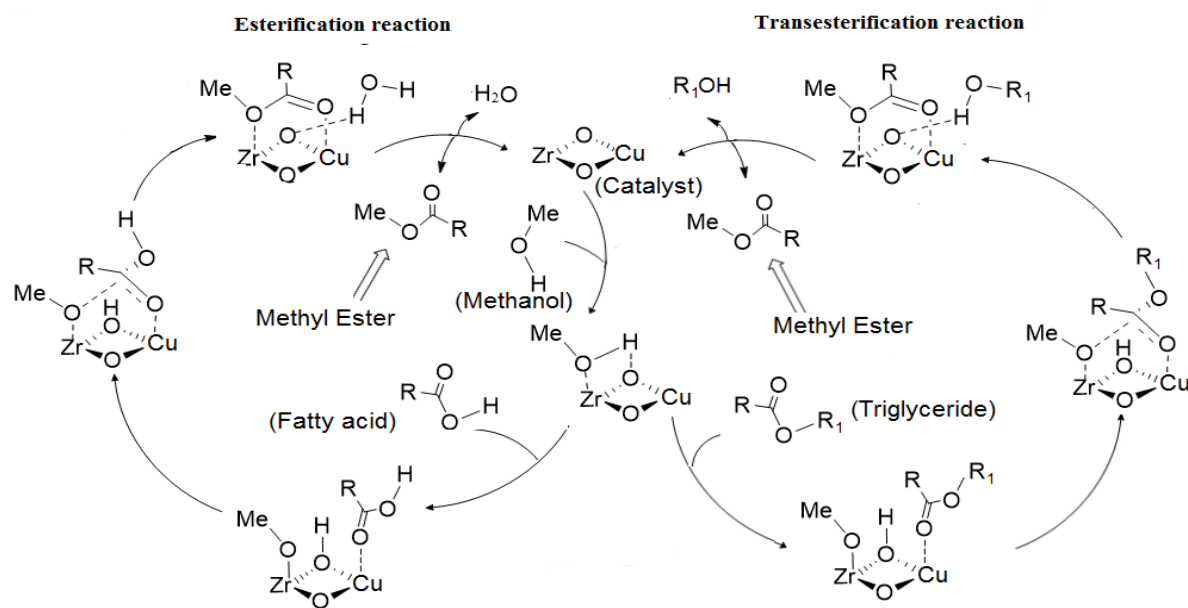


Figure 6.11. Plausible mechanism for the reactions

6.4.12 Reusability of catalysts

The heterogeneous solid acid catalysts reusability test is important because it demonstrates the benefit of utilizing a catalyst to lower the preparation cost for industrial use. To evaluate the catalyst reusability in the present study, 7%Cu/UiO-66 catalyst was centrifuged after each cycle, oven-dried at 100 °C for 8 hours after being washed with methanol, and then utilized for the next cycle. Under the optimal reaction condition (6 wt% catalyst and 20:1 methanol/WCO at 160 °C for 4 hours), the reaction was repeated six times, and the findings are exhibited in Figure 6.12. We found that even after three reuses, the catalyst activity could maintain a conversion of more than 80%. This result could be inferred that incorporating Cu into the UiO-66 cavities enhanced the stability of the catalyst and WCO conversion. XRD analysis was utilized to determine the stability of the synthesized catalyst, and the results are given in Fig. A.11. Based on Fig. A.11, the recycled catalyst XRD pattern was substantially comparable to that of the fresh catalyst, except for a decrease in peak intensity, indicating that the structure and the composition of the 7%Cu/UiO-66 catalyst were substantially preserved. However, the slight decrease in activity is likely due to leaching part of the active component into the reaction media. Based on the analysis above, the synthesized 7%Cu/UiO-66 catalyst exhibits good stability in biodiesel production. Table 6.3 compares the performance of various solid catalysts in biodiesel production using oleic acid/low-grade oils as the feedstock. It follows that when WCO was used as a feedstock, the performance of our catalyst is comparable to other studies.

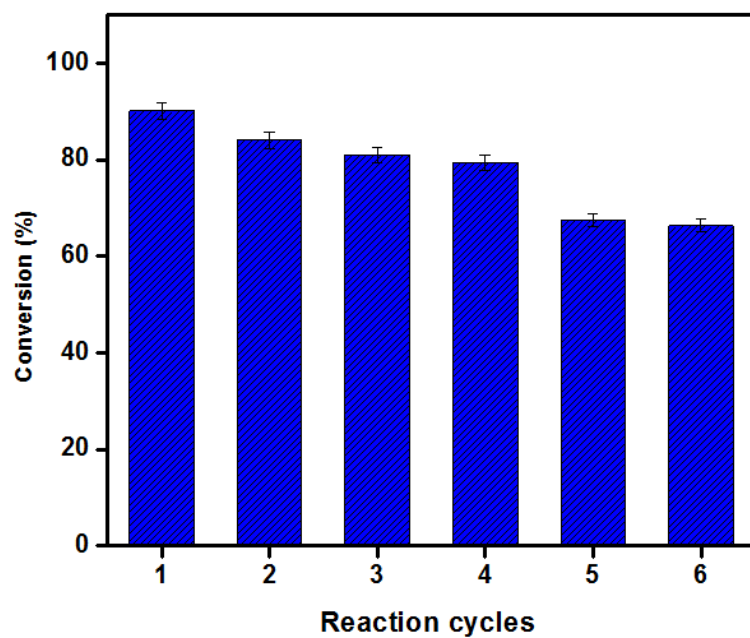


Figure 6.12. Effect of reusability

Table 6.3. Different solid catalysts performance in biodiesel production utilizing waste cooking oils/low grade material as a feedstock; comparison of literature

Catalyst	Operating conditions ^a	Performance	Reference
NiHSiW/UiO-66	3 h, 160 °C, 6 wt.%, 18:1	86.7% oil conversion	[338]
PMA/Fe-BTC	3 h, 160 °C, 10 wt.%, 16:1	72.3% oil conversion	[339]
Co-MOF	12 h, 60 °C, 2.5 wt.%, 200:1	83.7% oil conversion	[232]
MIL-101(Cr)@MBIAILs	4 h, 67 °C, 11 wt.%, 10:1	91% oil conversion	[340]
Sn _{1.5} PW/Cu-BTC-1	24 h, 160 °C, 7 wt.%, 20:1	87.7% oil conversion	[341]
Cu-MOF	1 h, 65 °C, 1 wt.%, 20:1	78.3% oil conversion	[342]
Ca-MOF	4 h, 100 °C, 10 wt.%, 45:1	78% oil conversion	[342]
Cu-MOF + Ca-MOF	1 h, 70 °C, 10 wt.%, 15:1	85% oil conversion	[342]
SO ₄ ^{2-/} TiO ₂ -SiO ₂	3 h, 200 °C, 4 wt.%, 9:1	90% oil conversion	[301]
SO ₄ ^{2-/} SnO ₂ -SiO ₂	3 h, 150, 4 wt.%, 15:1	92% oil conversion	[343]
HSiW-UiO-66	4 h, 160, 7 wt.%, 20:1	80.5% oil conversion	[320]

7%Cu/UiO-66	4 h, 160 °C, 6 wt.%, 20:1	90.1% oil conversion	This work
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^aThe operating conditions (time, temperature, catalyst amount and molar ratio)

6.5 Conclusion

In conclusion, Cu/UiO-66 catalysts prepared through a wet impregnation approach proved to be effective catalysts in the production of biodiesel from WCO. The as-prepared Cu/UiO-66 catalysts exhibited high catalytic activity. This is because of the appropriate pore size, large surface area and the synergistic effect between UiO-66 and copper oxide composite. The catalyst with a Cu loading of 7 wt.% (7%Cu/UiO-66) exhibited a high conversion of 90.10% under the optimal process conditions (6 wt% catalyst and methanol/oil ratio of 20:1 at 160 °C for 4 hours). Based on a kinetic investigation that revealed the reaction followed pseudo first-order kinetics, we estimated the activation energy to be 32.26 kJ/mol. This result suggests that the reaction is chemically controlled and not by mass transfer and diffusion constraints. Furthermore, the 7%Cu/UiO-66 catalyst displayed good stability, and after three cycles of reuse, WCO conversion was more than 80%. Therefore, the presented 7%Cu/UiO-66 catalyst has the potential to be utilized in industrial biodiesel production since it is recyclable and capable of converting cheap feedstocks into biodiesel.

CHAPTER 7

Synergy effect of bimetallic in porous MOF matrix for efficient production of biodiesel from waste cooking oils

7.1 Abstract

Metal-organic frameworks (MOFs) has gained much attention in the realm of catalysis due to their unique attributes, such as large porosity, high surface area, and adjustable properties. In this study, facile and efficient heterogeneous catalyst was prepared by modification of the copper-based metal-organic framework with zinc (Zn/Cu-BTC) and the composite was used as a catalyst for biodiesel production from waste cooking oil (WCO). The catalysts were characterized using XRD, FTIR, SEM, TEM, TGA and N₂ adsorption-desorption. The biodiesel produced was characterized using NMR and GC-MS. The Zn/Cu-BTC catalyst exhibits a high biodiesel conversion of 92.4% under optimal conditions of 4 wt% catalyst loading, 20:1 methanol/waste cooking oil molar ratio at 160 °C for 4 hours due to its bimetallic synergistic effect, appropriate pore size and high surface area. The Zn/Cu-BTC catalyst displayed good stability and reusability giving a biodiesel conversion of 84.1% after three reuses. In addition, our kinetic investigation showed that the reaction follows a pseudo-first order kinetic, with an activation energy (E_a) of 40.33 kJ/mol. Compared with other solid catalysts reported in the literature, Zn/Cu-BTC catalyst showed good WCO biodiesel conversion. The results of the current study substantiate that Zn/Cu-BTC is a promising solid catalyst in producing biodiesel from WCO.

7.2 Introduction

Due to the current conventional technologies and high energy content, the world relies heavily on energy derived from nonrenewable fuel resources. The increasing price of fossil fuels and severe environmental problems has sparked interest in developing alternative energy resources [344-345]. Renewable energy like wind energy, bioenergy and solar energy are potential alternatives to the energy sector challenges [346-347]. Renewable resources reduce global emissions and increase world energy production [347]. Among the alternative being considered today, waste materials have been utilized to produce biofuels, which can significantly impact the energy sector and enhance global socio-economic prospects [347]. Biodiesel is the most promising biofuel for replacing diesel engines [348]. Biodiesel has several benefits such as higher cetane number than diesel fuel, nontoxic, biodegradable, low exhaust emissions during the combustion process [349-352]. Biodiesel is produced by either transesterification of triglycerides or esterification of free fatty acids (FFAs) with alcohol in the presence of a suitable catalyst [353-354].

Biodiesel feedstock comes in a variety of forms: non-edible oil, edible oil, algal lipid, and waste cooking oil [17–20]. Currently, almost all biodiesel production begins with edible oil (such as soybean, sunflower, rapeseed corn, and rapeseed oil) as a feedstock because it is widely available from the established agricultural sector [17-18]. However, the vast cultivation of edible oil for biodiesel production can put the entire world at risk, in which the slightest planning error can have a substantial effect on the economy and food supply [1]. The limited agricultural land typically available for growing food would be compromised when the fuel economy and the food economy are both in competition for the same resources [21]. Biodiesel is produced using non-edible oils like *Jatropha*, *Karanja*, *Castor*, and *Mahua* because of its lower sulfur content, ready availability, lower aromatic content, and biodegradability [46]. However, non-edible is unfavorable as biodiesel feedstock because of the higher reactivity of its unsaturated fatty acid chain, lower volatility, and higher viscosity [46]. Waste cooking oil (WCO) could be used as a biodiesel feedstock instead of edible oil. WCO is released directly into the waterway or accumulated in the ground in most cafeterias, hotels, and other service industries [83]. Producing

biodiesel from WCO offers three possible solutions: environmental, waste management, and economic [250]. Biodiesel's high cost is the most significant barrier to its commercialization [289]. Biodiesel produced from WCO is a cost-effective source that can effectively reduce feedstocks cost [289].

Biodiesel is typically produced utilizing homogenous acid catalysts (e.g., H_2SO_4 or HCl) or alkali catalysts (like KOH or NaOH) [355-356]. Homogeneous catalysts are typically employed in commercial biodiesel production, but they are highly corrosive, toxic in nature, generate large amounts of effluent, and are difficult to recycle [357]. In order to circumvent the limitations of liquid catalysts, solid catalysts are being examined because of their unique advantages, including simple recovery and reuse for repeated reaction runs, high activity, noncorrosive nature, and ecofriendliness [358]. However, heterogeneous base catalysts are sensitive to water content (tolerate level: <0.06 wt.%) and FFAs (maximum: 2.0 wt.%) in the low cost raw materials, which could promote hydrolysis side reaction and saponification [293]. This would reduce both the fatty acid methyl ester conversion and catalytic activity [293]. Thus, the heterogeneous acid catalyst is preferred when dealing with low-cost raw materials containing substantial quantities of water and FFAs [293]. Various types of heterogeneous acid catalyst systems have been utilized, including carbon-based solid acids, magnetic $\text{Fe}_3\text{O}_4/\text{MCM-41}$, $\text{Fe}_3\text{O}_4@ \text{HKUST-1-ABILs}$, cation exchange resins, $\text{SLO}/\text{HZSM-5}$ zeolites, Cr-Al oxides, and solid superacids [302,359-363]. However, these reported catalysts have at least one of the following drawbacks, including lower conversion, high cost, and catalyst toxicity [364].

Metal-organic frameworks (MOFs) are a new type of solid material with various applications in scientific study, including electrochemistry magnetism, catalytic activities, and energy storage [235]. MOFs are heterogeneous materials that have well-structured coordinated bonds between organic ligands and metal ions storage [362-364]. MOFs have high catalytic efficiency, highly ordered structure, tunable pore size, tailorable functionalities, and high surface area, making them a viable option for various reactions [35-37]. The open metal sites in MOFs act as adsorption and Lewis acidic sites, and thus play a vital role in modulating the catalytic activity for different reactions [345,364].

Several studies have shown that MOF catalysts exhibit exceptional conversion efficiency in a wide range of industrially relevant reactions [362-364]. Nevertheless, transesterification and esterification processes have received less attention. Only a few types of MOFs have been studied in terms of biodiesel production, including Cr(III) terephthalate, Co(II) terephthalate, MIL-53(Fe), and Fe-BTC [345,365-366]. These MOF catalysts can provide good to excellent fatty acid alkyl esters (FAMES) conversion. The biodiesel conversion is achieved via a two-step transesterification/esterification of pre-esterified oil or a one-step esterification of fatty acid substrates [320,345,365-366], while the model reaction involving the simultaneous esterification and transesterification of WCO remains unexplored.

In this work, we prepared Zn/Cu-BTC composite with different weight percent loading of Zn. Various methods were used to characterize the prepared catalysts, including, FTIR, SEM, TEM, N₂ adsorption-desorption, TGA and XRD. Thereafter, the potential of the prepared catalysts was studied for the transesterification and esterification of WCO to produce biodiesel. Furthermore, the influence of various process variables such as reactant molar ratio, catalyst loading, reaction temperature and time were studied to optimize the reaction. Finally, the reaction kinetic parameters and catalyst reusability were explored.

7.3 Materials and methods

Materials, catalyst preparation procedure, biodiesel production procedure, biodiesel analysis and characterization methods used in this study explained previously in Chapter 3 (section 3.1, 3.2.4, 3.4,3.5 and 3.6).

7.4 Results and discussion

7.4.1 XRD analysis

The XRD patterns of the samples are depicted in Figure 7.1. The pattern of Cu-BTC have a peak in the range of 8–20° before loading, which is the characteristic peaks of Cu-BTC [367-369]. The XRD pattern of the prepared Cu-BTC sample is coincides with the literature [367-368]. The typical Cu-BTC diffraction peaks are apparent following the zinc loading (4%, 8%, and 10%, correspondingly) via impregnation, indicating that the catalyst preparation does not significantly influence support crystallinity. Nevertheless, when the Zn loading increases, the Cu-BTC diffraction peaks at 8–20° decreased. These results suggest that the zinc oxide particles were uniformly dispersed on surface of the Cu-BTC.

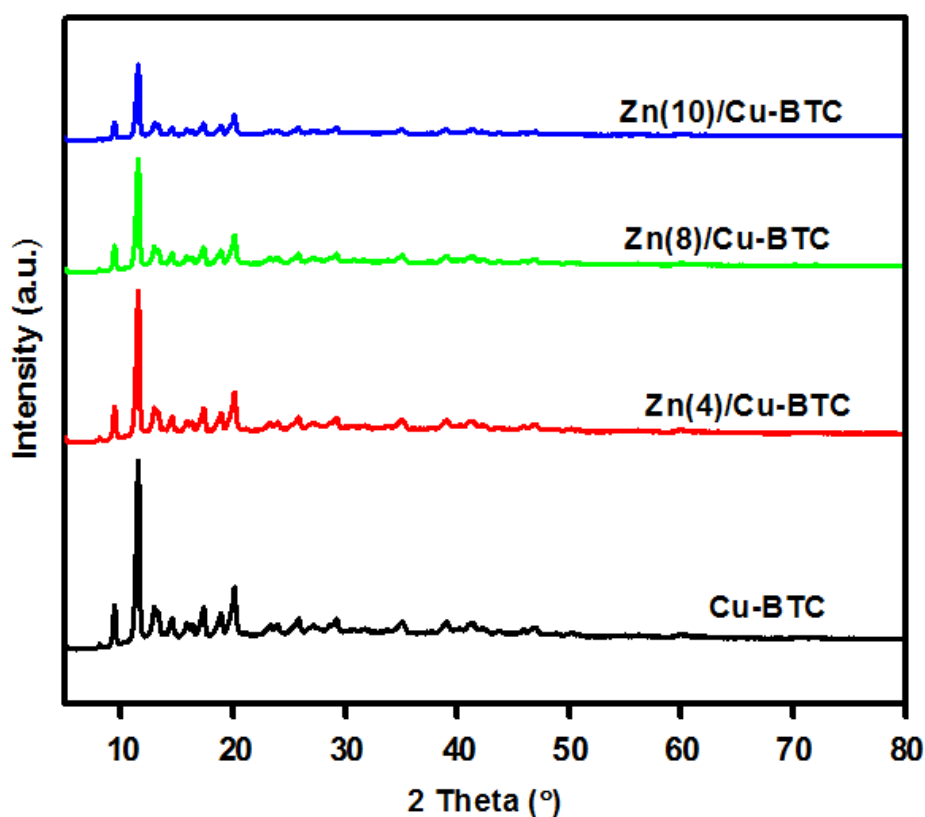


Figure 7.1. XRD patterns of the as-synthesized Cu-BTC and Zn-modified Cu-BTC samples

7.4.2 Nitrogen adsorption-desorption isotherms studies

Figure 7.2 depicts the nitrogen adsorption-desorption isotherms of the as-synthesized Cu-BTC and Zn-modified Cu-BTC samples. As depicted, the profile of the samples exhibited a type 1 isotherm according to the IUPAC [370]. Table 7.1 depicts the summary of textual features of the samples. Cu-BTC shows a high surface area and the pore volume of 912.40 m²/g and 0.49 cm³/g, respectively. The surface area and the pore volume of the Cu-BTC are comparable to the findings that were previously reported in the literature [371]. The surface area of Cu-BTC decreases after Zn loading into the Cu-BTC sample. As the Zn loading increases from 4 wt.% to 10 wt.%, the surface area of the Zn/Cu-BTC catalysts reduced (Table 7.1). For example, a surface area loss of 78.41 m²/g is noticed upon the incorporation of 4 wt.% of Zn, and with a further loss of 12.25 m²/g when the amount of impregnated Zn species increased to 8 wt.%, and with an additional loss of 43.21 m²/g is observed with the incorporation of 10 wt.% of Zn onto Cu-BTC. The reduction in surface area could be attributed to pore blockage caused by Zn deposition on the Cu-BTC support [372]. Also, the pore volume of Cu-BTC decreases following the Zn loading, which suggests that the impregnation-reaction approach successfully introduces Zn metal into Cu-BTC. Moreover, the pore size increased after the incorporation of Zn metal into the Cu-BTC sample. This increase in pore size may be ascribed to the collapsed micropores structure after the exchange metal ions [372-373].

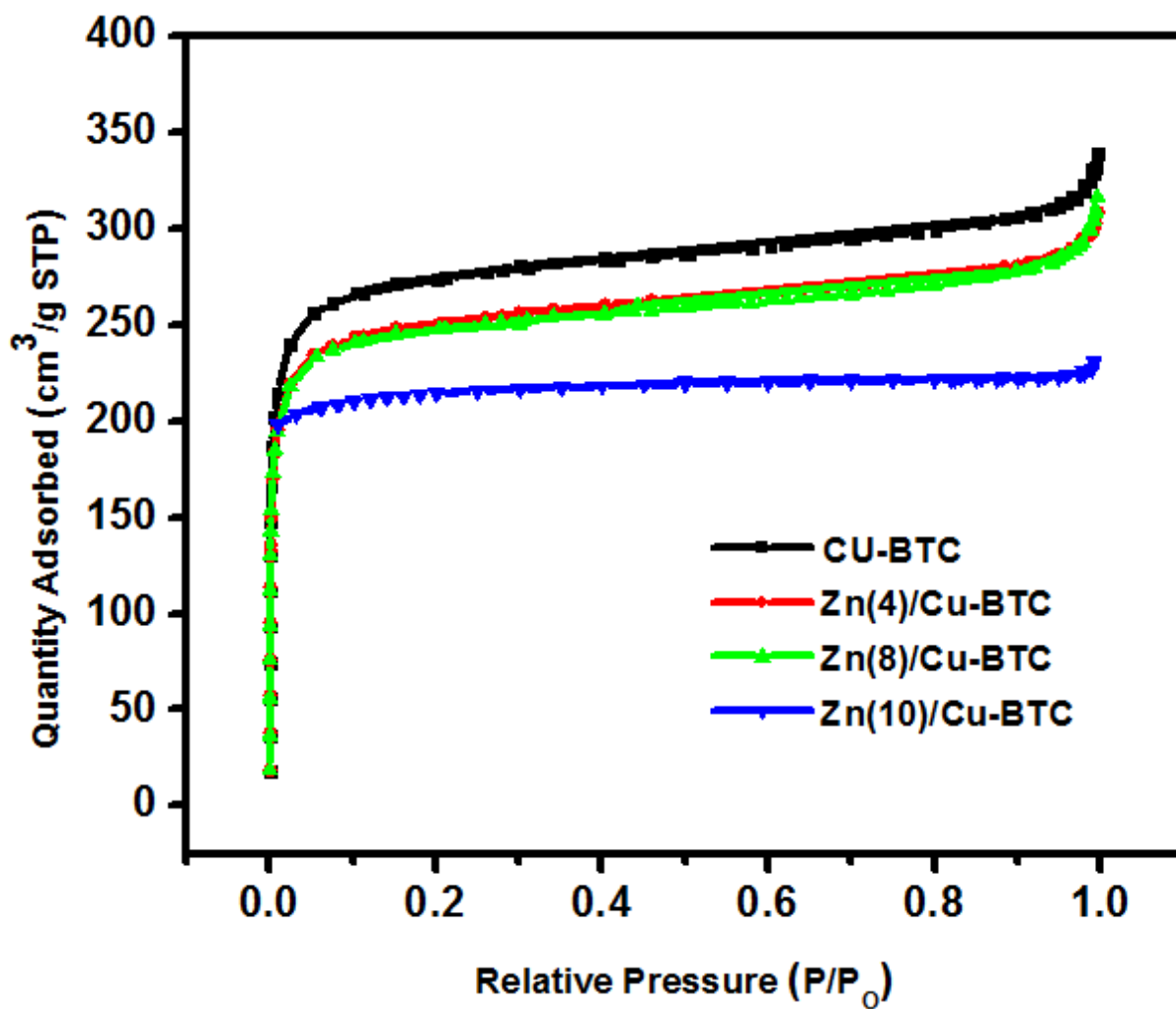


Figure 7.2. N₂ adsorption-desorption analysis of the materials

Table 7.1. Textural features of the materials.

Samples	S_{BET} (m ² /g)	V_{total} (cm ³ /g)	PS (nm)
Cu-BTC	912.40	0.49	4.30
4%Zn/Cu-BTC	833.99	0.45	4.48
8%Zn/Cu-BTC	821.74	0.44	5.06
10%Zn/Cu-BTC	778.53	0.35	4.85

7.4.3 FTIR analyses

The samples were analyzed using FTIR in order to characterize the functional groups present in their structure. Figure 7.3 depicts the FTIR spectra of as-synthesized Cu-BTC and Zn-modified Cu-BTC. For Cu-BTC, the typical C-O-Cu stretching vibration appeared at 1112 and 730 cm^{-1} , which confirm the formation of Cu-BTC [369,374–376]. The FTIR spectra of the Cu-BTC is consistent with the previous findings [377-378]. The absorption band at 1376 cm^{-1} is due to O-C-O stretching vibration [376]. The bands at 1643 cm^{-1} and 1454 cm^{-1} are associated with the C=O stretching and C=C stretching vibration [376-377]. The bands at 1554 cm^{-1} is ascribed to O-C-O stretching vibrations [377-378]. The FTIR spectra of Zn-modified Cu-BTC are comparable to Cu-BTC, indicating that the incorporation of Zn species into Cu-BTC support has no effect on the framework of the support. The band at 443 cm^{-1} is related to the zinc oxide stretching mode, suggesting that ZnO is incorporated into the zeolite framework and these results are consistent with the literature reports [214].

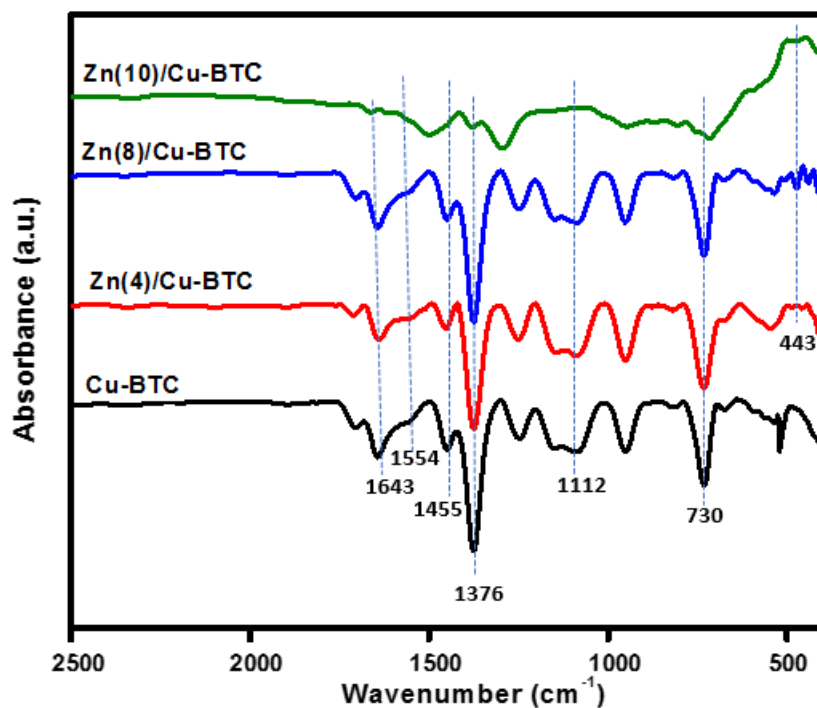


Figure 7.3. FTIR spectra of the materials.

7.4.4 Thermogravimetric analysis

Thermogravimetric analyses was performed on the as-synthesized Cu-BTC and Zn(8)/Cu-BTC catalyst (Figure 7.4). The thermogravimetric curve of as-synthesized Cu-BTC support and Zn(8)/Cu-BTC catalyst showed two main stages of mass loss (Fig. 7.4). The first stage of mass loss in the temperature range 50–120 °C can be ascribed to the loss of moisture [379]. During the second stage (between 120–300 °C), a weight loss was observed for synthesized Cu-BTC support and Zn(8)/Cu-BTC catalyst, which is related to Cu-BTC frameworks decomposition (decomposition of organic linker) [362, 377]. The TG curve showed essentially no noticeable mass loss from 100 to 300 °C, demonstrating the high thermal stability of Zn(8)/Cu-BTC catalyst. As shown, Zn(8)/Cu-BTC catalyst is a little more stable because the organic linkers decomposed at high temperatures. This increase in stability may be ascribed to strong effect of the metal-host matrix interaction. Hence, the findings show that the synthesized catalyst is thermal stable and can be employed to produce biodiesel.

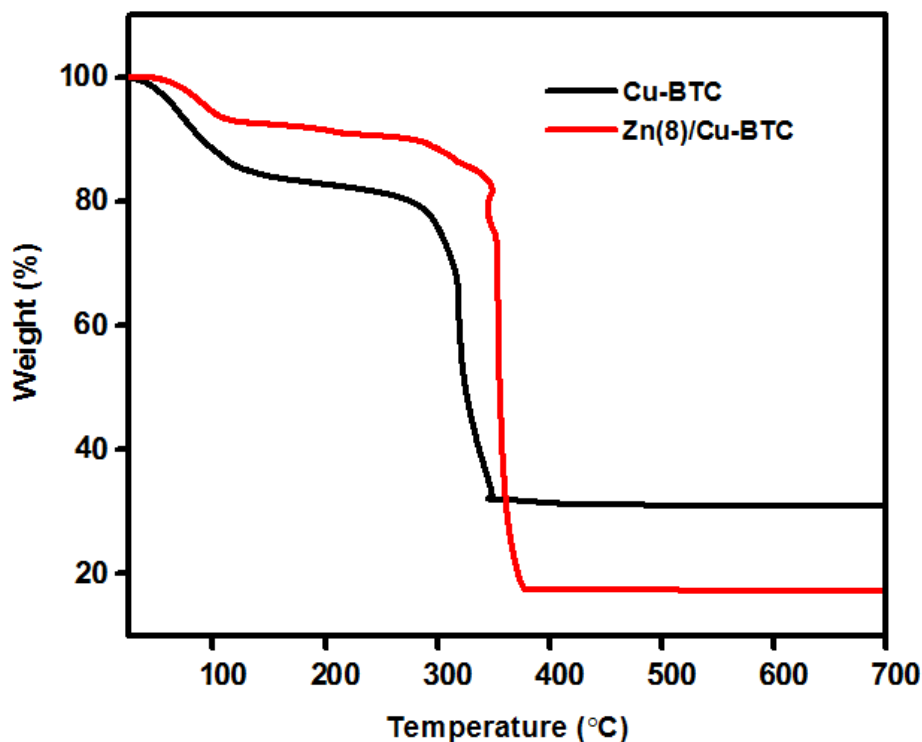


Figure 7.4. TG curve as-synthesized Cu-BTC and Zn(8)/Cu-BTC catalyst.

7.4.5 SEM and TEM studies

The SEM images of the Cu-BTC support and the catalysts are presented in Fig. 7.5. The as-synthesized Cu-BTC exhibited an octahedron shape (Figure 7.5a) [380]. The morphology of the Cu-BTC is comparable to the findings that were previously reported in the literature [380-381]. After zinc oxide had been loaded onto Cu-BTC (Zn/Cu-BTC), there is no substantial change in the shape of the particles (Fig. 7.5b-d). These results suggest that zinc oxide particles were evenly dispersed on the surface of the Cu-BTC. There is a rod-like shape on the MOFs morphologies, which may indicate the presence of ZnO nanorods.

TEM images of the synthesized Zn/Cu-BTC catalysts are depicted in Figure 7.5e-g. As shown, the images indicate that the Zn particles are well dispersed on the external surface of the Cu-BTC. Selected area electron diffraction of the TEM images (Figure 7.5e-g inset) supported the uniform distribution of Zn over Cu-BTC. The histograms in the Figure 7.5e-g inset suggests an estimated particle size of Zn varied over the range of 2-20 nm, and the average particle size for Zn(4)/Cu-BTC, Zn(8)/Cu-BTC and Zn(10)/Cu-BTC were 6.65 nm, 8.43 nm and 9.16 nm, respectively. The Zn particles were larger than the average pore size of Cu-BTC (4.30 nm according to BET analyses); thus, a substantial amount of Zn was deposited on the external surface of Cu-BTC. Moreover, the arrangement of Zn on the Cu-BTC without particle agglomeration suggests adequate dispersion of Zn over Cu-BTC. Therefore, much of the Zn sits on the external surface of the Cu-BTC.

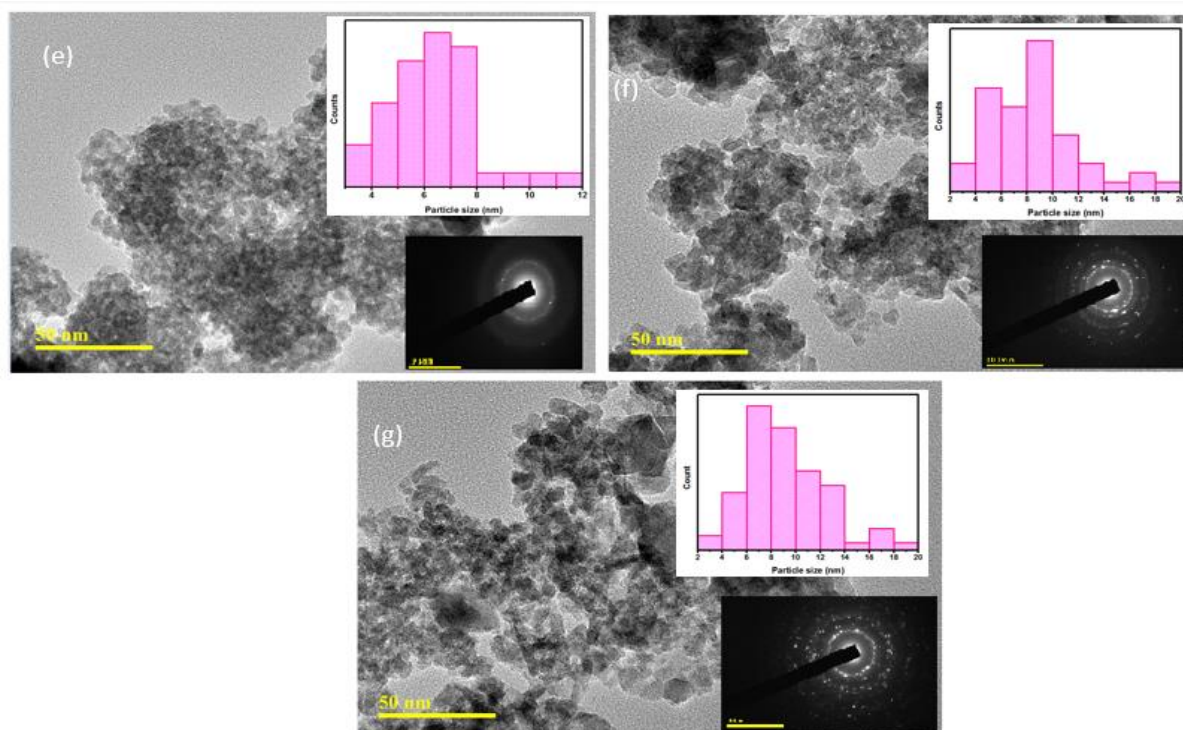
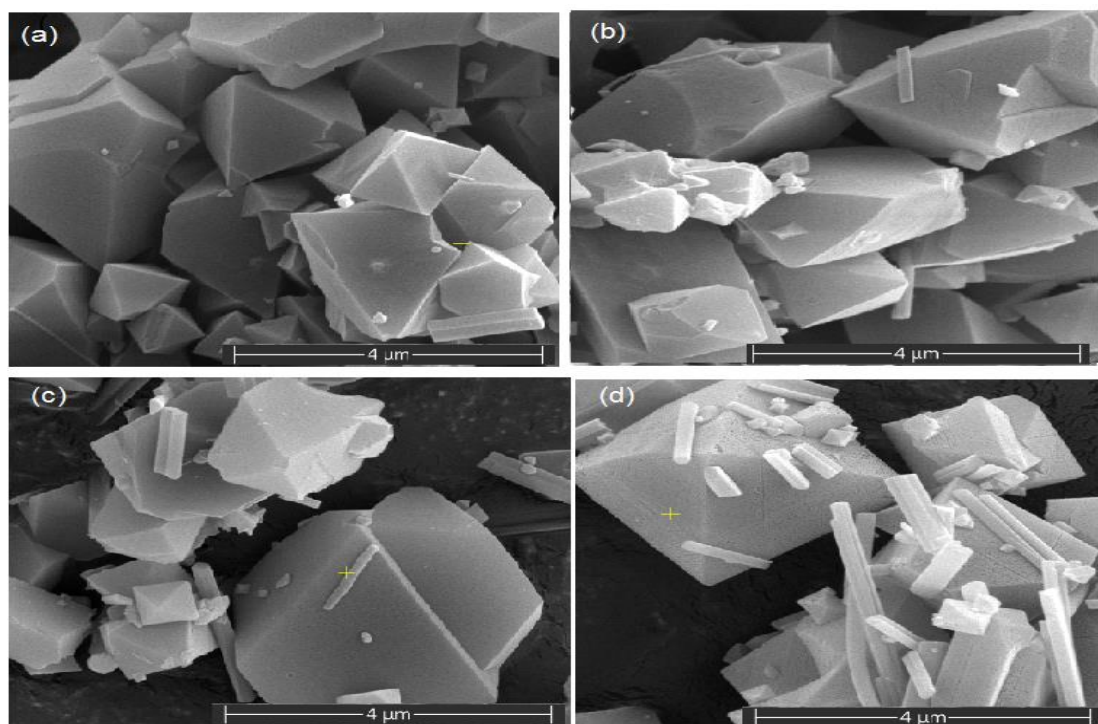


Figure 7.5. SEM images of the materials [a: as-synthesized Cu-BTC, b: Zn(4)/Cu-BTC, c: Zn(8)/Cu-BTC, and d: Zn(10)/Cu-BTC]. TEM (e-g) images of Zn(4)/Cu-BTC, Zn(8)/Cu-BTC and Zn(10)/Cu-BTC

7.4.6 Catalytic investigation

The performance of the prepared materials for WCO methanolysis for biodiesel production was investigated. The catalytic activities of Cu-BTC and Zn/Cu-BTC catalysts were evaluated at fixed process parameters (catalyst loading of 3 wt% and 16:1 methanol/WCO ratio for 2 hours at 150 °C). Fig. 7.6 depicts the biodiesel conversion using several synthesized catalysts. We found that the biodiesel conversion of Zn/Cu-BTC catalysts was significantly increased in comparison with that of the Cu-BTC (Figure 7.6). This increase in catalytic activity may be attributed to the large pore size and synergistic effect of double metals Cu(II) and Zn(II) on triglycerides molecules, which enhanced the adsorption of bulky triglycerides to reach the active sites during the simultaneous transesterification and esterification reaction. As shown, the biodiesel conversion increased with zinc loading to a maximum of 8 wt.%, after which the WCO biodiesel conversion reduced with further loading. The observed positive trend in the conversion with Zn loading might be linked to the appropriate pore size and the evenly dispersed Zn on the surface of the Cu-BTC. However, the incorporation of 10 wt.% of Zn onto Cu-BTC might block the pore and increase diffusion resistance during the mass transfer reactions, resulting in lower biodiesel conversion. In addition, high loading of Zn might have resulted in the formation of crystals with larger particle sizes, resulting in the agglomeration and eventually, blockage of catalyst pores [372]. Therefore, the optimum Zn loading was found to be 8%. Also, in order to avoid Zn agglomeration on the Cu-BTC support surface and to conserve raw materials, we utilized this Zn(8)/Cu-BTC as the solid acid catalyst for further studies.

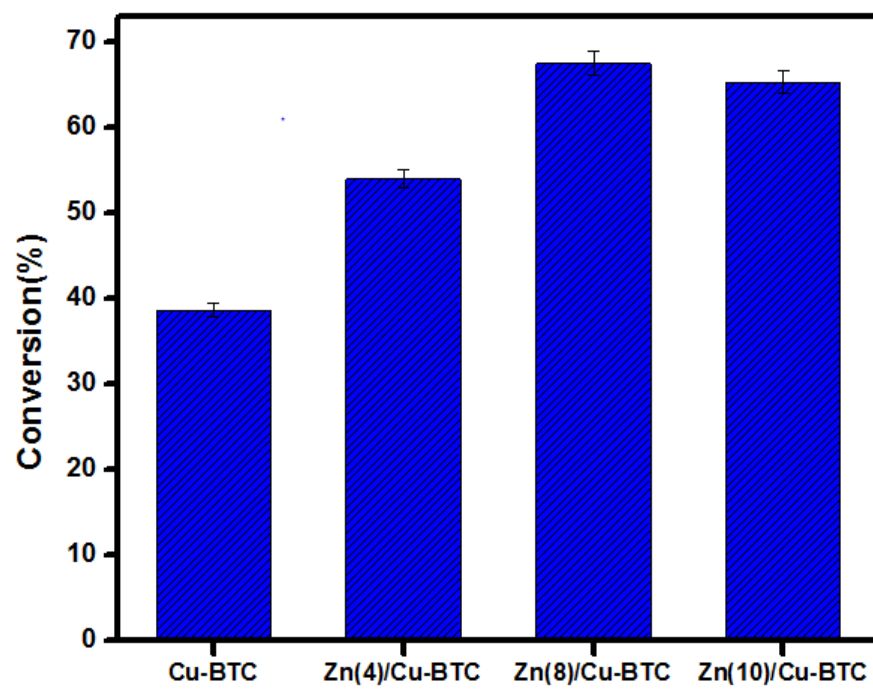


Figure 7.6. Catalysts evaluation for the production of biodiesel.

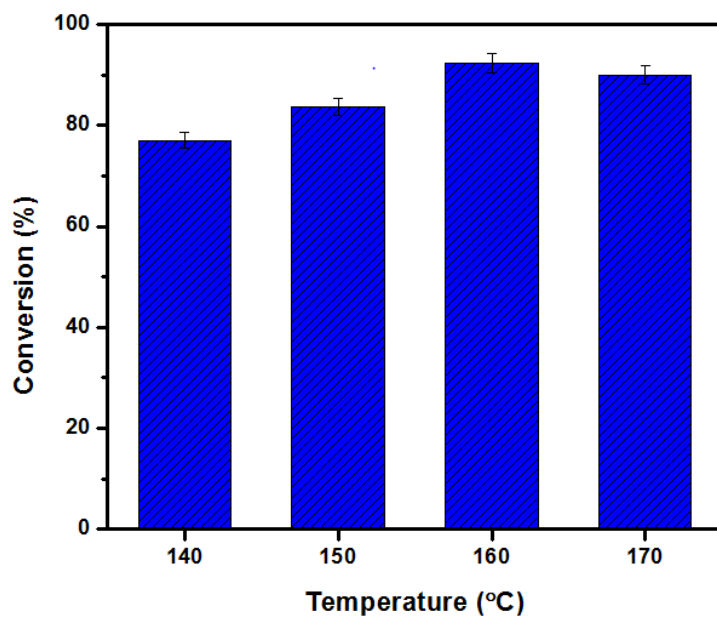
7.4.7 Effect of transesterification conditions

A. Effect of reaction time and temperature

In order to investigate the influence of reaction temperature on the conversion of biodiesel, some experiments were performed using Zn(8)/Cu-BTC catalyst at 140, 150, 160, and 170 °C with a catalyst amount of 4 wt% and methanol/WCO ratio of 20:1 at 4 hours (Figure 7.7a). The results showed that the conversion rate increased with temperature, reaching 92.4% at 160 °C. The rise in temperature raises the reaction rate constant and shifts the reaction to the product side. With increasing temperature, the mass transfer barrier between the catalyst and reactants decreases, allowing reactants to adsorb faster onto the catalyst's surface and diffuse faster into the catalyst's pores. At the temperature higher than 160 °C, the WCO conversion started to decrease marginally. Therefore, 160 °C was selected as the optimal reaction temperature.

The effect of reaction time as a process parameter for biodiesel production was also examined at 160 °C with a catalyst loading of 4 wt% and a methanol/WCO molar ratio of 20:1. As depicted in Fig. 7.7b, the results indicated that the WCO conversion increased with time and reached 92.4% at 4 hours. Longer reaction times allow reactants to permeate into the catalyst (where the reaction takes place). Thus, as reaction time increases, more reactants diffuse into catalyst molecules, resulting in a higher conversion of the reactants and the conversion of the FAME product. When the time rose beyond 4 hours until 5 hours, the WCO conversion decreased. This decrease in catalytic activity could be explained by reverse transesterification that occurs between glycerol and FAME as reaction time increases [228-229]. Hence, 4 hours is considered the optimal reaction time in the present study.

(a)



(b)

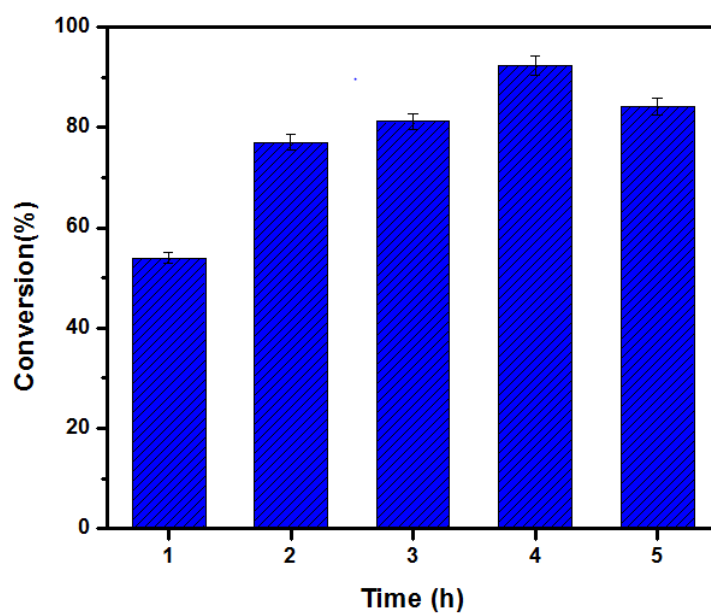


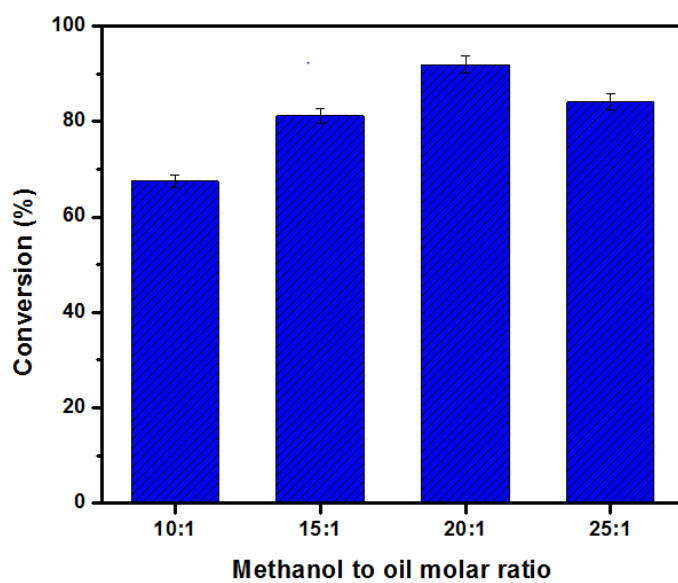
Figure 7.7 (a) effect of reaction temperature and (b) effect of reaction time on the conversion of WCO into biodiesel using Zn(8)/Cu-BTC catalyst.

B. Effect of catalyst loading and methanol to oil molar ratio

The effect of methanol/WCO molar ratio as a process parameter for biodiesel production was also investigated with a catalyst loading of 4 wt% at 160 °C for 4 hours. The results, as depicted in Figure 7.8a revealed that the WCO conversion was improved with increase in the methanol/WCO molar ratio. We observed that when the methanol/WCO molar ratio further increased beyond 20:1, the WCO conversion decreased. This finding indicates that transesterification is not favored by using excessive amounts of methanol. Furthermore, excessive methanol has various drawbacks, including high production costs and increased glycerol solubility in methyl ester, which may hinder the separation of glycerol and biodiesel [229]. Therefore, in this study, 20:1 methanol/WCO molar ratio was chosen as the optimal ratio.

The influence of catalyst loading on WCO biodiesel production was examined under optimal reaction conditions: methanol/WCO molar ratio of 20:1 at 160 °C for 4 hours. The biodiesel conversion increase with the increase of catalyst loading as depicted in Figure 7.8b. An increase in catalyst loading provides more active sites for the reaction, resulting in an increase in biodiesel conversion. When the catalyst loading increased from 2 to 4 wt%, biodiesel conversion steadily increased and reached a maximum of 92.4% (Figure 7.8b). Further increase in catalyst amount presumably decreased the biodiesel conversion due to the poor diffusion of reactants and products [382]. Therefore, 4 wt% is considered as the optimum catalyst loading.

(a)



(b)

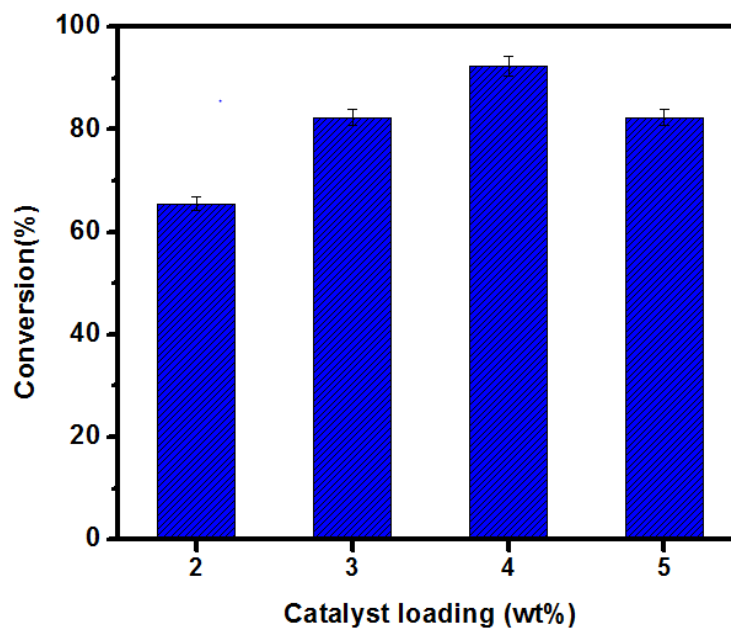


Figure 7.8. (a) effect of methanol to oil molar ratio and (b) effect of catalyst loading on the conversion of WCO into biodiesel using Zn(8)/Cu-BTC catalyst.

7.4.8 Biodiesel Characterization

The WCO biodiesel was characterized by ^1H NMR spectroscopy, and its spectrum is depicted in Figure A.12. The typical signal of methoxy protons was seen as a singlet at 3.65 ppm while a triplet of α -CH₂ protons was observed at 2.26 ppm. These two signals are unique for confirming the presence of methyl esters in biodiesel. Other observed signals were at 5.28 ppm due olefinic hydrogen, a signal at 1.58 ppm related to β -carbonyl methylene protons, a signal at 1.26 ppm related to methylene protons of the carbon chain, and at 0.85 ppm due to terminal methyl protons, which are consistent with the literature report [224,383].

Figure A.13 depicts a representative ^{13}C NMR spectrum of WCO biodiesel. The characteristic peaks of C–O were observed at 51.38 ppm and ester carbonyl (–COO–) at 174.26 ppm. The unsaturation in methyl esters was indicated by the peaks at 131.88 and 127.08 ppm. Other signals at 14 ppm are attributable to the terminal carbon of methyl groups, and signals between 22–34 ppm are ascribed to FAME's long-chain methylene carbons [223-224].

The composition of WCO biodiesel was further investigated using the GC-MS technique to identify the various esters that comprised the sample. Figure A.14 depicts the GC-MS chromatogram while Table A4 lists the biodiesel sample identified components. The sample of biodiesel contained both saturated and unsaturated FAMES

Table 7.2 shows the fuel properties of the biodiesel that was produced along with a comparison to the ASTM D6751 standard. These properties conform to the quality requirements recommended by ASTM D6751, which suggests that the as-produced biodiesel could be used as either a neat fuel or blended with petroleum diesel.

Table 7.2**The properties of the biodiesel in comparison with the ASTM standards**

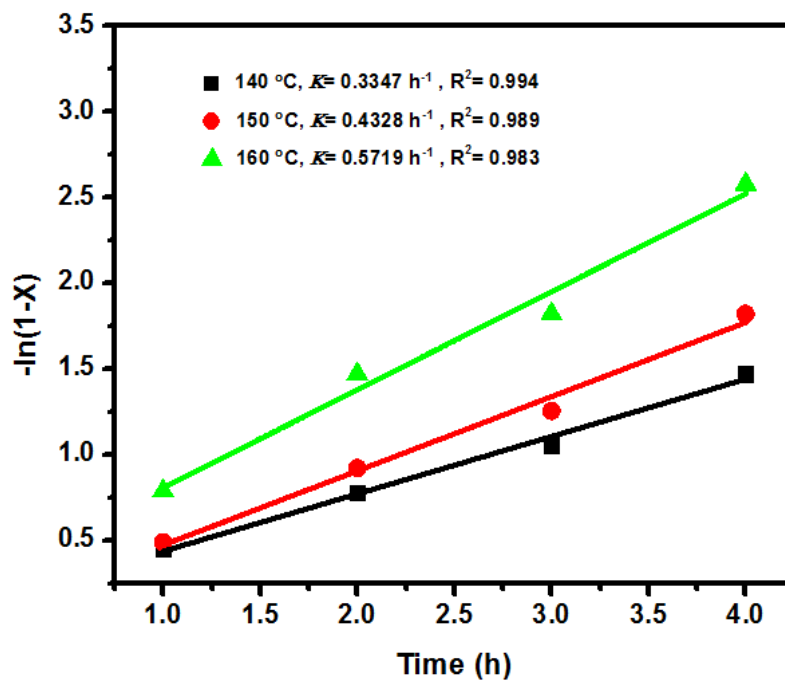
Fuel properties	ASTM method used	ASTM D6751 Biodiesel	Prepared biodiesel
Kinematic viscosity (40 °C, mm ² /s)	D445	1.9-6.0	5.49
Density (40 °C, g/cm ³)	D5002	0.86-0.90	0.876
Specific gravity (40 °C, g/cm ³)	D287	0.88	0.879
Flash point (°C)	D93	100-170	145
Acid value (mg KOH/g)	D664	0.5	0.2

7.4.9 Kinetic studies of biodiesel production

Independent experiments were conducted under the optimum WCO conversion conditions for the kinetic study: methanol/WCO ratio of 20:1, 4 wt% catalyst loading, and reaction temperature was varied in each experiment (140 °C, 150 °C, 106 °C). The reverse reaction may be ignored since methanol was used in excess, and the reaction is assumed to be governed by the pseudo-first-order model [230-231]. Thus, equation (4.1) fits the reaction rate constant, and the Arrhenius equation (4.2) is utilized to compute the activation energy (E_a) needed for the reaction [230].

Figure 7.9a depicts a first-order plot of $-\ln(1-X)$ vs. *time*. The linear regression was used to obtain the k at different temperatures, and it was discovered that k increases with increasing reaction temperature. Due to the improved mass transfer effect, it is obvious that increasing the temperature increases the reaction. According to the Arrhenius plot ($\ln k$ against $1/T$), the E_a of the reaction was 40.33 kJ/mol (Figure 7.9b). Several studies have showed that chemically controlled reactions typically have E_a higher than 25.0 kJ/mol, while diffusion-limited reactions have a lower E_a (10 to 15 kJ/mol) [233,335-337]. Therefore, these findings show that the reaction is chemically controlled in the present study due to the high E_a (40.33 kJ/mol).

(a)



(b)

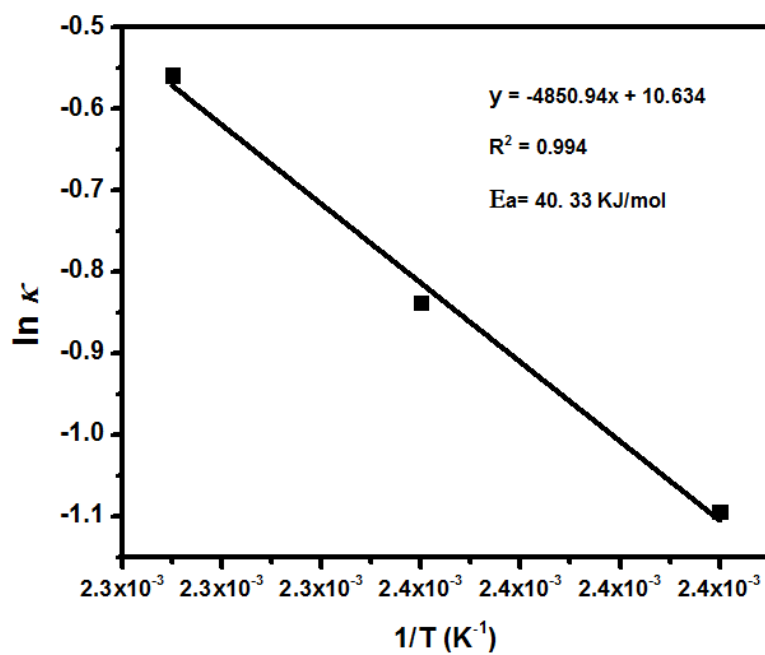


Figure 7.9. (a) A plot of $-\ln(1-X)$ vs. time and (b) An Arrhenius graph showing the relationship between k and $1/T$.

7.4.10 Plausible mechanism

Figure 7.10 illustrates a plausible mechanism for WCO's simultaneous transesterification and esterification. Typically, methanol establish coordination with the metal atom of the catalyst. Triglyceride/fatty acid molecule attached to the Cu atom of the catalyst. The interaction is promoted by delocalization of electron, which forms a resonance between oxygen atoms of the fatty acid/triglyceride. Methanol and triglyceride/fatty acid have positions that are close to each other so that their interaction can occur facilely. The nucleophilic oxygen atom from methanol hydroxyl group then attacks the electrophilic carbon at the triglyceride/fatty acid ester group thus transesterification/esterification occurs. The nucleophilic attack produces glycerol as by-products of the transesterification and water molecule as by-product of esterification reaction. Finally, the produced methyl ester detached from the surface of the catalyst via electron delocalization at the oxygen atom; thus, fatty acid methyl esters as the main product are obtained. After the catalytic process was completed, the active species of the deprotonated catalyst is regenerated for another catalytic cycle.

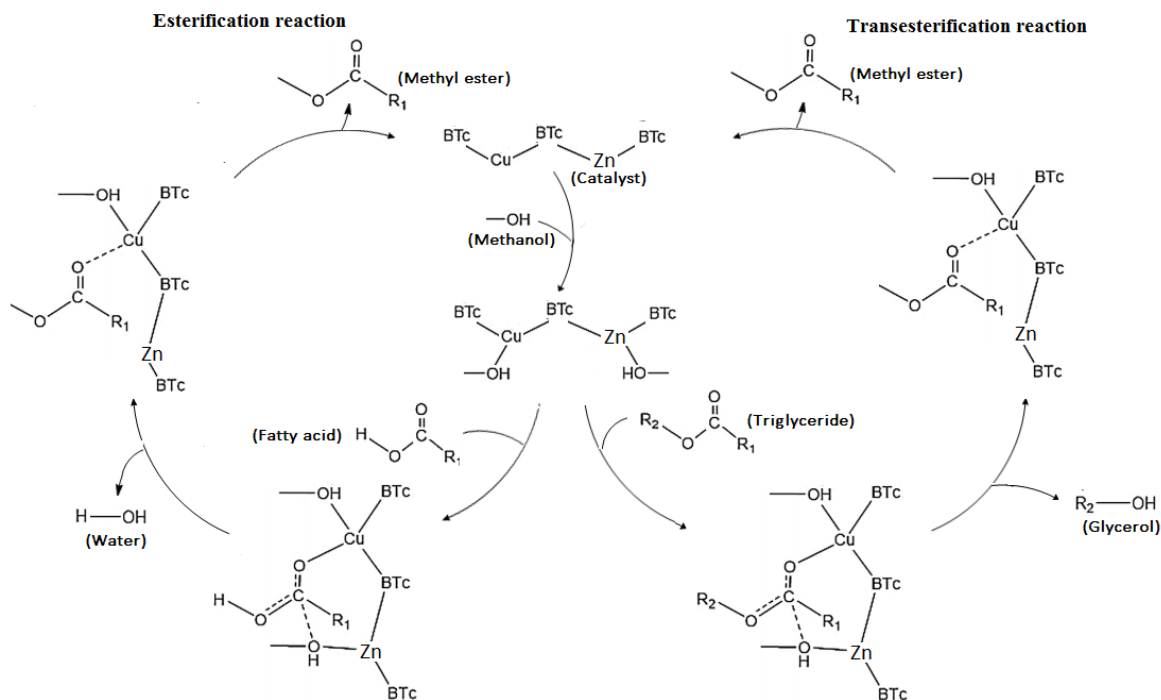


Figure 7.10. Plausible mechanism for the simultaneous transesterification and esterification

7.4.11 Reusability of catalysts

Reusability is an appealing feature in the use of heterogeneous catalysts. After each catalytic cycle, used Zn(8)/Cu-BTC catalyst is regenerated by centrifugation, washed with methanol, oven-dried at 100 °C for 8 hours and then utilized for the next cycle. Therefore, the reusability of Zn(8)/Cu-BTC catalyst was investigated for six cycles (Figure 7.11). We found that even after three reuses, the catalyst activity could maintain a conversion of more than 80%. Nevertheless, the catalytic activity reduced slightly so that at the sixth cycle, the WCO conversion was 73%. To evaluate slight deactivation, XRD analysis was employed to evaluate catalyst stability (see Fig. A.15). According to the characterization result, the XRD pattern of the six recovery catalyst is substantially comparable to that of the fresh catalyst, indicating that the Zn(8)/Cu-BTC catalyst has better recyclability. However, the slight decrease in activity is ascribed to the leaching part of the active species during repeated reactions [384]. The recycling practice demonstrates that Zn(8)/Cu-BTC catalyst is capable of continuous biodiesel production.

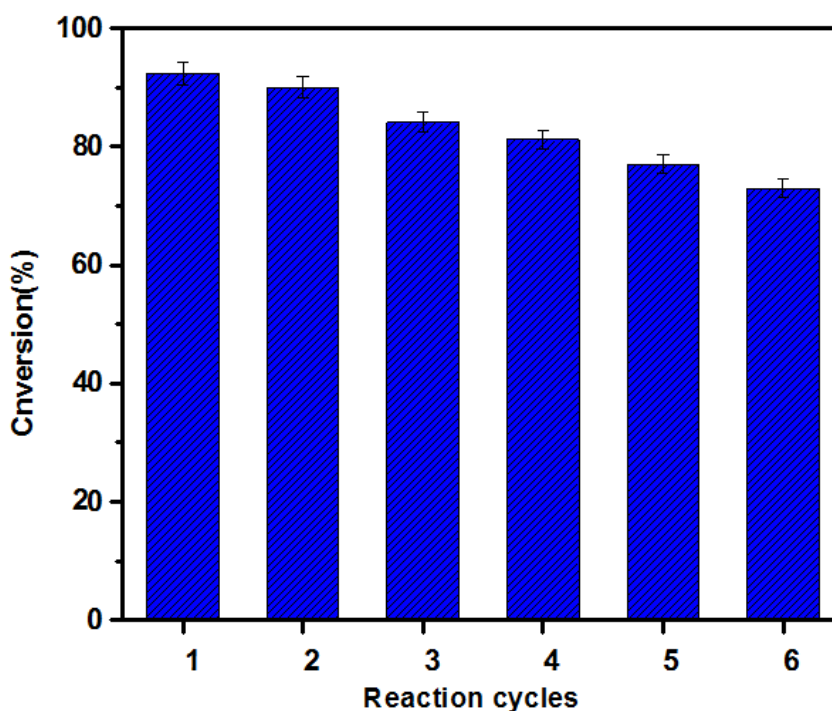


Figure 7.11. Effect of reusability.

Table 7.3 compares the performance of different heterogeneous catalysts in biodiesel production using low-grade/waste oils as feedstock. Our catalysts' performance is comparable to other studies

Catalyst	Operating conditions ^a	Performance	Reference
Cu-MOF + Ca-MOF	1 h, 70 °C, 10 wt.%, 15:1	85% oil conversion	[342]
SO ₄ ⁻² /TiO ₂ -SiO ₂	6 h, 200 °C, 3 wt.%, 16:1	92% oil conversion	[111]
Zn ₃ La ₁	3 h, 200 °C, 2.3 wt.%, 36:1	96% oil conversion	[234]
Sn _{1.5} PW/Cu-BTC	24 h, 160 °C, 7 wt.%, 20:1	87.7% oil conversion	[232]
12-Tungstophosphoric acid supported on zirconia	10 h, 200 °C, 3 wt.%, 9:1	90% FAME yield	[236]
H-ZSM-5	4 h, 100 °C, 10 wt.%, 45:1	55% oil conversion	[132]
H-ZSM-5 (1.0 M citric acid modified)	4 h, 100 °C, 10 wt.%, 45:1	84% oil conversion	[237]
Co-MOF	12 h, 60 °C, 2.5 wt.%, 200:1	83.7% oil conversion	[340]
S-La ₂ O ₃ /Na-Y-800 (S = surfactant modified)	1 h, 70 °C, 10 wt.%, 15:1	84% oil conversion	[238]

CaO/Zeolite	1.25 h, 8 wt.%, 30:1	90.5% oil conversion	[239]
Zn(8)/Cu-BTC	4 h, 160 °C, 4 wt%, 20:1	92.4% conversion	This work

^aThe operating conditions (time, temperature, catalyst amount and molar ratio)

7.5 Conclusion

Zn/Cu-BTC catalysts were successfully developed as the solid catalyst for biodiesel production. Characterization of these catalysts was affirmed using XRD, FTIR, SEM, TEM TGA and N₂ adsorption-desorption. The Zn/Cu-BTC catalysts exhibited excellent catalytic activity in producing biodiesel from WCO due to their high surface area, appropriate pore size and bimetallic synergistic effect. A high conversion of 92.4% was achieved using the Zn(8)/Cu-BTC catalyst under the optimal process conditions (4 wt% catalyst and methanol/oil ratio of 20:1 at 160 °C for 4 hours). From the experimental data, kinetic parameters were obtained. The results show that the reaction followed pseudo-first-order kinetics with an activation energy (E_a) of 40.33 kJ/mol. In addition, the Zn(8)/Cu-BTC catalyst displayed good stability, and after three cycles of reuse, WCO conversion was 84.1%. This study opens the possibility of doping different MOFs with various metal ions, aiming to improve their properties for energy and environmental applications. Thus, Zn/Cu-BTC catalyst has the potential to be utilized in industrial biodiesel production since it is recyclable and capable of converting low grade feedstocks into biodiesel.

CHAPTER 8

Conclusions and Recommendations

8.1 Conclusions

This thesis explored new catalyst that can catalyze simultaneously esterification-transesterification reactions for efficient biodiesel production. The main findings of the work can be summarized as:

1. Metal oxides supported catalysts were successfully synthesized using wet impregnation techniques and were utilized as a solid acid catalyst in the production of biodiesel.
2. Among the studied catalysts (pure β -zeolite, ZnO- β -zeolite and SO_4^{2-} /ZnO- β -zeolite), SO_4^{2-} /ZnO- β -zeolite catalyst offers the highest biodiesel conversion: 96.9%. This promising performance was ascribed to its large surface area, high acidity, and high dispersion of the active phase of the SO_4^{2-} /ZnO- β -zeolite.
3. Desilicated zeolite-supported ZrO_2 catalyst showed high activity for transesterification reaction due to its large pore volume, high surface area, and high dispersion of ZrO_2 on the desilicated zeolite support with improved acidity and high number of active sites: the order of biodiesel conversion among the catalysts is $\text{ZSM-5/ZrO}_2(0.2\text{M}) > \text{ZSM-5/ZrO}_2 > \text{ZSM-5}$.
4. The maximum biodiesel conversion of 90.1% was achieved under the optimum reaction condition with 7%Cu/UiO-66 supported catalyst due to its appropriate pore size, large surface area and the synergistic effect between UiO-66 and copper oxide composite.
5. An optimum loading of 8 wt% Zn species on Cu-BTC supported catalyst improved biodiesel conversion up to 92.4 % due to the high surface area, appropriate pore size and bimetallic synergistic effect of the Zn(8)/Cu-BTC catalyst.

6. The catalytic performance of all the catalysts agreed with their physical and chemical properties as supported by the various techniques including XRD, BET, FTIR, Pyridine-FTIR, TGA, TEM, NH₃-TPD and SEM.
7. The as-produced biodiesel properties satisfy the standard fuel specification requirements of ASTM6751, which suggests that the as-produced biodiesel could be used as either a neat fuel or blended with petroleum diesel.
8. The catalysts displayed good stability and found the catalysts were reusable without much loss of catalytic activity.
9. After comparing the performance of our catalyst with some heterogeneous acid catalysts from the literature, it can be noted that the catalysts exhibited promising activity for biodiesel production.
10. A plausible mechanism has been suggested for the simultaneous transesterification and esterification reactions
11. Kinetic studies show that the reaction exhibits a pseudo-first order kinetic model and activation energies of 38.58 kJ/mol, 32.26 kJ/mol and 40.33 kJ/mol were obtained using $\text{SO}_4^{2-}/\text{ZnO-}\beta\text{-zeolite}$, 7%Cu/UiO-66 and Zn(8)/Cu-BTC catalysts, respectively, this result suggests that the reaction is chemically controlled and not by mass transfer and diffusion constraints.

8.2 Recommendations

The following points are recommended for further research work:

1. An appropriate catalyst synthesis cost estimation method need to be established.
2. The heterogeneous acid catalyzed biodiesel production process should be tested in the presence of co-solvents (e.g., ethanol, THF) and process sustainability study should be conducted for this.
3. Technoeconomic analysis of the process should be carried out to determine a more reliable economic evaluation of the production process.
4. The excess methanol used in the biodiesel production should be recycled properly to reduce biodiesel production cost.
5. It is recommended to prepare the catalyst by equilibrium adsorption method to minimize pore blockage.

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APPENDIX A

ADDITIONAL DATA

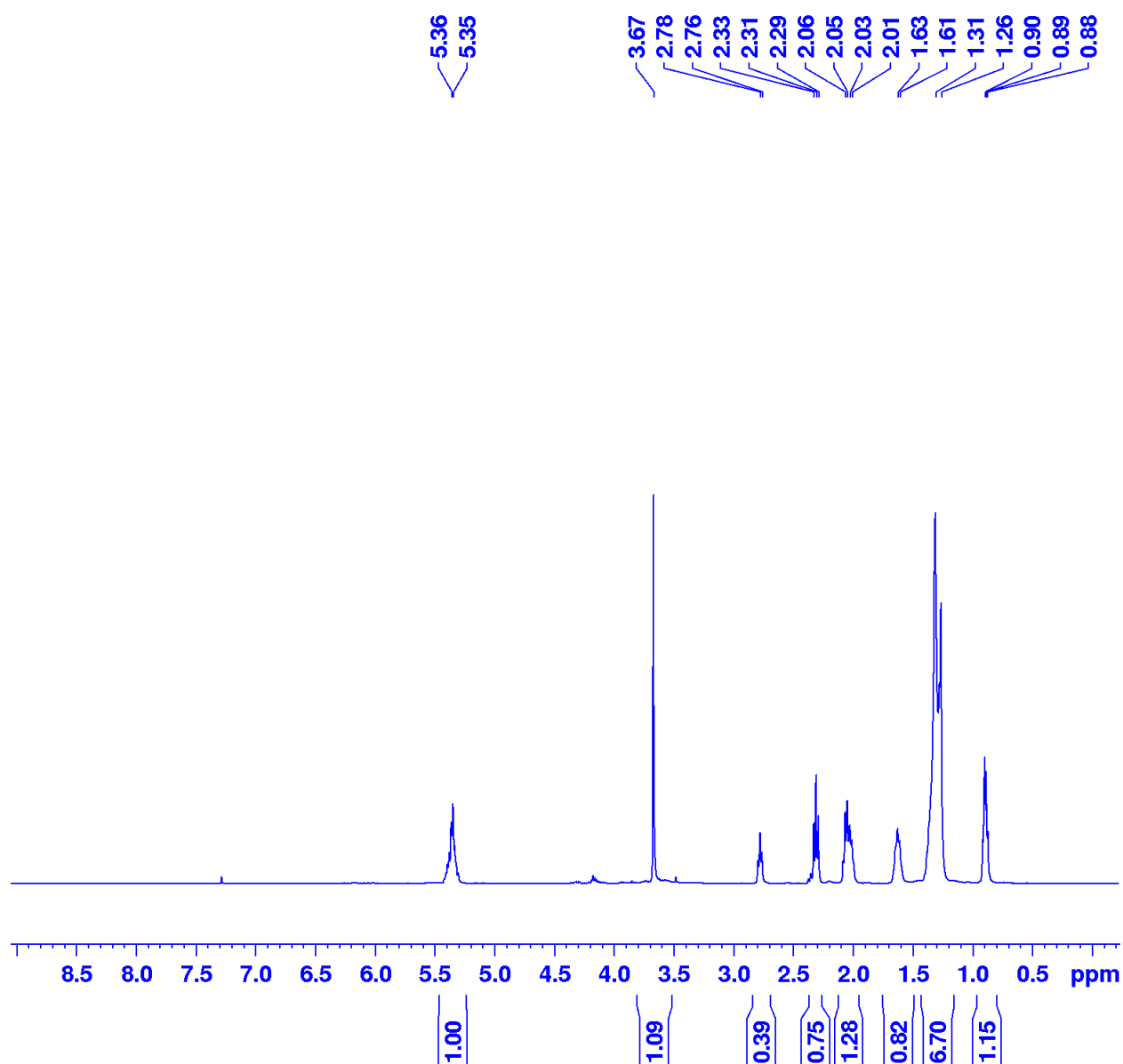


Figure A.1. ^1H NMR spectrum of biodiesel obtained following simultaneous transesterification and esterification with $\text{SO}_4^{2-}/\text{ZnO}$ - β -zeolite catalyst

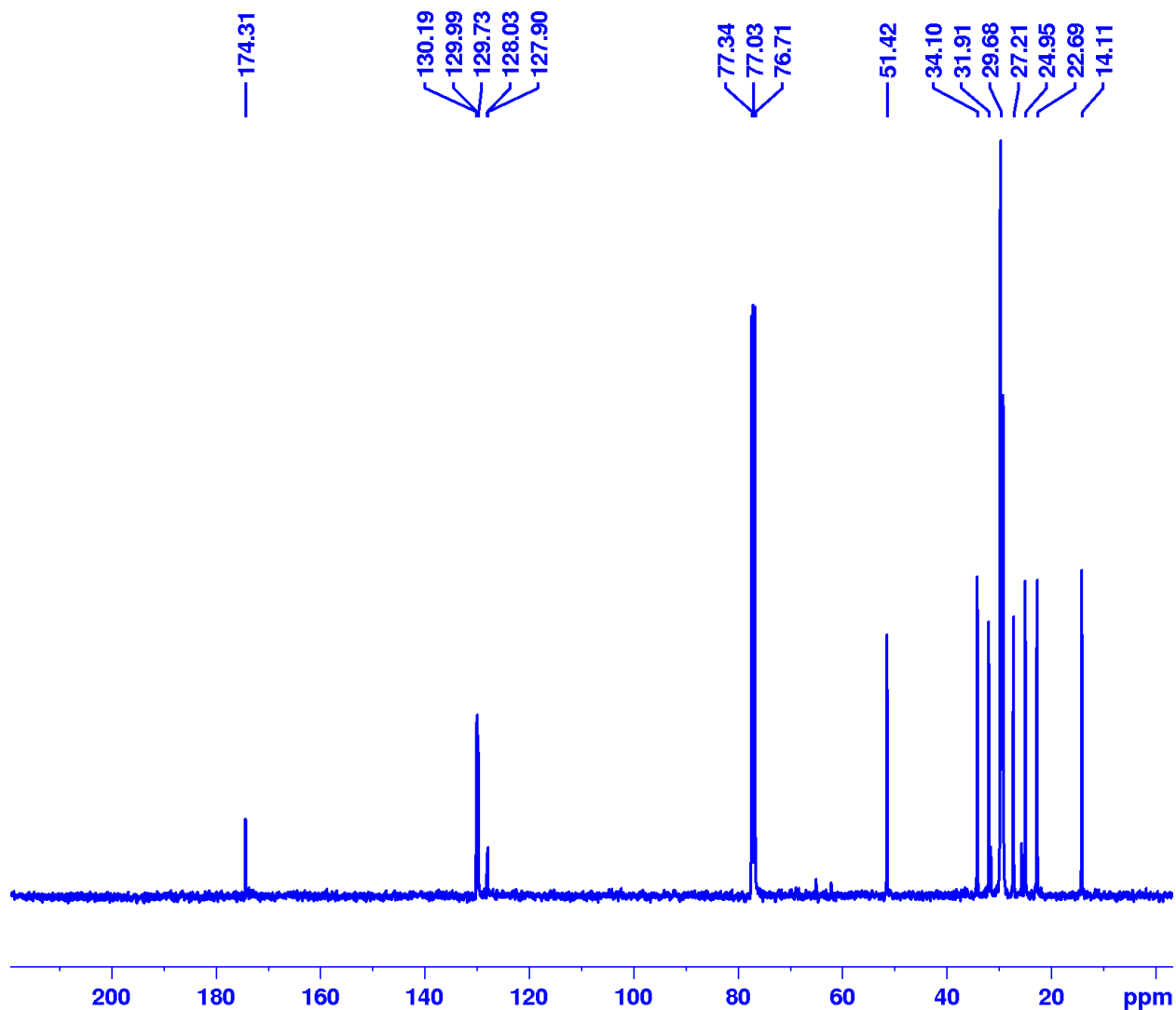


Figure A.2. ^{13}C NMR spectrum of biodiesel obtained following transesterification with $\text{SO}_4^{2-}/\text{ZnO-}\beta\text{-zeolite}$ catalyst

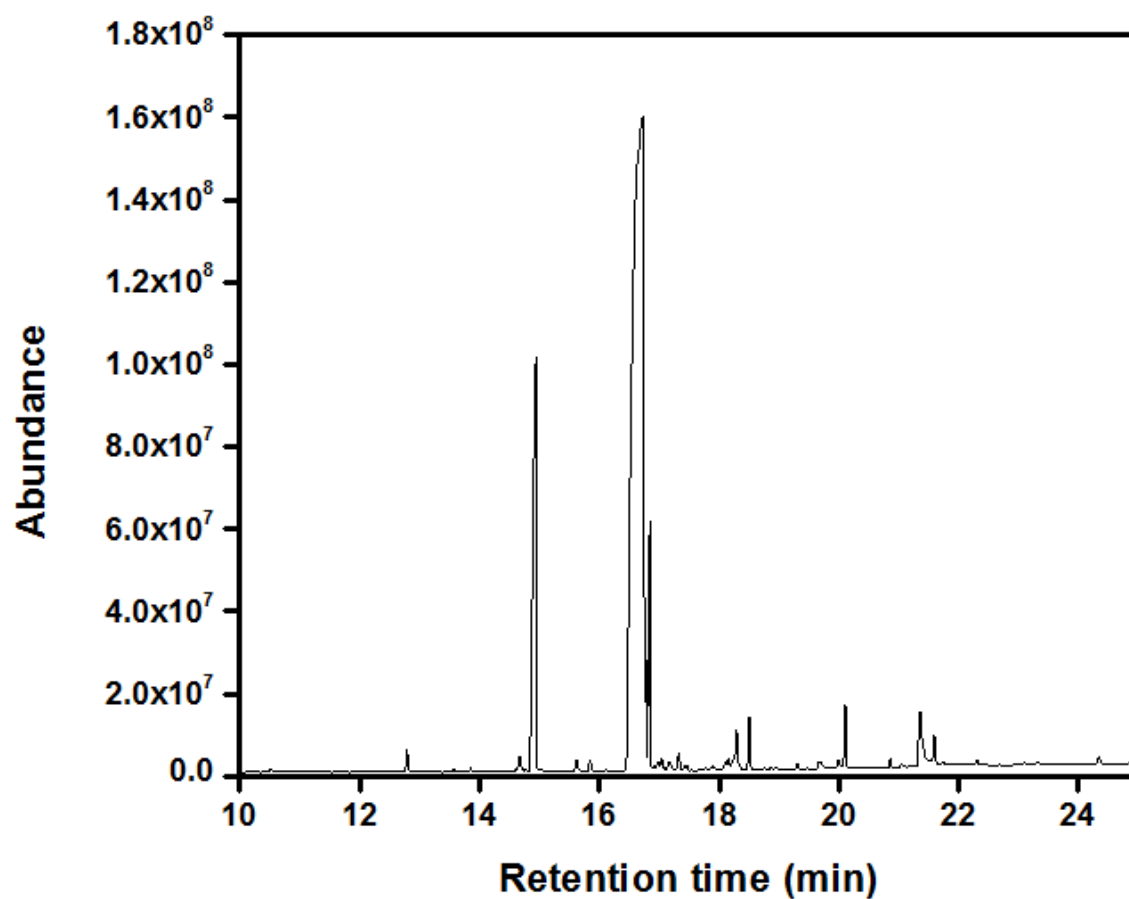


Figure A.3. GC/MS analysis of FAME produced from simultaneous transesterification and esterification of waste cooking oil using $\text{SO}_4^{2-}/\text{ZnO-}\beta\text{-zeolite}$ catalyst under optimal conditions (section 3.4 of the main manuscript): 3 wt.% catalyst loading, 1:15 soybean oil/methanol molar ratio for 8 h at 200 °C. Table A1 below shows what each peak represents

Table A.1. Biodiesel profile obtained following the simultaneous transesterification and esterification of waste cooking oil with $\text{SO}_4^{2-}/\text{ZnO-}\beta\text{-zeolite}$ catalyst

Peak Number	Retention time (min)	Library Match (%)	Compound Name
1	12.80	94	Tridecanoic acid, methyl ester
2	14.67	97	Hexadecanoic acid, methyl ester
3	14.94	94	Pentadecanoic acid, 14-methyl-, methyl ester
4	15.84	98	Heptadecanoic acid, methyl ester
5	16.73	99	7-Octadecenoic acid, methyl ester
6	16.77	93	9,12,15-Octadecatrienoic acid, methyl ester
7	16.84	90	Heptadecanoic acid, 15-methyl-, methyl ester

8	18.29	93	9-Octadecenoic acid (Z)-, methyl ester
9	18.50	95	Nonadecanoic acid, 11-methyl-, methyl ester
10	20.10	96	Docosanoic acid, methyl ester
11	20.86	99	Tricosanoic acid, methyl ester

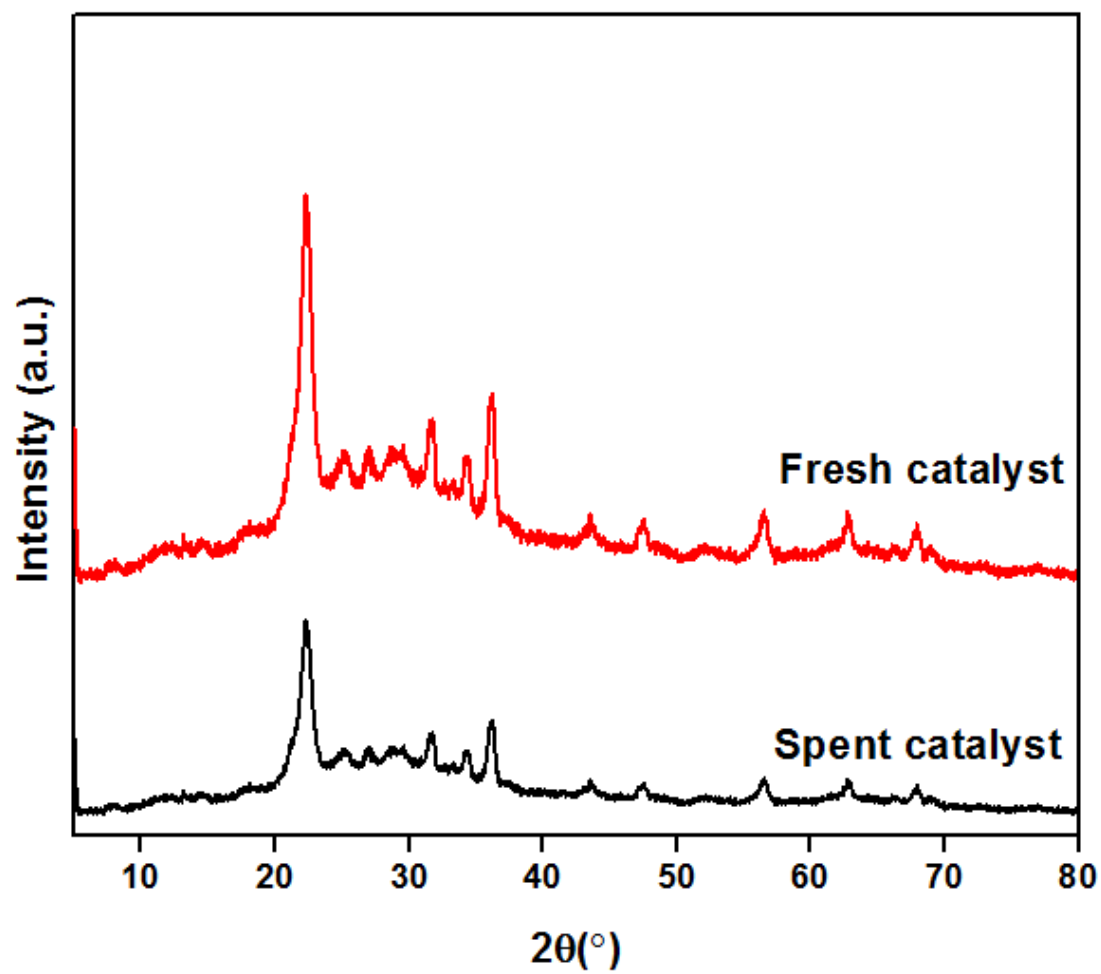


Figure A.4. The XRD patterns of the fresh and spent (after five cycles of use) $\text{SO}_4^{2-}/\text{ZnO}-\beta\text{-zeolite}$ catalyst.

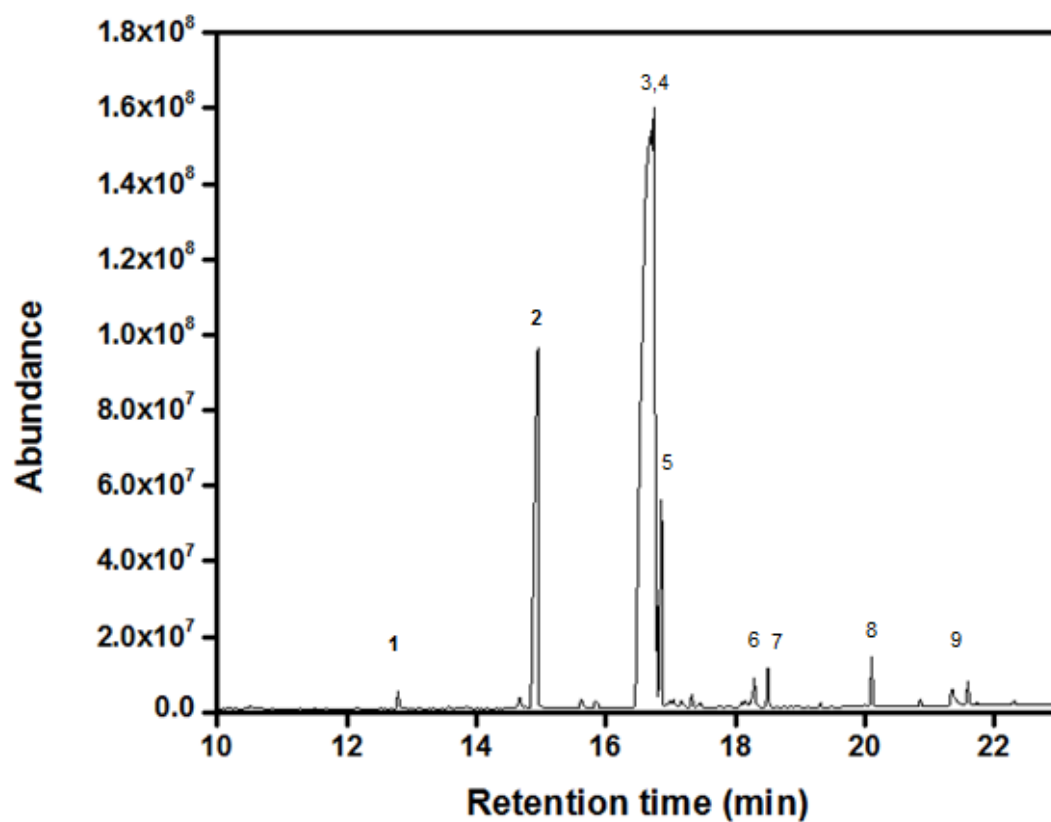
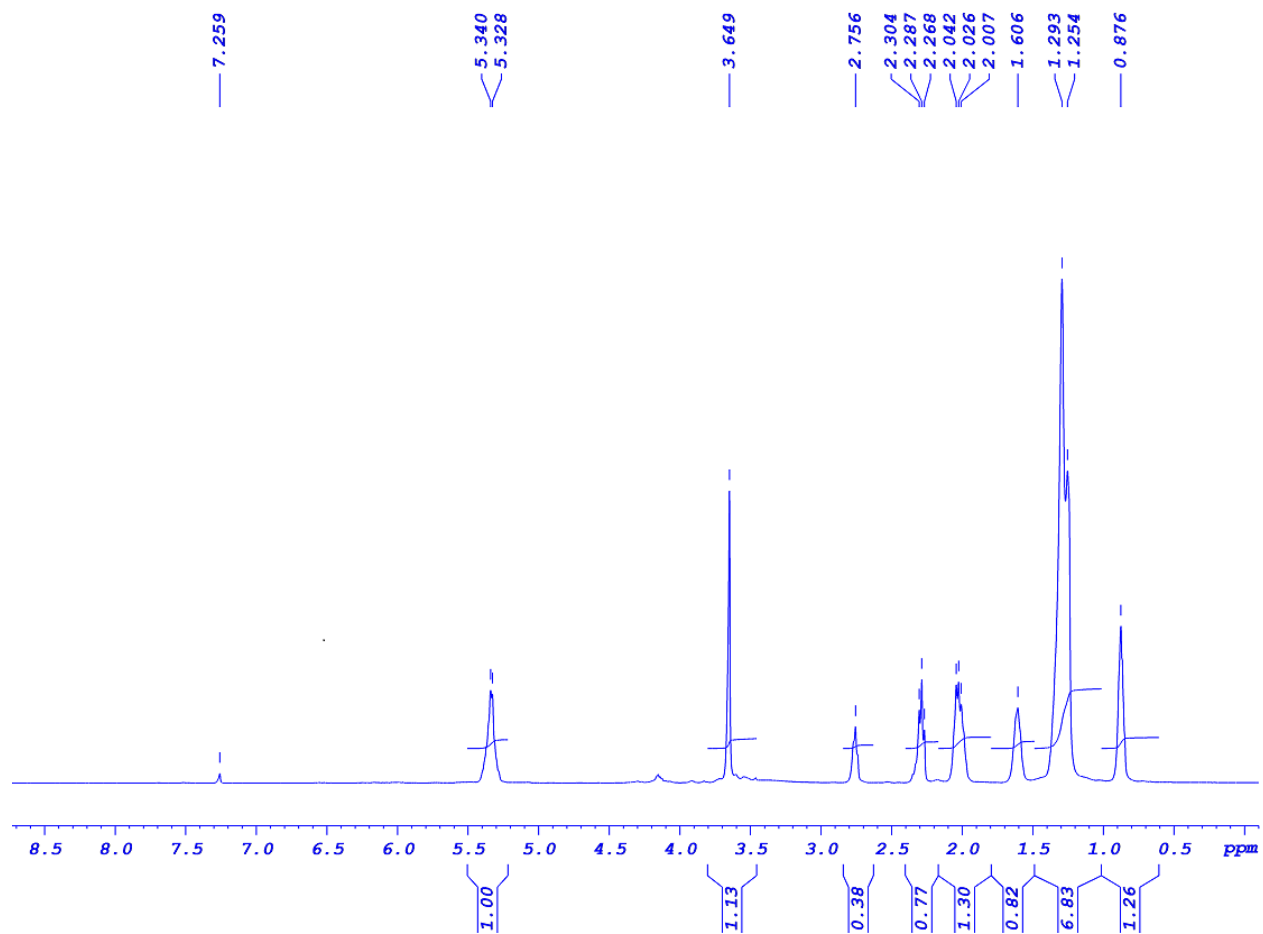


Figure A.5. GC/MS analysis of FAME produced from transesterification of soybean oil using ZrO₂/ZSM-5(0.2M) catalyst under optimal conditions: 1.0 wt% catalyst loading, 1:16 soybean oil/methanol molar ratio for 4 h at 200 °C. Table S1 below depicts what each peak represents

Table A.2. Biodiesel profile obtained following the transesterification with ZrO₂/ZSM-5(0.2M) catalyst

Peak Number	Retention time (min)	Library Match (%)	Compound Name
1	12.79	93	Tridecanoic acid, methyl ester
2	14.95	93	Hexadecanoic acid, methyl ester
3	16.70	96	9,12-Octadecadienoic acid, methyl ester
4	16.74	99	9-Octadecenoic acid, methyl ester
5	17.17	93	9,12,15-Octadecatrienoic acid, methyl ester
6	18.28	93	9-Octadecenoic acid, methyl ester
7	18.50	91	Nonadecanoic acid, methyl ester
8	20.10	95	Docosanoic acid, methyl ester
9	21.59	99	Tetracosanoic acid, methyl ester

(a)



(b)

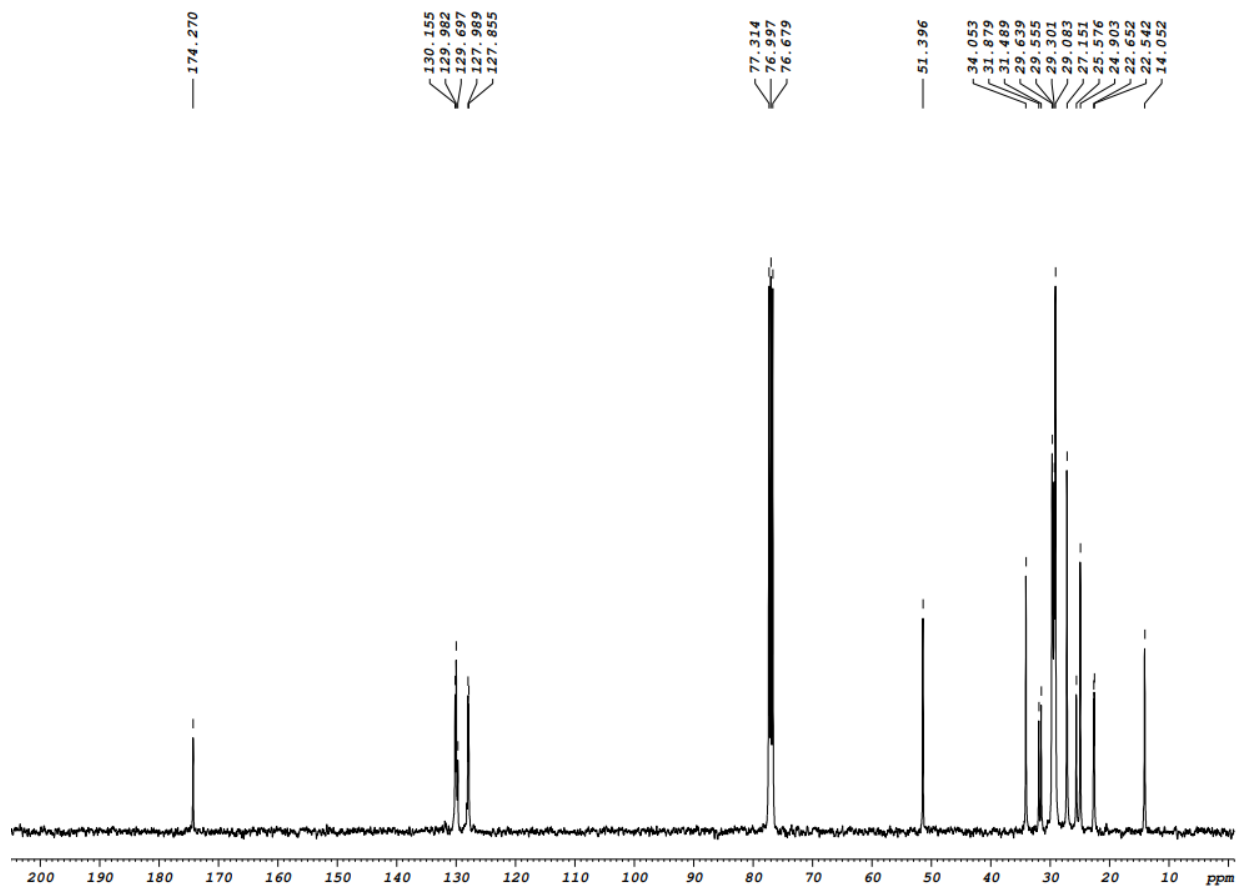


Figure A.6. (a) ^1H NMR spectrum of biodiesel obtained following transesterification with $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalyst; (b) ^{13}C NMR spectrum of biodiesel obtained following transesterification with $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalyst

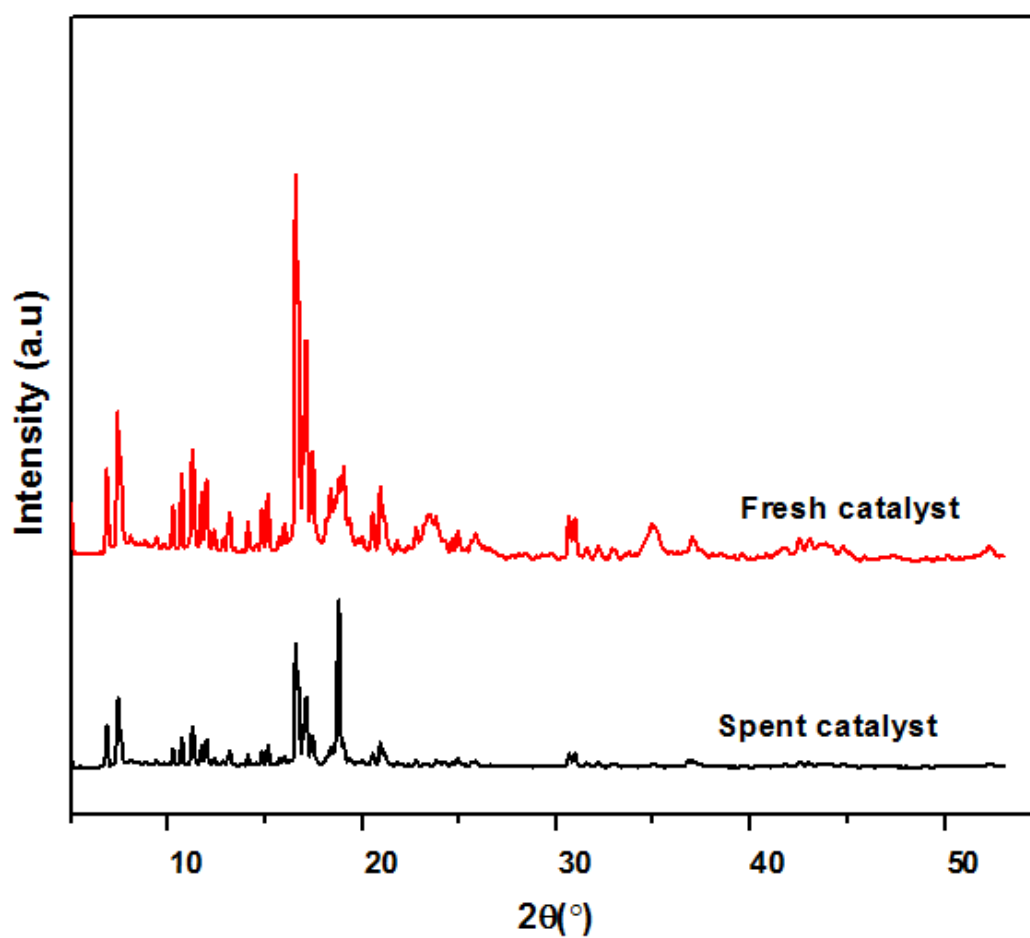
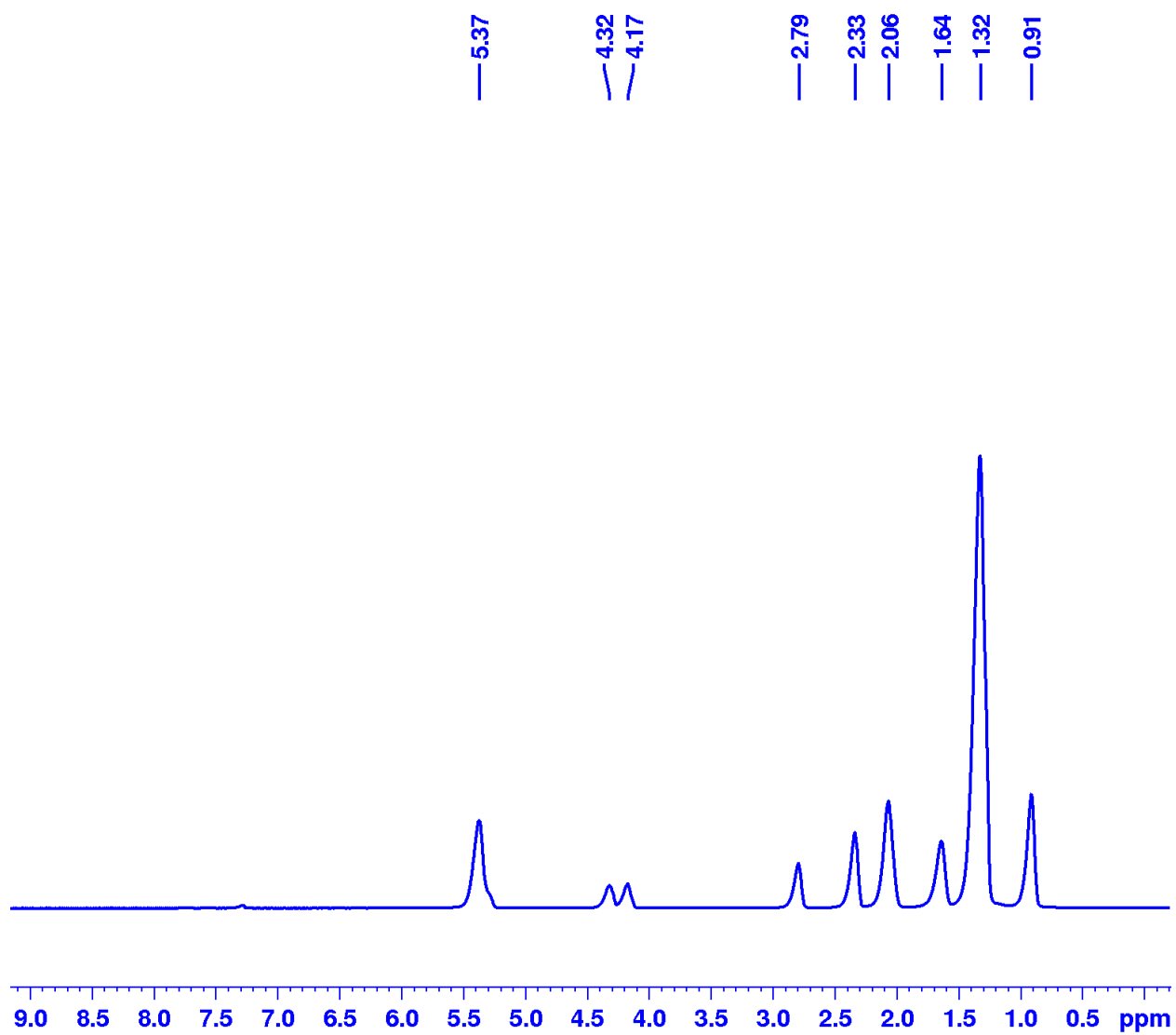


Figure A.7. The XRD patterns of the fresh and spent $\text{ZrO}_2/\text{ZSM-5}(0.2\text{M})$ catalyst.

(a)



(b)

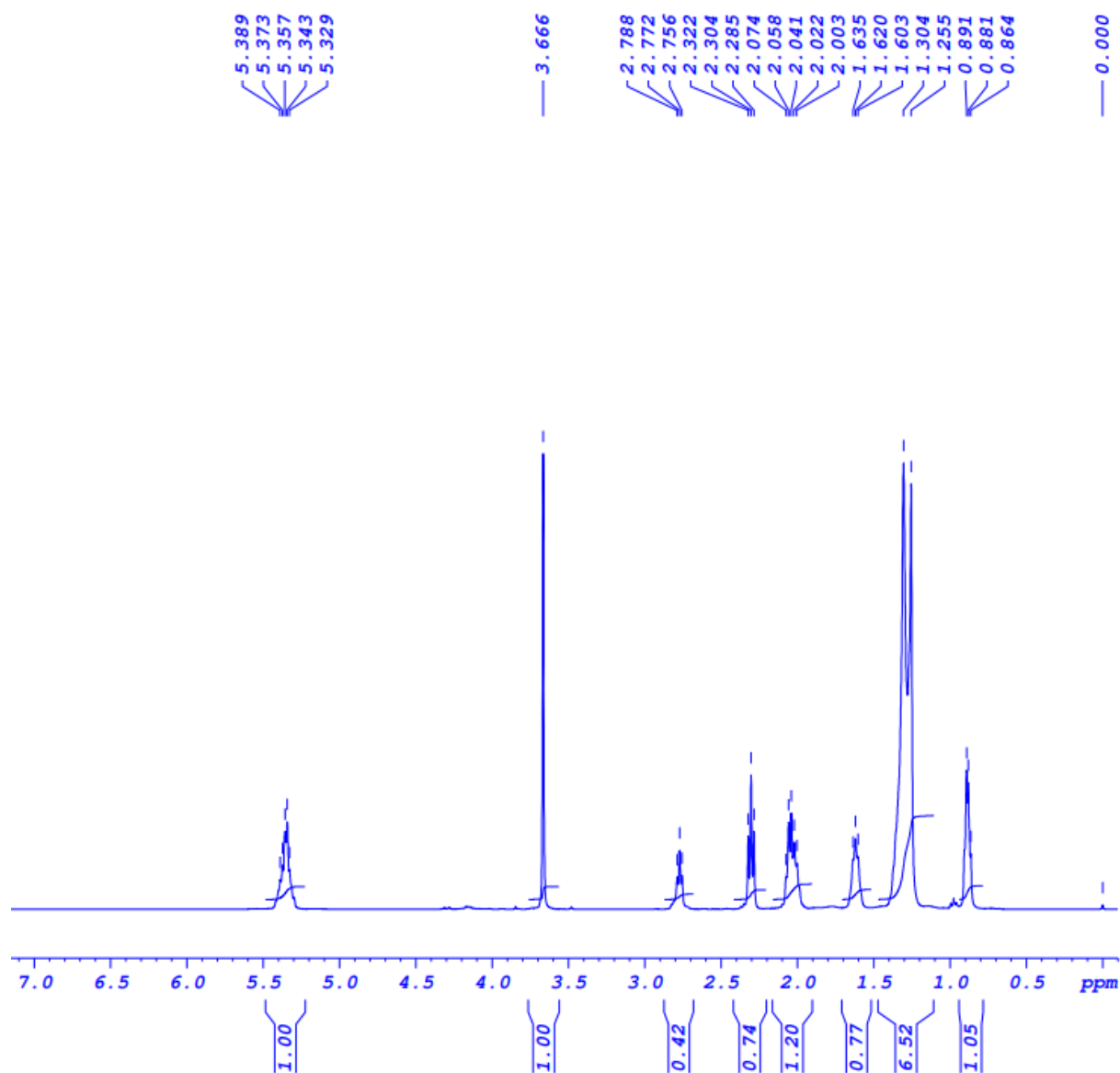
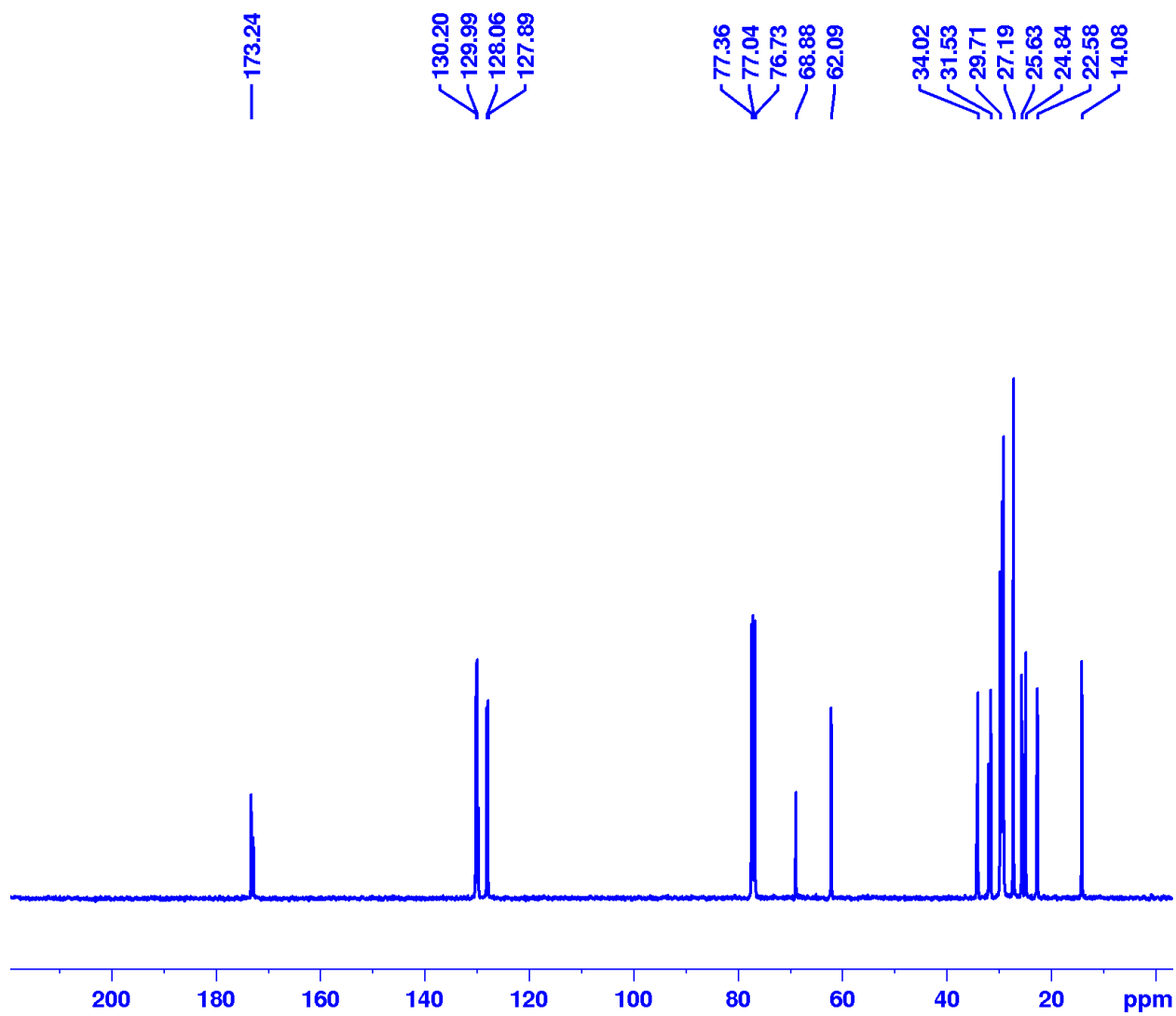


Figure A.8. (a) ^1H NMR spectrum of WCO (b) ^1H NMR spectrum of biodiesel obtained following simultaneous transesterification and esterification with 7% Cu/Uio-66 catalyst

(a)



(b)

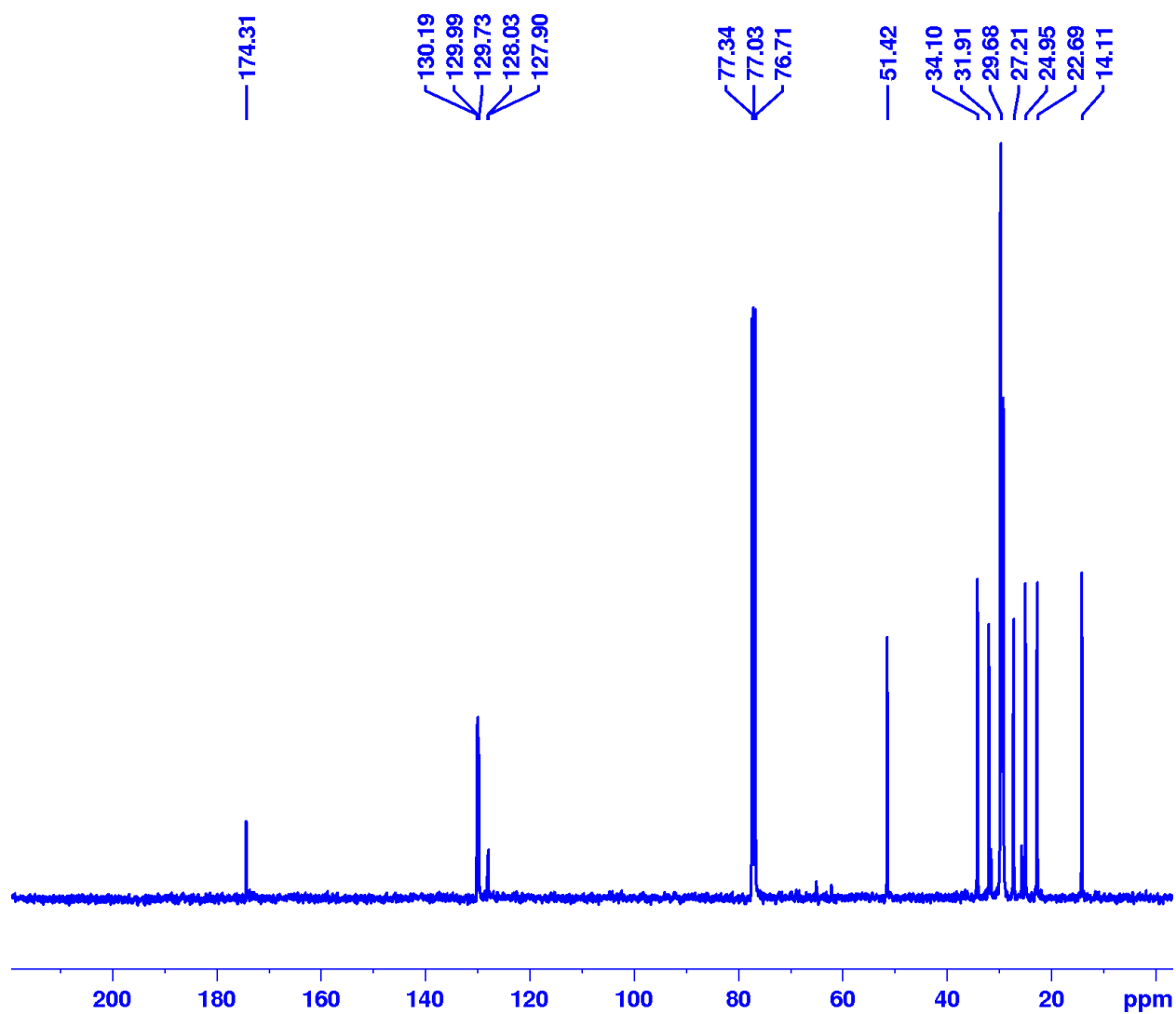


Figure A.9. (a) ^{13}C NMR spectrum of WCO (b) ^{13}C NMR spectrum of biodiesel obtained following simultaneous transesterification and esterification with 7% Cu/UiO-66 catalyst

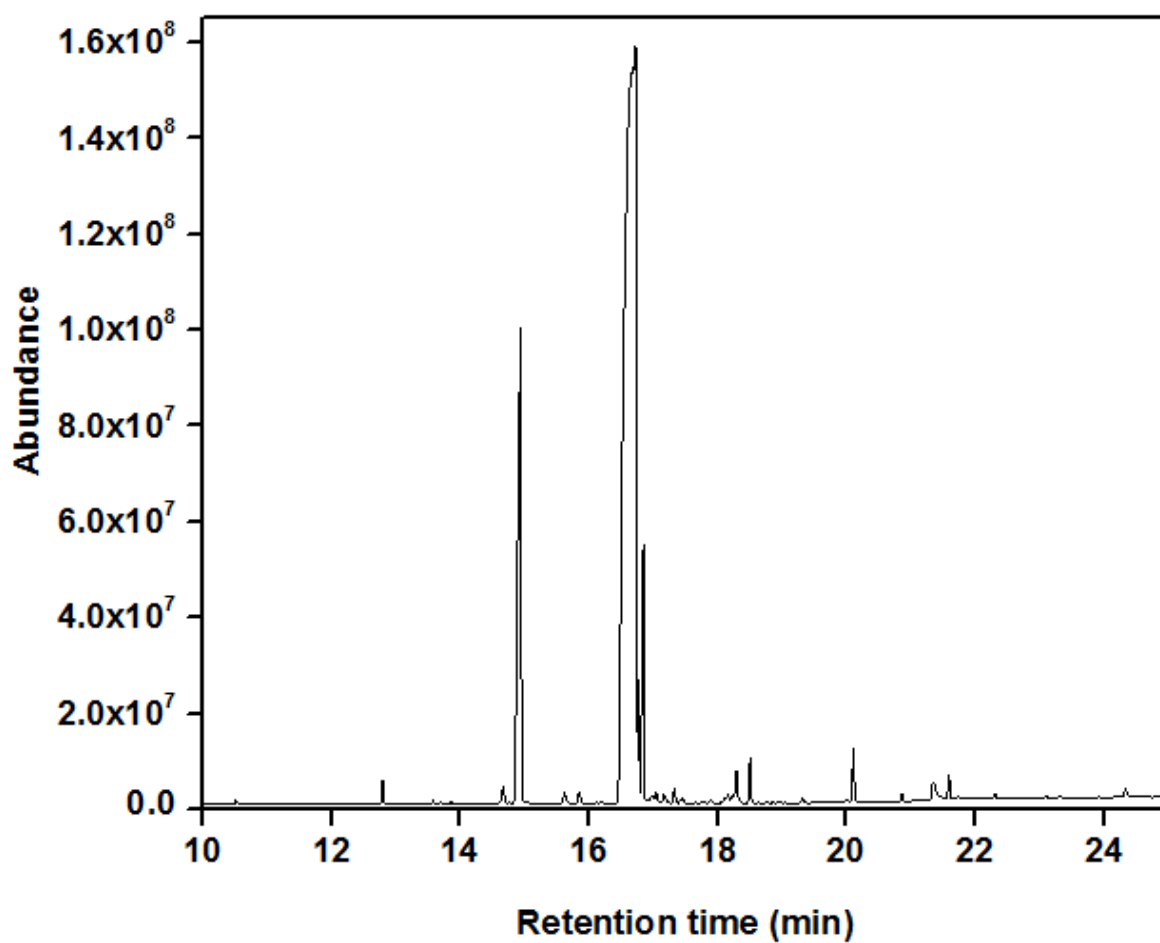


Figure A.10. GC/MS analysis of FAME produced from simultaneous transesterification and esterification of WCO using 7%Cu/Uio-66 catalyst under optimal conditions: 6 wt% catalyst loading, 20:1 methanol/WCO molar ratio for 4 h at 160 °C. Table S1 below shows what each peak represents

Table A.3. Biodiesel profile obtained following the simultaneous transesterification and esterification of WCO with 7% Cu/UIO-66 catalyst.

Peak Number	Retention time (min)	Library Match (%)	Compound Name
1	12.79	95	Tridecanoic acid, methyl ester
2	14.67	97	Hexadecanoic acid, methyl ester
3	14.93	93	Pentadecanoic acid, 14-methyl-, methyl ester
4	15.84	96	Heptadecanoic acid, methyl ester
5	16.72	99	7-Octadecenoic acid, methyl ester

6	16.77	90	9,12,15-Octadecatrienoic acid, methyl ester
7	16.84	90	Heptadecanoic acid, 15-methyl-, methyl ester
8	18.29	93	11-Eicosenoic acid, methyl ester
9	18.50	95	Nonadecanoic acid, 11-methyl-, methyl ester
10	20.10	96	Docosanoic acid, methyl ester
11	20.86	99	Tricosanoic acid, methyl ester
12	21.59	99	Tetracosanoic acid, methyl ester

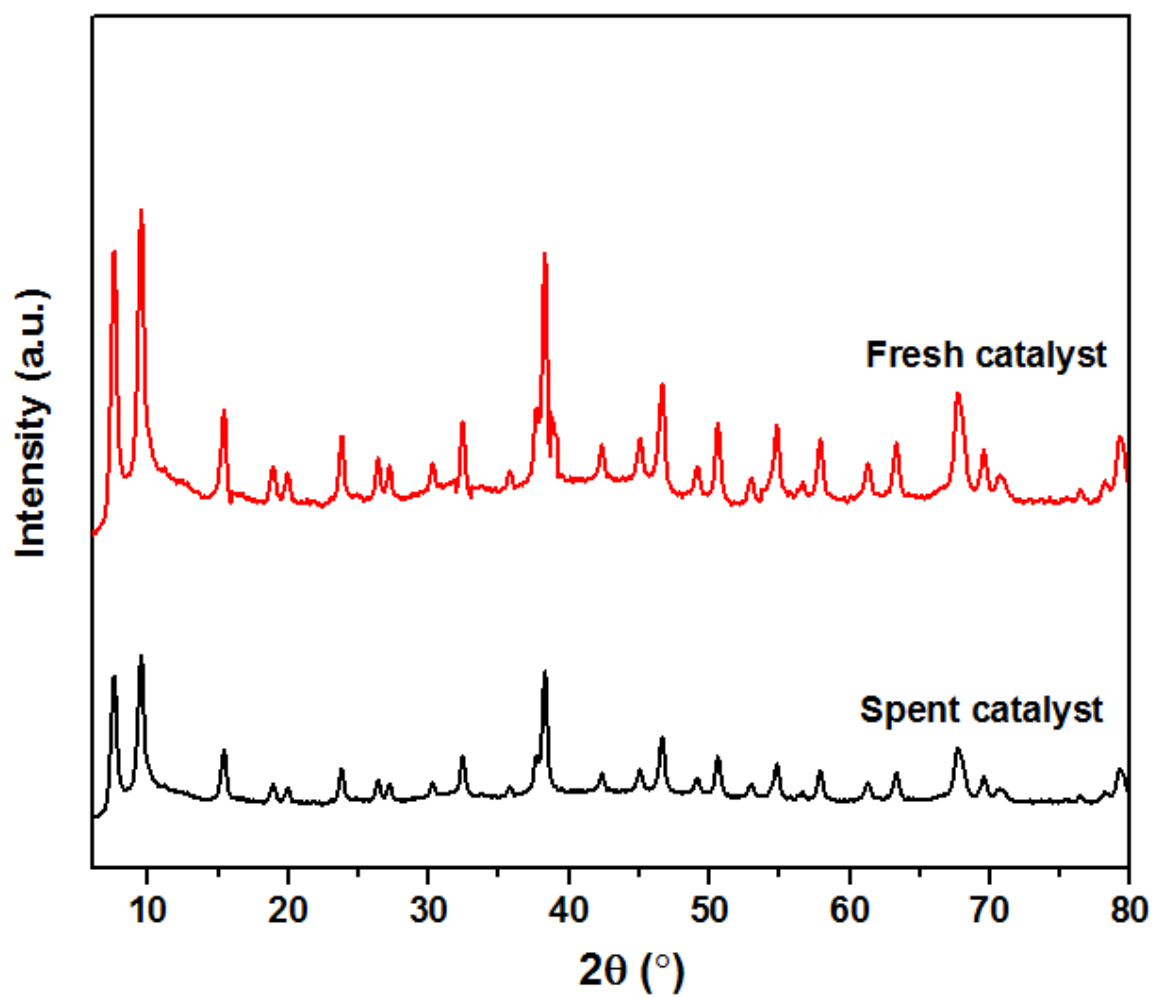


Figure A.11. The XRD patterns of the fresh and spent (after six experiments) 7%Cu/UiO-66 catalyst

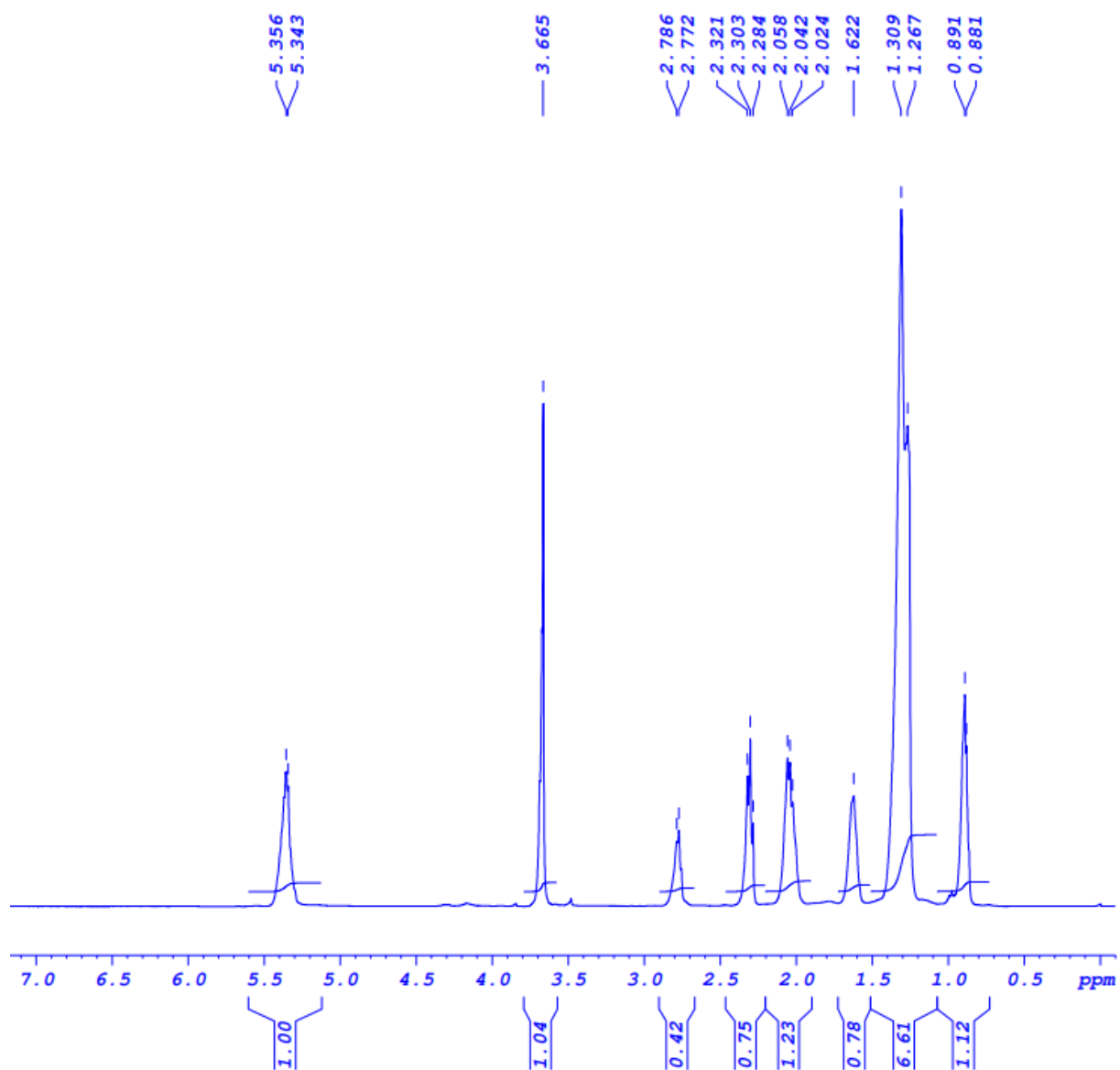


Figure A.12. ^1H NMR spectrum of biodiesel obtained following simultaneous transesterification and esterification with Zn(8)/Cu-BTC catalyst.

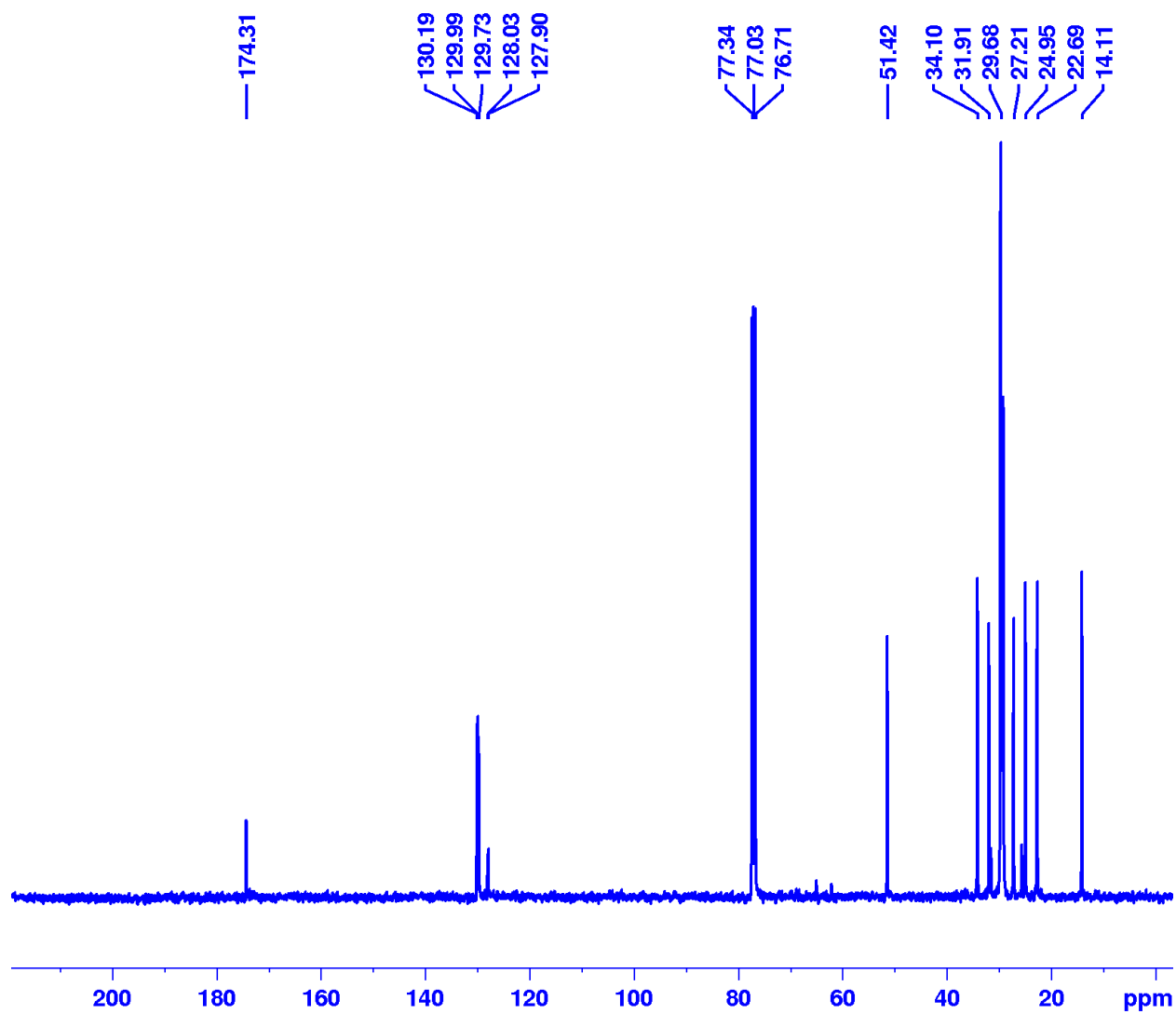


Figure A.13. (a) ^{13}C NMR spectrum of biodiesel obtained following simultaneous transesterification and esterification with Zn(8)/Cu-BTC catalyst

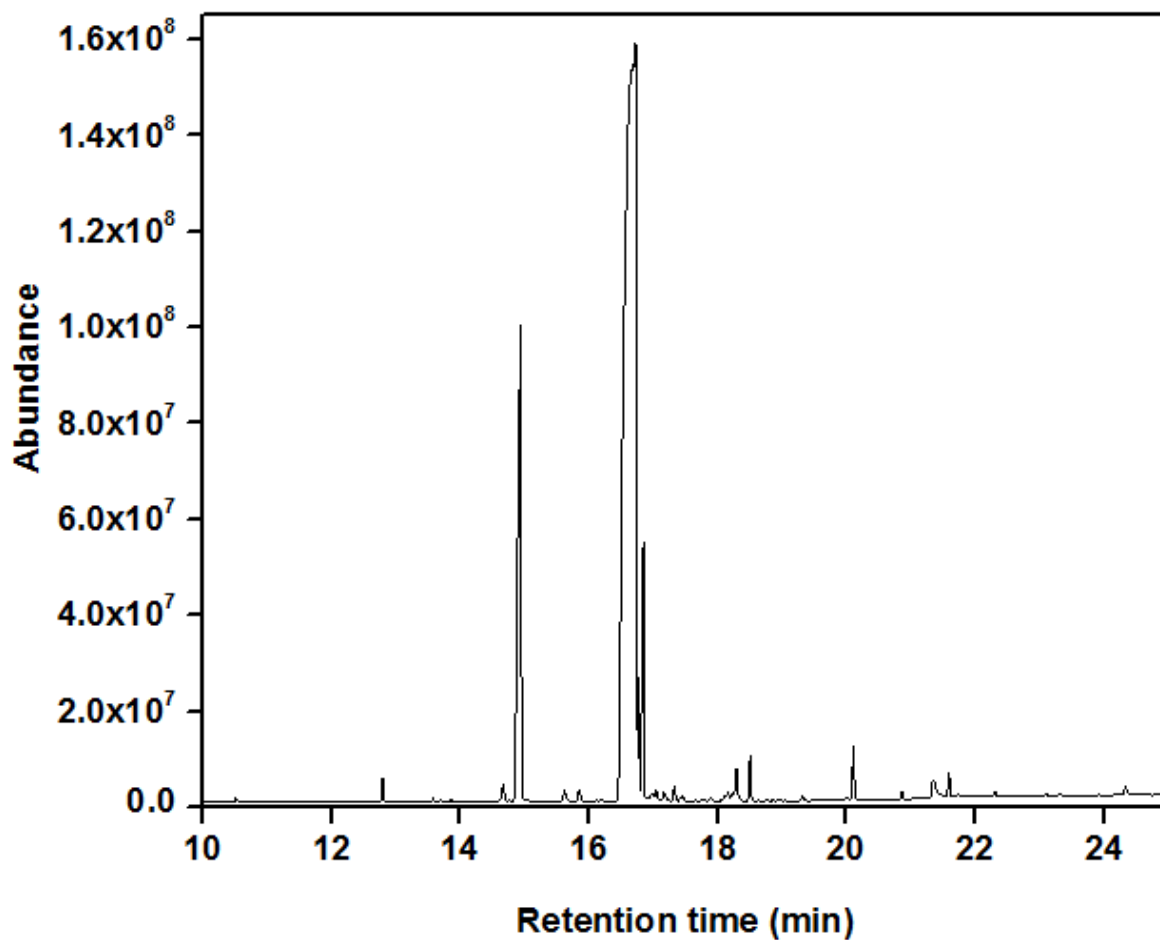


Figure A.14. GC/MS analysis of FAME produced from simultaneous transesterification and esterification of WCO using Zn(8)/Cu-BTC catalyst under optimal: 4 wt% catalyst loading, 20:1 methanol/WCO molar ratio for 4 h at 160 °C.

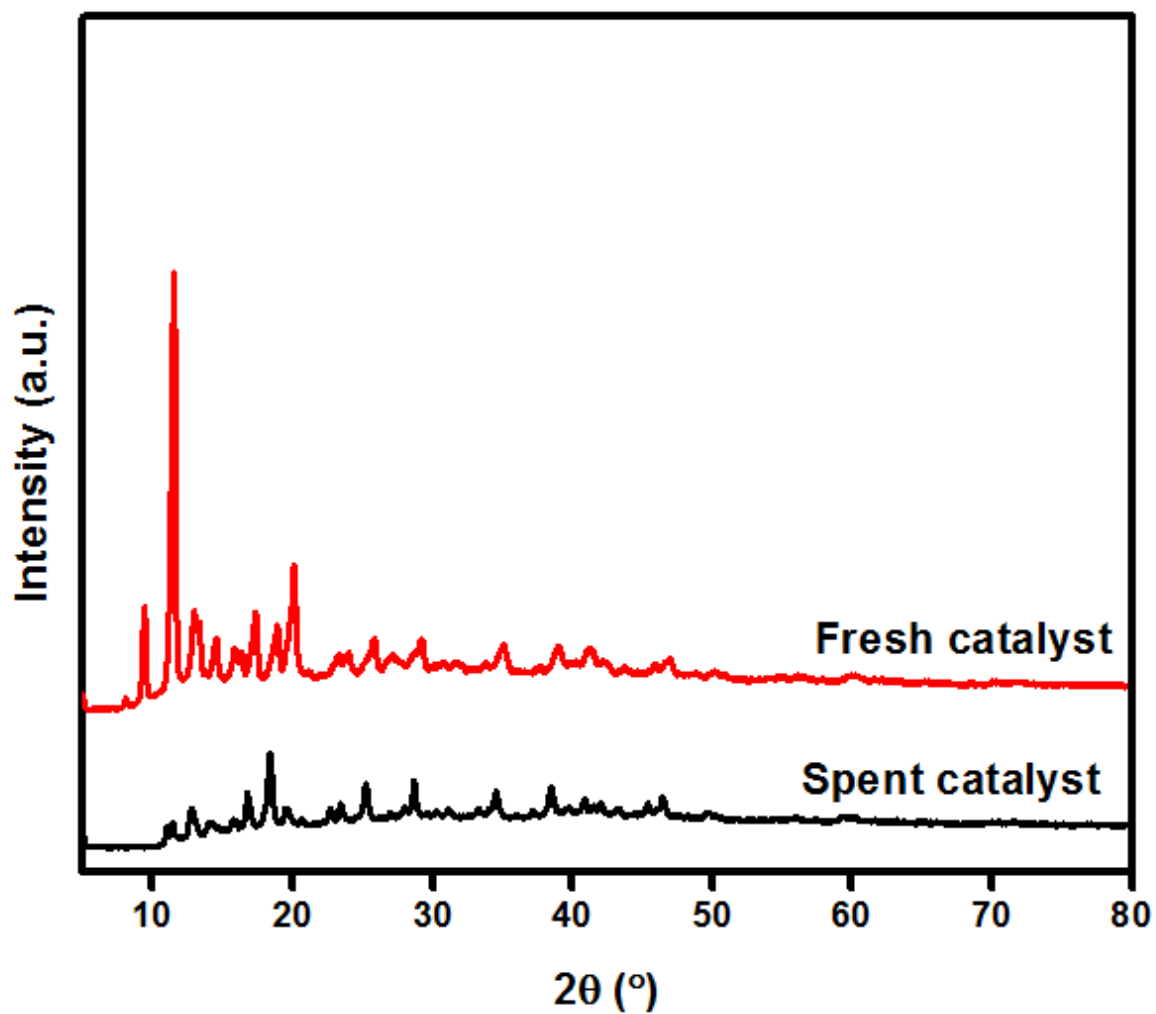


Figure A.15. The XRD patterns of the fresh and spent (after six experiments) Zn(8)/Cu-BTC catalyst.

Table A.4. Biodiesel profile obtained following the simultaneous transesterification and esterification of WCO with Zn(8)/Cu-BTC catalyst.

Peak Number	Retention time (min)	Library Match (%)	Compound Name
1	12.79	95	Tridecanoic acid, methyl ester
2	14.67	97	Hexadecanoic acid, methyl ester
3	14.93	93	Pentadecanoic acid, 14-methyl-, methyl ester
4	15.84	96	Heptadecanoic acid, methyl ester
5	16.72	99	7-Octadecenoic acid, methyl ester
6	16.77	90	9,12,15-Octadecatrienoic acid, methyl ester
7	16.84	90	Heptadecanoic acid, 15-methyl-, methyl ester
8	18.29	93	11-Eicosenoic acid, methyl ester
9	18.50	95	Nonadecanoic acid, 11-methyl-, methyl ester
10	20.10	96	Docosanoic acid, methyl ester

11	20.86	99	Tricosanoic acid, methyl ester
12	21.59	99	Tetracosanoic acid, methyl ester

|

Vitae

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Publications under Review/Preparation

1. Biodiesel production from waste cooking oil via sulfated-metal oxide supported β -zeolite, **B.O. Yusuf**, S.A. Oladepo, S.A. Ganiyu, *ACS Omega*, In Press, **2023**
2. Zr-modified desilicated ZSM-5 catalysts as highly active and recyclable catalysts for production of biodiesel: Insight into improved catalyst properties, acidity and dispersion through desilication, **B.O. Yusuf**, S.A. Oladepo, S.A. Ganiyu, *Fuel*, 351 (2023) 128729
3. Synthesis and evaluation of Cu/UiO-66 metal-organic frameworks as a solid catalyst for biodiesel production from waste cooking oil, **B.O. Yusuf**, S.A. Oladepo, S.A. Ganiyu, A.M.P. Peedikakkal. (Under preparation)
4. Synergy effect of bimetallic in porous MOF matrix for efficient production of biodiesel from waste cooking oils, **B.O. Yusuf**, S.A. Oladepo, S.A. Ganiyu, A.M.P. Peedikakkal. (Under preparation)
5. Use of biocatalysts, homogeneous and heterogeneous catalysts in the production of biodiesel by transesterification: A review, **B.O. Yusuf**, S.A. Oladepo, S.A. Ganiyu. (Under preparation)

General Publications

1. “Concentration-Dependent Study of Nucleic Acid Blockers Used for Sequence-Specificity Enhancement in Nucleic Acids Detection”, S.A. Oladepo, **B.O. Yusuf**, A. Nzila, S. Saravanan, A. Albaiz, *Arab. J. Sci. Eng.*, In Press, 2023
2. “Comparative Study of Thermal Stability and On/Off Fluorescent Signaling Characteristics of Self-Quenching Smart Probes”, S.A. Oladepo, **B.O. Yusuf**, H. Alzaindeen, *Arab. J. Sci. Eng.*, In Press, 2020.
3. Detection of Several Homologous MicroRNAs by a Single Smart Probe System Consisting of Linear Nucleic Acid Blockers, S.A. Oladepo, **B.O. Yusuf**, *Molecules*, 2019, 24, 3691.
4. Simple Protocol for Sequence-Specific Detection of Mixed-Base Nucleic Acids Using a Smart Probe with NABs. S.A. Oladepo, **B.O. Yusuf**, *Anal. Biochem.* 2019, 568, 53-56.