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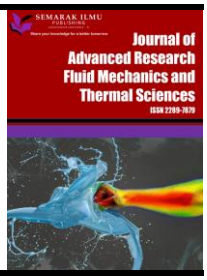

Zno Loaded *Singgora* Roof Tiles as Heterogeneous Catalyst for Waste Cooking Oil Biodiesel

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ABSTRACT

This study aimed to utilize the waste cooking oil (WCO) into biodiesel using a novel waste *Singgora* roof tiles wet impregnated with zinc oxide (ZnO) as a heterogeneous catalyst. The motivation behind this choice stems from the non-recyclable nature of Singgora roof tiles and their potential applicability in biodiesel synthesis. The catalyst was characterized by X-ray Fluorescence (XRF) and scanning electron microscopy (SEM) with energy-dispersive X-ray diffractometer (EDX). A two-step transesterification method was employed to reduce the concentration of free fatty acids (FFA) in the WCO. The process started by treating the WCO with sulfuric acid (H_2SO_4) to diminish the levels of free fatty acid (FFA), followed by the utilization of the *Singgora* roof tiles catalyst in the subsequent step. A maximum yield of 96.96% biodiesel was obtained under the optimal conditions, which included a methanol-to- oil ratio of 12:1, a catalyst concentration of 1 wt.%, a reaction temperature of 65 °C, and a 2-hour reaction time. The quality of the biodiesel produced was analyzed according to biodiesel standards specified in the ASTM D6751, EN 14214, and AOCS, and were within the ranges. The study demonstrates the potential of using *Singgora* roof tiles as a heterogeneous catalyst in biodiesel production, offering a promising approach to repurposing non-recyclable materials and advancing sustainable biodiesel production methods.

1. Introduction

The world's energy needs are growing daily, depleting natural resources like fossil fuels at an alarming rate. In addition, this scenario results in changes to the world's climate, which was thought to be one of the planet's most pressing problems in the twentieth century [1]. Fossil fuels may supply 65% of the world's energy by 2050. The supply of non-renewable fossil fuels is finite and will eventually run out because they were produced from decaying plants and animals millions of years ago. Finding alternative fuels that will reduce the reliance on imported crude oil and contribute to

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sustainable environmental protection is urgently needed. It is advocated that using biofuels or biodiesel will help cut greenhouse gas emissions from industry and transportation [2].

Biodiesel, also known as fatty acid methyl ester (FAME) has several advantages over regular diesel fuel. It comes from long chains of free fatty acids (FFA) of triacylglycerol (TAG) found in oils from both edible and non-edible sources, like animal fats or used cooking oil [3]. Currently, more than 90% of biodiesel is made from conventional biofuels, mainly sourced from food crops such as sugar cane, starch-based ethanol, FAME, straight vegetable oil, and hydro-treated vegetable oil from palm, rapeseed, or soybean oil. To address sustainability concerns, there was a growing use of alternative sources like non-food crop-derived advanced biofuels, which produce fewer greenhouse emissions and do not compete with food crops for land [4]. For biodiesel to be practical, it must have low production costs and be produced on a large scale, where a significant part of the expenses is related to raw materials. To reduce cost costs, using waste cooking oil (WCO) instead of edible oils in biodiesel production is a viable solution [5].

There are several well-established techniques available for making biodiesel fuel. Modifying vegetable and animal fats to reduce their viscosities is necessary to create a product appropriate for diesel engine fuel. This modification can be accomplished through various methods resulting in higher quality of biodiesel. These methods include direct usage and blending, microemulsions, pyrolysis, and transesterification. Transesterification is a commonly used process for producing biodiesel that involves using alcohol typically methanol or ethanol to convert fats or oils. This process is aided by a suitable catalyst. In this transformative process, a range of catalysts, such as homogeneous, heterogeneous, or enzyme catalysts, can be used [6]. Transesterification is also considered the best method to use in biodiesel production because of its high-yield of biodiesel production, low acid value, and compatibility with compression ignition engines [7].

Homogeneous catalysts such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) are commonly used in biodiesel production but come with challenges like difficulty in recycling some of them, excessive costs, and low efficiency, leading to a lot of wastewaters. The utilisation of heterogeneous catalysts has the potential to enhance biodiesel production processes and mitigate certain challenges commonly associated with homogeneous catalysts [8]. Heterogeneous catalysts have garnered significant interest owing to their capacity to generate elevated biodiesel yields and their potential for reusability in contrast to homogeneous catalysts. Heterogeneous catalysts are widely acknowledged as an environmentally friendly technology due to their capacity for facile separation from biodiesel and glycerol via filtration. This separation process removes the necessity for neutralisation and effectively mitigates the environmental consequences associated with the generation of wastewater [9].

This study utilised *Singgora* roof tiles, a clay-based roofing material, as a heterogeneous catalyst to produce biodiesel. The highest concentration components inside the Singgora roof tiles are silica (SiO_2), aluminium oxide (Al_2O_3), and iron (III) oxide (Fe_2O_3) [10]. *Singgora* roof tiles are frequently employed as a roofing material for a diverse range of structures, including palaces, mosques, and private residences. Nevertheless, these tools possess certain constraints, including their thin structure, lightweight, and susceptibility to fracturing. Due to these characteristics, they often end up as construction waste with no possibility for reuse. Nonetheless, the potential of *Singgora* roof tiles as a heterogeneous catalyst for biodiesel production has been largely unexplored. To date, there has been a notable absence of research investigating the use of *Singgora* roof tiles as solid catalysts in biodiesel production. In response to this issue, this study was done to explore the viability of utilizing waste *Singgora* as the main heterogeneous in boosting the performances of biodiesel production from WCO. Thus, this represents the first-ever research endeavour focused on harnessing *Singgora* roof tiles for applications in the biofuel sector.

The use of *Singgora* roof tiles as catalysts in biodiesel production offers a multifaceted approach to environmental sustainability and resource efficiency. Recycling discarded roofing materials, effectively reduces waste and lessens the demand for new resources. This waste repurposing demonstrates efficient resource utilization and waste reduction. Thus, the use of *Singgora* roof tiles exhibits cost-effectiveness compared to synthetic catalysts as they are repurposed from discarded or rejected tiles. *Singgora* roof tiles also consist of unique compositions, often rich in silica that provide a reactive surface area for catalyzing reaction. In this research, the *Singgora* roof was fused with Zinc Nitrate Hexahydrate (Zn $(NO_3)_2.6H_2O$) by the wet-impregnation method as a precursor to produce zinc oxide (ZnO). The wet impregnation method was used for Zn $(NO_3)_2.6H_2O$ as it is highly soluble in water due to its hexahydrate form. Therefore, wet impregnation was effective when dealing with soluble precursors. The two-step transesterification method was utilized in this biodiesel production, starting with oil pre-treatment and transesterification.

2. Material and Methods

2.1 Materials

The raw WCO was obtained from the Hospital Melaka's Dietetic and Food Service Department. The waste *Singgora* roof tiles were collected from a resident's house in Ayer Keroh, Melaka and all the chemicals such as pure methanol (MeOH, 99%), sulphuric acid (H_2SO_4, 98%), and Zinc Nitrate Hexahydrate (Zn $(NO_3)_2.6H_2O$) were supplied by Polyscientific Chemicals Sdn Bhd, Melaka.

2.2 Methods

2.2.1 Catalyst preparation

Sandpaper was employed to clean the surface of the *Singgora* roof tiles, removing any dirt. It is more efficient to use sandpaper as it is easier to remove deposits or impurities, especially when the contaminants have adhered strongly to the surface. Subsequently, the cleaned samples were crushed and ground into a fine powder (< 1mm) using a pestle, mortar, and dry blender. Following that, the *Singgora* powder was subjected to fusion with zinc oxide (ZnO) through the wet impregnation method. The *Singgora* powder was blended with a 1% weight concentration of zinc nitrate hexahydrate (Zn $(NO_3)_2.6H_2O$) in 100 ml of distilled water, and the mixture was stirred for 4 hours. Zn $(NO_3)_2.6H_2O$ was commonly used as a precursor in chemical procedures or catalyst synthesis to produce ZnO because of its eco-friendly and simple method, high potential in producing diverse morphologies of ZnO and more soluble than ZnO in water [11,12]. So, it can provide more uniform distributions of zinc ions on the catalyst support during the wet impregnation process. After that, the sample was initially dried in the oven for 24 hours at 100 °C. Following that, it underwent a calcination process in a furnace, gradually reaching 900 °C with a heating rate of 10 °C/min over 4 hours. This calcination process accelerated the catalytic reaction as the total surface area and the number of active places can be increased on the surface of the catalyst and the Zn $(NO_3)_2.6H_2O$ was converted into ZnO because of the heat treatment [6,13]. All *Singgora*/ZnO catalyst samples were stored in a sealed glass jar to protect them from contaminated by carbon dioxide (CO_2) and moisture. Figure 1 illustrates the flow chart detailing the experimental procedure.

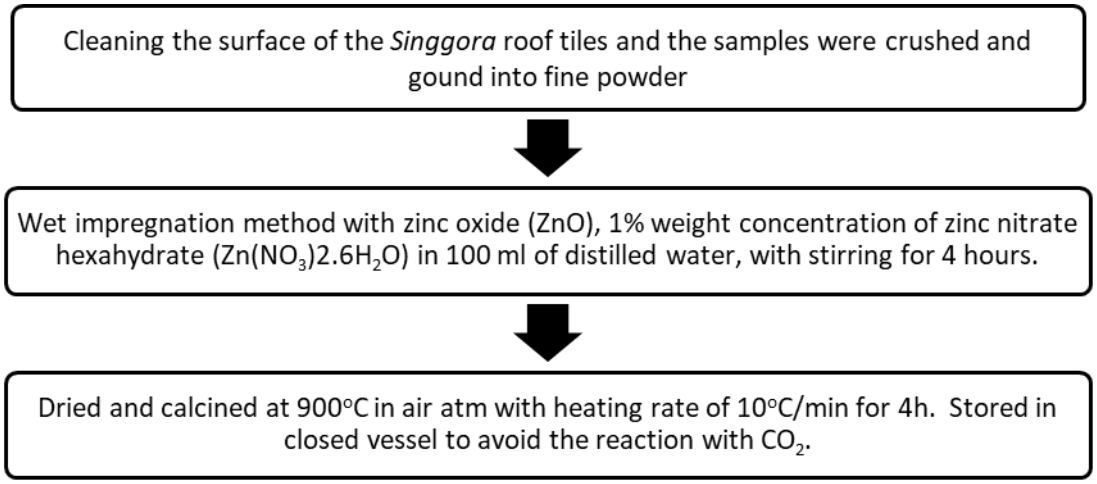

Fig. 1. Catalyst making process flow

2.2.2 Catalyst characterization

The elemental chemical composition analysis of the *Singgora*/ZnO catalyst was tested using X-ray fluorescence spectroscopy (XRF) using the Epsilon3-XL device. Using X-ray equipment, high-energy X-rays were applied to the material, causing inner electrons to be displaced and vacancies to form as a result. These gaps were filled by higher-level electrons that released X-rays unique to each element. These X-rays were analysed by a detector to find the types and concentrations of elements in the substance. XRF has become a popular non-destructive elemental analysis technique in various sectors. Energy Dispersive X-ray spectroscopy (EDX) model JSM-6010PLUS/LV in conjunction with scanning electron microscopy (SEM) was used to investigate the elemental composition and surface morphology of the catalyst. SEM-EDX was a sophisticated imaging and analytical technique that focused an electron beam on the sample. High-resolution images were produced by secondary electrons, and information on the sample's elemental composition was disclosed by X-rays. Using an energy-dispersive X-ray detector, the apparatus measured the energy and intensity of these X-rays, allowing for precise identification and measurement of the constituent components in the material.

2.3 Acid Esterification and Transesterification

The acid esterification or pre-treatment step was utilized to reduce the free fatty acid (FFA) content in feedstock oils to prevent the formation of soap during the transesterification process [14]. The initial acid value of the WCO was 4.26 mg/KOH and the FFA of 2.13%. Previous research by Keskin *et al*., [15] also mentioned that two-step treatment was necessary when the acid value of the broiler rendering fat is 5.2 mg/KOH and the free fatty acid level was higher than 1%. The process was carried out using a conventional heating method. It involved mixing 200 ml of WCO, a 0.375% volume concentration of H_2SO_4 as the acid catalyst, and a 12:1 molar ratio of MeOH to the oil in a beaker. The mixture was stirred at 65 °C for 1 hour [16]. Afterwards, the solution was transferred to a separator funnel and left overnight for the separation of methanol and fats from the oil. After the separation process, the methanol and fats were discarded and the oil was extracted. The oil was filtered by using filter paper to remove any impurities inside the oil. The acid value for this pre-treatment process was reduced to 0.79 mg/KOH.

The transesterification process consisted of several key steps, including pre-heating the raw feedstock, mixing the catalyst with methanol, conducting the transesterification reaction, and then performing separation and filtration [17]. This process also was carried out using a conventional

heating method. The esterification of WCO involved a chemical reaction where triglycerides present in the WCO reacted with methanol in the presence of the heterogeneous catalyst which was *Singgora* roof tiles. The production began with a 1-hour pre-heating of the acid ester oil to eliminate excess water. In a beaker, 100 g of acid ester oil, a 12:1 molar ratio of methanol- to oil, and a 1% weight concentration of *Singgora*/ZnO catalyst (1 g) were mixed and stirred at 65 ˚C for 2 hours in a controlled temperature water bath. Utilizing just a 1% weight concentration of the *Singgora*/ZnO catalyst yields a significant amount of biodiesel, while a 12:1 methanol-to- oil molar ratio was chosen because it delivers optimal results in various conditions. After the reaction was completed, the mixture was filtered with a filter cloth to separate the solid catalyst and the product was transferred to a separation funnel and was left for 24 hours. Following this period, three layers were formed inside the funnel; methanol, biodiesel, and glycerine. The biodiesel was extracted and collected inside an Erlenmeyer flask while the other layers were discarded. The biodiesel oil was filtered to remove any heterogeneous catalyst or other impurities. The final biodiesel product was heated to over 100 °C to eliminate the remaining moisture and methanol [18].

2.4 Biodiesel Characterization

The physicochemical properties of the biodiesel produced were tested according to ASTM D6751, American Oil Chemists' Society (AOCS) and EN 14214. Gas Chromatography-Mass Spectrometry (GCMS) (Agilent Technologies 7890A) was used to analyse the composition of fatty acid methyl ester (FAME) of the biodiesel oil [19]. GCMS works by first separating the components of the sample using gas chromatography and then analyzing those separated components based on their mass-to-charge ratios using mass spectrometry.

3. Result and Discussion

3.1 Catalyst Characterization

This section discusses the results gained from the characterization of the catalyst. The methods used for the characterization process were XRF and SEM-EDX. The details of the results are discussed in the next subsection.

3.1.1 XRF

XRF was used to analyse the elemental chemical composition of the *Singgora*-ZnO catalyst and raw *Singgora* roof tiles. Table 1 shows that silica dioxide (SiO_2) is the predominant mineralogical component at 55.15 wt.% followed by aluminium oxide (Al_2O_3) at 19.18 wt.% and ferric oxide, at 4.825 wt.%. Hassan and Harun [20] also stated that in 2013, the highest compounds found inside the *Singgora* were Silica and Alumina. Both materials are modelled after the *Singgora* clay body, which becomes stronger when fired in a kiln [20]. There was a significant increase and decrease of compounds after being calcined such as SiO_2, Al_2O_3 and Fe_2O_3 and some of the compounds occurred after calcination such as MnO, Y_2O_3, SnO_2, and more. This is because, after calcination, there were some changes on the surface of the catalyst. Hence, there have been refinements made to certain catalyst components. The presence of a higher content of ZnO in the calcined catalyst confirmed the successful execution of the wet impregnation method.

Table 1
XRF Spectrometry of raw *Singgora* roof tiles and calcined *Singgora/*ZnO catalyst

Compound	Concentration (%)	
	Raw *Singgora*	Calcined *Singgora/*ZnO catalyst
SiO_2	29.13033	55.149
Al_2O_3	8.19233	19.177
Fe_2O_3	7.03467	4.852
K_2O	1.53800	1.741
ZnO	0.01023	1.284
TiO_2	0.84300	0.889
P_2O_5	0.15000	0.264
Ag_2O	0.10063	0.069
ZrO_2	0.03897	0.031
BaO	0.02197	0.016
Rb_2O	0.01625	0.015
V_2O_5	0.01322	0.013
Cr_2O_3	0.01382	0.012
Ga_2O_3	-	0.007
Eu_2O_3	-	0.007
PbO	0.01104	0.006
MnO	-	0.006
Y_2O_3	-	0.005
SnO_2	-	0.005
ThO_2	-	0.005
SrO	-	0.004
Yb_2O_3	-	0.004
Nb_2O_5	-	0.003
CuO	-	0.003
As_2O_3	-	0.001
MgO	0.06278	-

3.2 SEM-EDX Analysis

Figure 2 shows the SEM-EDX analysis of raw *Singgora* roof tiles and *Singgora*/ZnO 1% 900˚C. The SEM analysis was used to determine the morphological traits and particle size of the synthesized catalyst and support. While EDX was used to examine the elemental composition of the samples. The SEM image of raw *Singgora* roof tiles (a) appeared as fine and some are moderately flat surfaces. while the SEM image of *Singgora*/ZnO showed some irregular crystallization shapes on the morphology monograph. These changes happened due to the loading of 1% ZnO and calcination at 900˚C. As for EDX analysis, the raw *Singgora* sample revealed a composition of 50.49% of silicon (Si), 8.94% of aluminium (Al), 31.34% of oxygen (O), and 9.23% of potassium (K). As for *Singgora*/ZnO, the elements were Si (49.33%), Al (24.53%), and O (26.14%). Due to the surface cover limitation of EDX, the zinc (Zn) element cannot be detected as the loading was low (1%) and the content may not have dispersed completely over *Singgora*. Therefore, the XRF test was conducted as it can analyse a larger volume of samples.

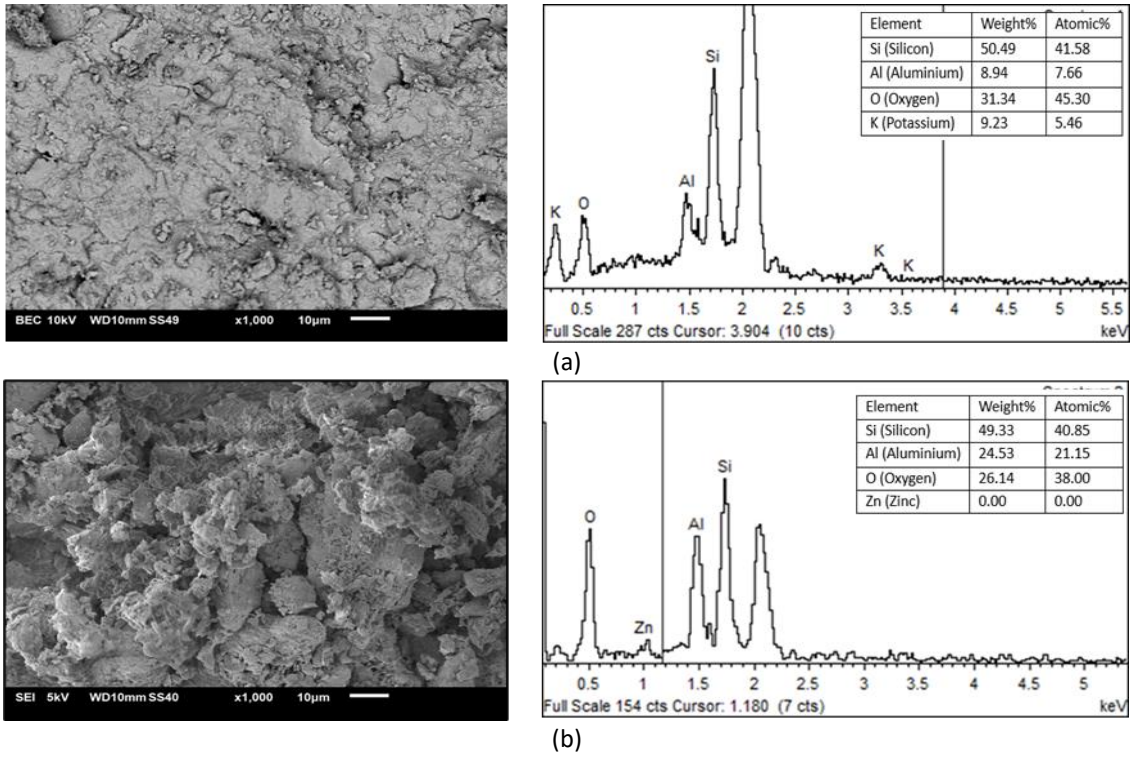

Fig. 2. SEM image and EDX analysis of (a) raw *Singgora* roof tiles and (b) *Singgora*/ZnO 1% obtained by calcination at 900 °C

3.3 FAME Compounds

3.3.1 Gas Chromatography-Mass Spectrometry (GCMS)

All the Fatty Acid Methyl Ester (FAME) compounds of the produced biodiesel identified by the GCMS (Agilent Technologies 7890A) were tabulated in Table 2 while the chromatograph of FAME was illustrated in Figure 3. Significant quantities of oleic, palmitic and linoleic acids are present in the produced biodiesel. The 9-Octadecenoic acid commonly known as oleic acid (C18:1) was found to be the largest compound (40.99%) followed by 38.15% of hexadecenoic acid or palmitic acid (C16:0), and 9.12-Octdecadienoic acid also known as linoleic acid (C18:3) having 10.77% yield. The total of the *Singgora*-ZnO biodiesel yield was achieved at 96.96%. The presence of a higher content of oleic acid monounsaturated in the WCO methyl ester indicated that the produced biodiesel has lower volatility. Conversely, a higher concentration of palmitic acid can significantly increase the cetane number.

Table 2
FAME Composition for B100 *Singgora*-ZnO

#Peak	Retention Time	Chemical Name	Yields (%)
2	13.5372	11-Hexadecenoic acid ME	0.9761
3	13.7505	Hexadecenoic acid ME	38.1489
4	15.5418	9,12-Octadecadienoic acid ME	10.7738
5	15.6092	9-Octadecenoic acid ME	40.9984
6	15.6654	11-Octadecenoic acid ME	1.1533
7	15.8844	Octadecanoic acid ME	4.1742
9	17.4903	Eicopentaenoic acid ME	0.7323
FAME Total			96.96

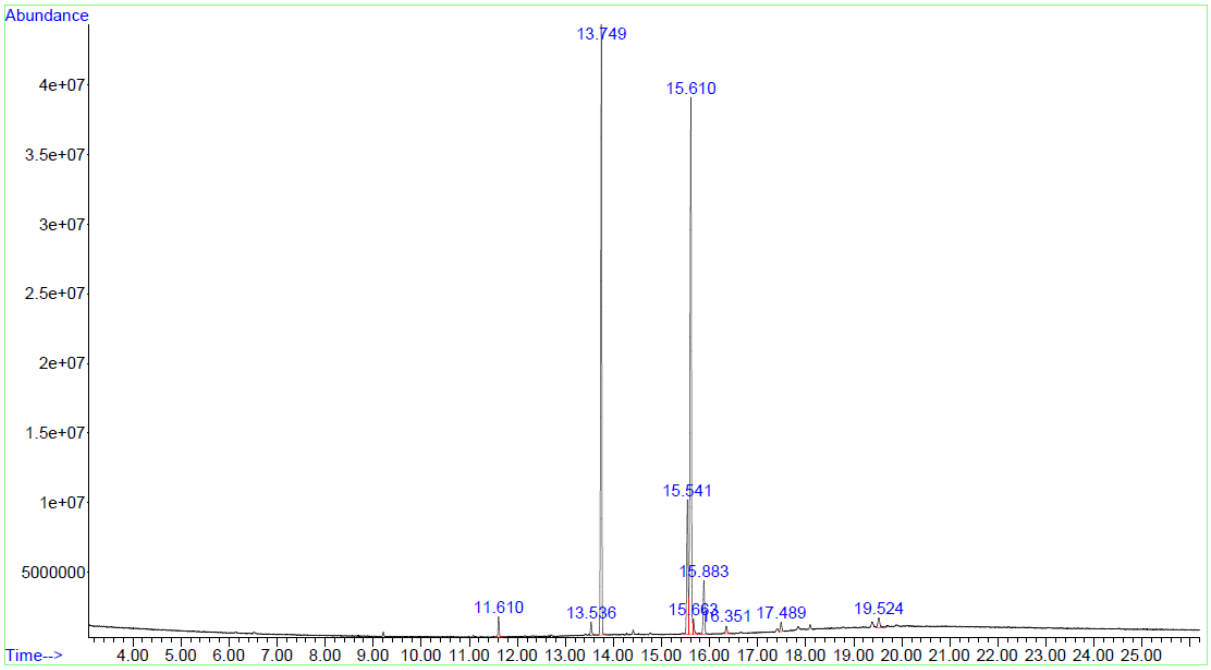

Fig. 3. Gas chromatography of Singgora/ZnO biodiesel

3.3.2 Biodiesel properties

Table 3 implies the physicochemical properties of the produced WCO methyl ester. For the data confirmation, several tests were assigned, such as acid number, kinematic flash point, and density. The assessments were determined using the ASTM D6751, EN 14214, and American Oil Chemists' Society (AOCS) methods [21]. The acid value is a crucial parameter in the production of biodiesel, serving as an initial indicator to evaluate the quality of both the raw feedstock and the methyl ester. To avoid some common issues associated with high FFA content, reducing the acid value under limits was essential. The methyl esters produced will be negatively impacted by soap formation, degumming, and end-product separation, and ultimately reduce the overall production yield. Lowering the acid number also indicates that it can be safely used in engines without causing corrosion to the metallic engine components. The flashpoint parameter also holds significant importance in the context of biodiesel and other fuels, as it serves as a crucial indicator of the fuel's safety, storage requirements, and transportation considerations [22]. The presence of free fatty acids and water content in biodiesel production can have negative effects, such as the formation of soap and decreased catalyst efficiency. Important properties such as IV and SV are some of the fuel properties that are strongly influenced by the composition of fatty acids. A higher IV can potentially decrease the engine lifespan but offer improved viscosity properties, especially in colder climates while the SV reflects the proportion of fatty acids in the average molecular weight. These factors can potentially reduce the overall conversion efficiency [23].

Table 3
Comparison of biodiesel properties with ASTM standard

Properties	Testing Method	Result	Range	
			ASTM D6751	EN14214
Acid Value	ASTM D664	0.224 mg	0.5 max	0.5 max
Density	ASTM D1298	872 kg/m^3	880	860-900
Flashpoint	ASTM D93	195 °C	130 min	101 min
Water Content	EN ISO 12937	0.021 %V	0.05%V max	0.05 %V max
Iodine value	AOCS Cd 1c-85	66 g/100g	-	120 max
Saponification value	ASTM D5558	195.4 mg/KOH	370 max	-

4. Conclusions

This research focused on incorporating waste cooking oil and waste *Singgora* roof tiles into clean and quality biodiesel and showed a tangible example of sustainable practice. The biodiesel process was performed by the two-steps transesterification method. The composition and morphology of the catalyst were tested by using XRF and SEM-EDX. The findings also indicate that the primary component within the *Singgora* roof tiles is silica (SiO_2). ZnO was used as support to the Singgora roof tiles catalyst. The results from the experiments showed that the parameters for the maximum yield of 96.96% biodiesel were recorded at a 12:1 methanol to oil ratio, a 1% catalyst concentration, a reaction temperature of 65°C, and a reaction time of 2 hours. All the physical properties tests were within the standards indicating that *Singgora* roof tiles have the potential to serve as a heterogeneous catalyst in biodiesel production. Further research can be explored to find additional applications of *Singgora* in the biodiesel industry.

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