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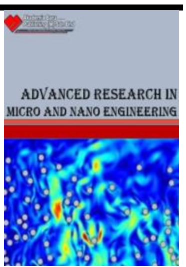

Catalytic Potential of *Singgora* Roof Tiles in Transesterification for Sustainable Biodiesel

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ABSTRACT

The study centred around the uitilization of *Singgora* roof tiles as a heterogeneous catalyst in the production of biodiesel via the transesterification process. The motivation behind this choice stems from the non-recyclable nature of *Singgora* roof tiles and their potential applicability in biodiesel synthesis. To enhance the catalytic properties, zinc oxide (ZnO) is incorporated using the wet impregnation technique during catalyst preparation. The catalyst was characterized by XRF and SEM-EDX. A two-step transesterification method is employed to mitigate the levels of free fatty acid (FFA) in waste cooking oil (WCO). The initial step involves treating the WCO with sulfuric acid (H_2SO_4) to reduce FFA. Subsequently, the *Singgora* roof tiles catalyst is utilized in the second step. A high yield of FAMEs, specifically 96.96%, was achieved 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 reaction time of 2 hours. The quality of the biodiesel produced was analyzed according to biodiesel standards such as ASTM D6751, EN 14214, and AOCS, and it met all the required standards. 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 as stated by Jikol *et al.*, [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

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oil and contribute to 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, alternatively referred to as fatty acid methyl ester (FAME), presents a multitude of advantages in comparison to conventional diesel fuel. The substance in question originates from extensive sequences of free fatty acids (FFA) or triacylglycerol (TAG) found in edible or non-edible oil sources, including animal fats or discarded cooking oil [3]. The current production of biodiesel predominantly consists of conventional biofuels, which are derived from food crops, accounting for over 90% of the total output. This category comprises feedstock such as sugar cane, starch-based ethanol, FAME, straight vegetable oil, and hydro treated vegetable oil sourced from palm, rapeseed, or soybean oil. The increasing use of alternative feedstock, like non-food crop-derived advanced biofuels, addressed sustainability concerns by offering lower greenhouse gas emissions than fossil fuels and avoiding competition with food crops for agricultural land [4]. For biodiesel to be viable, it needs low production costs and a substantial production scale, with a significant portion of expenses linked to raw materials. Therefore, the utilisation of waste cooking oils (WCO) as a substitute for edible oils in the production of biodiesel proves to be a viable approach to reducing the expenses associated with raw materials [5].

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 [6]. 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 [7].

This study utilised *Singgora* roof tiles, a clay-based roofing material, as a heterogeneous catalyst to produce biodiesel. *Singgora* roof tiles as shown in Figure 1 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. By repurposing discarded roofing materials, it effectively reduces waste and lessens the demand for new resources. This waste repurposing demonstrates efficient resource utilization and waste reduction. *Singgora* roof will be fused with ZnO by the wet-impregnation method. The two-step transesterification method will be utilized in this biodiesel production, starting with oil pre-treatment and transesterification. The oil composition was tested by GCMS, and the physical properties were tested according to ASTM D6751, EN 14214 and AOCS standards.

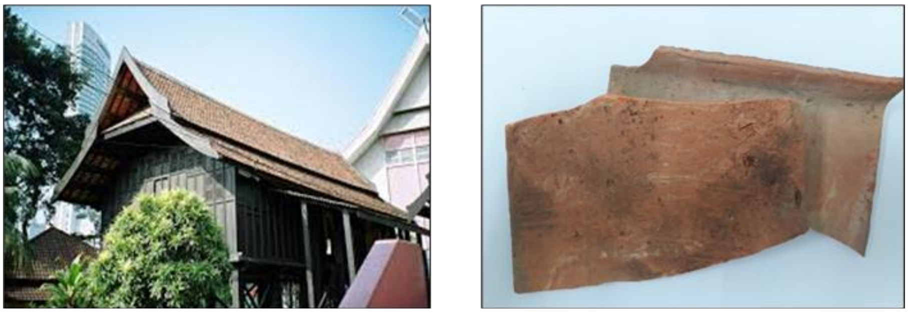


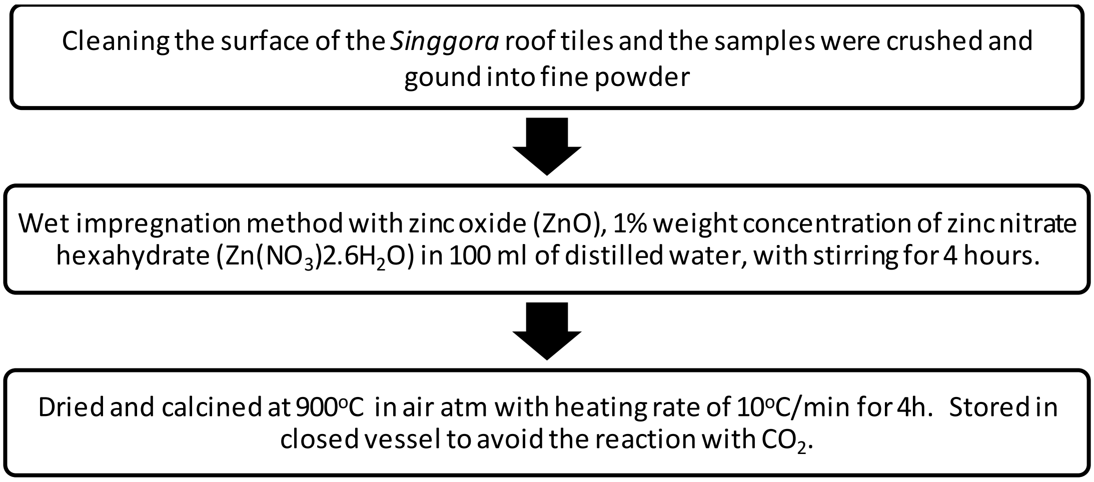
Fig. 1. *Singgora* roof tiles

2. Methodology

The raw WCO was obtained from the Hospital Melaka's Dietetic and Food Service Department and all the chemicals such as 99.9% pure methanol (MeOH), 98% sulphuric acid (H_2SO_4), and Zinc Nitrate Hexahydrate were supplied by Polyscientific Chemicals Sdn Bhd, Melaka. The waste *Singgora* roof tiles were collected from a resident's house in Ayer Keroh, Melaka.

2.1 Catalyst Preparation

Sandpaper was employed to clean the surface of the *Singgora* roof tiles, removing any dirt. Subsequently, the cleaned samples were crushed and ground into a fine powder 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. The sample was initially dried in the oven for 24 hours at 100 °C to remove excess moisture. 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 and converted $Zn\ (NO_3)_2.6H_2O$ into ZnO. 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 2 illustrates the flow chart detailing the experimental procedure.



Cleaning the surface of the *Singgora* roof tiles and the samples were crushed and gound into fine powder

Wet impregnation method with zinc oxide (ZnO), 1% weight concentration of zinc nitrate hexahydrate ($Zn(NO_3)2.6H_2O$) in 100 ml of distilled water, with stirring for 4 hours.

Dried and calcined at 900^oC in air atm with heating rate of 10^oC/min for 4h. Stored in closed vessel to avoid the reaction with CO_2.

Fig. 2. Catalyst making process flow

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. The catalyst surface morphology and elemental composition were performed using scanning electron microscopy (SEM) combined with Energy Dispersive X-ray spectroscopy (EDS) model JSM-6010PLUS/LV. The test was done at the Material Lab, Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka.

2.3 Acid Esterification and Transesterification

The acid esterification or pre-treatment step is utilized to reduce the free fatty acid (FFA) content in feedstock oils to prevent the formation of soap during the transesterification process [8]. 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 ratio of MeOH to the oil in a beaker. The mixture was stirred at 65 ˚C for 1 hour [9]. Afterwards, the solution was transferred to a separator funnel and left overnight to separate the methanol from the oil. The extracted oil was then prepared for transesterification.

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 [10]. The process 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 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 transferred to a separation funnel and left for 24 hours. Following this period, three layers were formed inside the funnel; methanol, biodiesel, catalyst, and glycerine. The biodiesel was extracted, while the other layers were discarded. The final biodiesel product was heated to over 100˚C to eliminate the remaining moisture and methanol [11].

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) was used to analyse the composition of fatty acid methyl ester (FAME) of the biodiesel oil [12].

3. Result and Discussion

3.1 X-ray Fluorescence (XRF)

XRF was used to analyse the elemental chemical composition of the *Singgora*-ZnO catalyst and raw *Singgora* before heat treatment. 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 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 [13].

Table 1
XRF Spectrometry of uncalcined *Singgora* and calcined *Singgora/*ZnO catalyst

Compound	Concentration (%)	
	Uncalcined *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 Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM-EDX)

The sample of the *Singgora*/ZnO catalyst was observed using a JSM-6010PLUS/LV SEM-EDX under x1000 magnification. The catalyst was sputtering coated with metal before being tested for SEM-EDX to allow electron conductivity to obtain a higher quality of image scanning [14]. In the SEM micrograph shown in Figure 3, the catalyst samples displayed visible voids or pores spread across the surface. The catalyst had a flat structure with strips appearing at consistent intervals. The EDX analysis in Figure 4 showed that the highest component is Si, followed by Al and Zn which is compatible with XRF results.

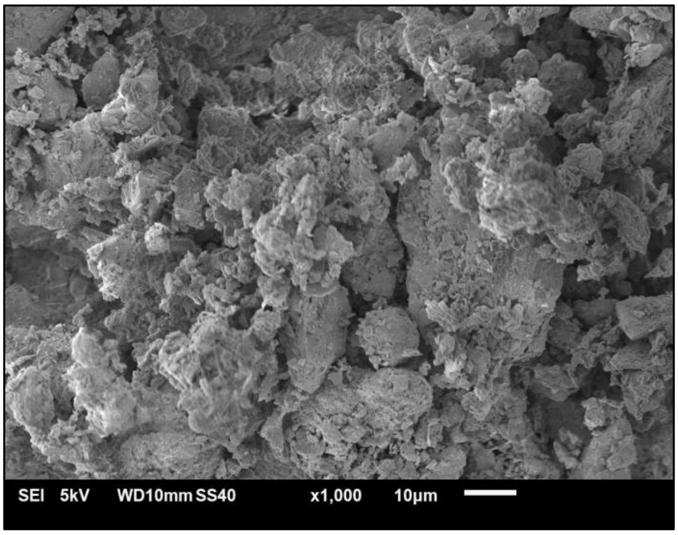


Fig. 3. SEM image (5 kV) of *Singgora*/ZnO Catalyst obtained by calcination at 900˚C

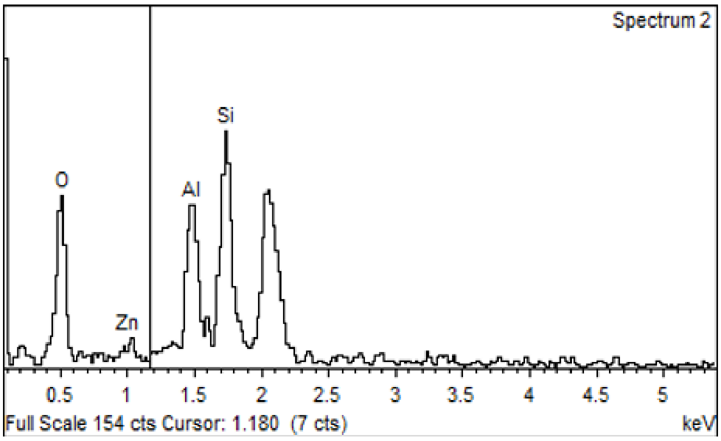


Fig. 4. EDX analysis

3.3 Biodiesel Characterization

Several tests, including acid value, flash point and water content were carried out in the Faculty of Technology Engineering Mechanical and Manufacturing (FTKMP) at Universiti Teknikal Malaysia Melaka (UTeM) laboratories. The initial acid value for the raw WCO was measured at 4.26mg KOH/g. The composition of the biodiesel oil sample was analyzed using GCMS at the Central Laboratory of Universiti Malaysia Pahang (UMP). Iodine value (IV) and saponification value (SV) tests were conducted at Intertek Testing Services, Port Klang.

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. 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 optimum conversion 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	0.9761
3	13.7505	Hexadecenoic acid	38.1489
4	15.5418	9,12-Octadecadienoic acid	10.7738
5	15.6092	9-Octadecenoic acid	40.9984
6	15.6654	11-Octadecenoic acid	1.1533
7	15.8844	Octadecanoic acid	4.1742
9	17.4903	Eicopentaenoic acid	0.7323
FFA Conversion			96.96

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 [15]. 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 [16]. 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 [17].

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 ^{o}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

Incorporating waste cooking oil and waste *Singgora* roof tiles into clean and quality biodiesel serves as a tangible example of sustainable practice. 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). The results from the experiments showed that the optimum 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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