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PRODUCTION OF FATTY ACID METHYL ESTER FROM WASTE COOKING OIL UTILIZING SULFONATED TiO_2-SiO_2 CATALYST

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Abstract

Biodiesel is a sustainable, renewable, biodegradable, and non-toxic diesel fuel replacement that can easily be synthesized through the esterification reaction. Waste cooking oil (WCO) has been utilized as a feedstock for biodiesel production. However, there is difficulty to convert feedstock into biodiesel using basic catalyst due to high levels of free fatty acid (FFA). Therefore, sulfonated TiO_2-SiO_2 has been used as a solid acid catalyst via the esterification reaction. The aim of this study is to determine the effect of reaction time and catalyst loading on the production of fatty acid methyl ester (FAME) using sulfonated TiO_2-SiO_2 catalyst from WCO. Characterization using SEM-EDX confirmed the presence of Ti, Si, O, and S in the catalyst and revealed the rough surface of the impregnated sulfonated TiO_2-SiO_2. Hammett indicators analysis indicated that the catalyst was in a moderate acidity range. WCO was esterified with methanol using sulfonated TiO_2-SiO_2 as solid acid catalyst to produce biodiesel. The reactions were refluxed at 90 ºC with 3 wt% catalyst loading and 9:1 methanol to oil ratio while varying the reaction time (1 to 5 h). Meanwhile for the effect of catalyst loading (1 to 5 wt%), the reaction temperature, reaction time and methanol-to-oil ratio were constant at 150 ℃, 2 h, and 15:1, respectively. In this study, it was found that the highest FAME yield obtained from the effect of catalyst loading was 67.07% with optimum conditions of 3 wt% catalyst loading, 15:1 methanol to oil ratio, and a reaction temperature of 150 ºC for 2 h. The gas chromatography-mass spectrometry (GC-MS) results showed that eight peaks corresponding to the methyl ester group were found in the product, indicating that the FFA can be converted to methyl ester using sulfonated TiO_2-SiO_2 in the esterification reaction.

Keyword: Esterification, Fatty Acid Methyl Ester, Waste Cooking oil

Introduction

The demand for petroleum fuel has risen because of population growth and rapid industrial development although it can have various negative environmental consequences, necessitating the search for an alternative fuel that is both eco-friendly and highly sustainable. Hence, their use has resulted in massive environmental pollution. By 2040, global energy demand will be around 30% more than it was in 2010 (Rajendiran and Gurunathan, 2020). The implementation of economically feasible alternative fuels is required for long-term development. As a result, there is a growing interest in alternative fuels like biodiesel or also known as FAME (Arumugam and Ponnusami, 2019). Biodiesel has been proven to be more environmentally beneficial than fossil fuels due to lower emissions during burning and higher biodegradability (Parangi and Mishra, 2020). Biodiesel is a promising alternative fuel for the transportation and mechanized agriculture industries since it is renewable, environmentally friendly, and nontoxic.

Biodiesel is a long-chain fatty acid methyl ester (FAME) produced via transesterification of triglycerides (TAG) or esterification of free fatty acids (FFA) (Arumugam and Ponnusami, 2019). Vegetable oils and animal fats contain many types of fatty acids, including palmitic, myristic, stearic, oleic, linoleic, and linolenic. Therefore, the esterification reaction is used to produce biodiesel by converting FFA to alkyl ester through a reaction with alcohol (Naghmash et al., 2022).

The cost of feedstocks contributes to around 70–90% of the entire cost of biodiesel production and waste oils, such as waste cooking oil, might minimize these costs. Biodiesel production from WCO is environmentally favourable because it recycles WCO and produces less polluting biofuel. It replaces some petroleum oil imports and reduces the cost of waste treatment. The production of biodiesel from WCO offers three benefits which are in terms of economy, environment, and waste management (Attari et al., 2022). WCO is typically dumped since it is unfit for human consumption. Therefore, the feedstock may be easily obtained due to the availability of WCO. Additionally, it benefits the disposal of oil, which, if not removed, would otherwise lead to soil damage (Jayaraman et al., 2022*)*.

For biodiesel production, acidic and basic catalysts are commonly used. The acid catalysts are significantly less active than the base catalysts. However, when the percentage of FFA in oil approaches 1%, the acid catalyst becomes more effective. Typically, acid catalysts hinder the foaming of soap. Acid catalyst facilitates the hydrolysis of ester bonds in triglycerides to form carboxylic acid and glycerol. Hydrogen ion generated by acid catalyst may accelerate the hydrolysis reaction. The acid-catalyzed process is a slower reaction, hence, it requires high temperature and pressure (Maheswari et al., 2022). It is well known that the traditional homogeneous catalysts are used in the esterification of fatty acids process, such as mineral acids, H_2SO_4 (Ibrahim, 2021).

Homogeneous catalysts are more well-known in the industrial world because they are easily accessible, have a high reaction rate, and react immediately. However, there are a lot of limitations to utilizing a homogeneous catalyst because the esterification process results in biodiesel having a high sulphur content that can exceed 10 ppm when using a homogeneous acid catalyst (H_2SO_4). Sulfur oxide are categorized as emission substances that endanger human health. The increased setup required for product recovery and washing when using homogeneous base catalysts (KOH, NaOH) results in large wastewater production (Maulidiyah et al., 2022). Homogeneous alkali catalysts are efficient for vegetable oils with FFAs and moisture concentrations of less than 0.5 or 0.3%, respectively. Low-quality feedstocks have high FFAs and moisture content, which saponifies the homogenous alkali catalysts and makes them inactive (Kaur et al., 2018). Meanwhile, heterogeneous catalyst provides rapid recycling and reusing (Endalew et al., 2011), can handle both high FFAs and moisture content, involves simple preparation, requires low cost, and has potential for high biodiesel conversion (Gardy et al., 2016). Most acid catalysts exhibit good catalytic activity, but their optimization of method and reusability are often inadequately explored.

Rice husk ash (RHA) as biomass has a prospective function as an amorphous silica precursor due to its high silica content (87-99%) and abundant availability. RHA is a byproduct of rice husk combustion that has emerged as a key material for material research. Each tonne of rice produces 200 kg of rice husk (RH), which, with complete burning, yields 40 kg of RHA. Recently, around 146 million tonnes of RHA were produced annually on a global scale, and attempts are being made to address this environmental problem by implementing this material as support (Hindryawati et al., 2014).

Many researchers produce the silica from rice husk because the silica (SiO_2) is made from biomass waste, which is inexpensive and widely accessible (Banurea et al., 2020; Hindarso et al., 2021; Sawasdeea et al., 2022). Hence, in this study, solid acid catalyst that is highly active, stable, and affordable was produced for the esterification of WCO into methyl esters.The active catalyst needs to have a large surface area so that the reactants and products could transfer mass quickly and have good active phase dispersion (Embong et al., 2016).
The use of titanium dioxide (TiO_2) nanoparticles as catalyst support is due to its advantageous qualities, such as acidity, broad band gap, high surface area, low cost, high availability, improved redox selectivity, excellent mechanical and chemical stability, high reactivity, low toxicity, and great reusability. The ability of acid catalysts to enhance esterification of FFA without soap formation is particularly important for biodiesel production using inexpensive raw materials. Recycled vegetable oils could be used as economical feedstocks for biodiesel production in the context of sustainable chemistry. This benefits the reduction of environmental pollution and facilitates inexpensive biodiesel production (Gardy et al., 2017). In this study, sulfonated TiO_2-SiO_2 catalyst was utilized to produce FAME via esterification reaction. The effect of catalyst loading and reaction time on the production of FAME were also investigated.

Materials and Methods

Waste cooking oil was collected from the household. Rice husk was collected from BERNAS factory, Kelantan. Titanium dioxide (analytical reagent), hydrochloric acid (37 %), sulfuric acid (96 %), methanol (grade AR) from HmbG, methyl heptadecanoate from Merck and n-Hexane (anhydrous, ≥99.8 %) from R&M chemicals.

Preparation of sulfonated TiO_2-SiO_2 catalyst

The RH was weighed using an electronic balance for 50 g, and was washed with distilled water and filtered to eliminate dirt. After washing, RH was mixed with 0.4 M hydrochloric acid (HCl) at a ratio of 50 g of RH to 500 ml of HCl, then stirred and dried at 110 ºC for three hours. The HCl acid was washed out of the RH with pure water. The RH was re-dried in an oven at 110°C for 3 h. RH was burned at 550˚C for 6 hours to obtain white rice husk ash (RHA) (Shahrim Mustafa et al., 2015).

The weight ratio for TiO_2:SiO_2 is 3:1. Approximately 30 g of TiO_2 was slowly added to the 2.0 M H_2SO_4 solution until the solid dissolved completely. The solution was then treated with 10 g of SiO_2 powder. The mixture was stirred at 600 rpm for 6 h. The solid precipitate obtained was filtered and calcined at 500˚C for 4 h with a heating rate of 10 ºC/min (Embong et al., 2016).

Characterization of catalyst

The catalyst produced was examined for elemental analysis and surface morphology using Scanning Electron Microscope (SEM) under 5K x magnifications. The acid strength of the catalyst was tested using Hammett indicators. The following Hammett indicators were used: crystal violet (H_= 1.8), bromophenol blue (H_= 4.6) and methyl red (H_= 6.2). About 25 mg of the catalyst was shaken with 1 mL of a solution of Hammett indicator diluted in methanol and left to equilibrate for 2 h, and changes in colour were observed (Embong et al., 2016).

Pre-treatment Waste Cooking Oil

Waste cooking oil (WCO) was collected from the household. The solid particles and other impurities were removed from the WCO obtained by a filtration technique. The filtered WCO was heated at 110˚C for three hours while being stirred to remove its water content. The WCO from pre-treatment was kept in a clean glass bottle (Mohd Shohaimi and Marodzi, 2018).

Esterification Reaction

The esterification reaction was carried out in a round-bottom flask with the constituent. The reaction was refluxed with methanol to WCO molar ratio of 9:1, and a varied reaction time of 1, 2, 3, 4, and 5 h at a reaction temperature of 90ºC and a 3 wt% catalyst loading. (Purwasusanti et al., 2016). The esterification reaction was conducted with a condenser immersed in an oil bath.

The method was repeated with another parameter, which is catalyst loading. The esterification reaction was carried out in a round-bottom flask with the constituent, 10 g of waste cooking oil, a methanol to WCO molar ratio of 15:1, and the desired catalyst loading of 1, 2, 3, 4, and 5 wt% at a reaction temperature of 150˚C with a 2 h reaction time.
Centrifugation was used to separate the product mixture to recover the wasted catalyst. The layer of FAME was washed with hot distilled water multiple times to eliminate contaminants such as glycerol and methanol. After transferring the FAME into the beaker, it was heated at 100 °C for 2 min to eliminate excess water from the washing procedure (Lokman Nolhakim et al., 2021). Then, the methyl esters produced were determined by using chromatography-mass spectroscopy (GC-MS) for analysing the compositions of product.

Gas chromatography (GC) analysis

About 0.1 g of the internal standard (methyl heptadecanoate) was mixed with 10 mL of n-hexane to produce 10 000 ppm of the internal standard. Then, 0.125 g of sample (FAME) was dissolved in 2.5 mL of internal standard and 10 mL of n-hexane.

The methyl esters produced were determined by using 6890A Agilent gas chromatography-mass spectroscopy (GC-MS) with a mass spectrometry (MS) detector with a column BPX5 (30 m x 0.25 mm x 0.25 µm). Methyl heptadecanoate was used as an internal standard and the peaks of the methyl esters were detected by their respective standards. The GC oven temperature was held at the initial temperature of 120 °C for 2 min, increased to the end temperature of 270 °C at a rate of 6 °C/min, and then held at this constant temperature for 1 minute, for a total run time of 28.0 minutes. The injector and detector temperatures were 250 °C. At a flow rate of 12.0 mL/min, helium was used as the carrier gas. FAME content of the biodiesel was identified using NIST mass spectroscopy (MS) library programme.

Equation to calculate ester content:

$$C = \frac{(\Sigma A) - AEI}{AEI} \times \frac{CEI \times VEI}{m} \times 100\%$$

Where:
$A\Sigma$ = total peak area of the FAME
AEI = peak area of internal standard
CEI = concentration, in mg/mL, of the internal standard solution
VEI = volume, in mL of the internal standard solution

m = mass, in mg, of the sample

Result and Discussion

Characterization of catalyst using SEM-EDX and Hammett Indicator Analysis

The SEM image in **Figure 1(a)** showed TiO_2 has rough, with a crystalline coarse and porous structure that is useful for catalytic support material. The surface morphology of SiO_2, as viewed in **Figure 1(b)**, exhibited a smooth surface with a cylindrical-like structure. The surface morphology of **Figure 1(c)** showed up to reflect a combination of image of TiO_2 and SiO_2. The rough surface of the impregnated sulfonated TiO_2-SiO_2 catalyst is seen in the SEM image. The result was caused by the TiO_2-SiO_2 catalyst filling up the spaces in the pores in the TiO_2 and being distributed homogeneously throughout the surface of the material. It seemed to be composed of several brittle particles that had clumped together to create clusters. The image shows a rough surface which included a few gaps and tiny fractures, and the presence of cylindrical-like particles. These may be a result from the activation activity, which might have filled in the gaps and produced a special morphological surface (Hanif et al., 2023).

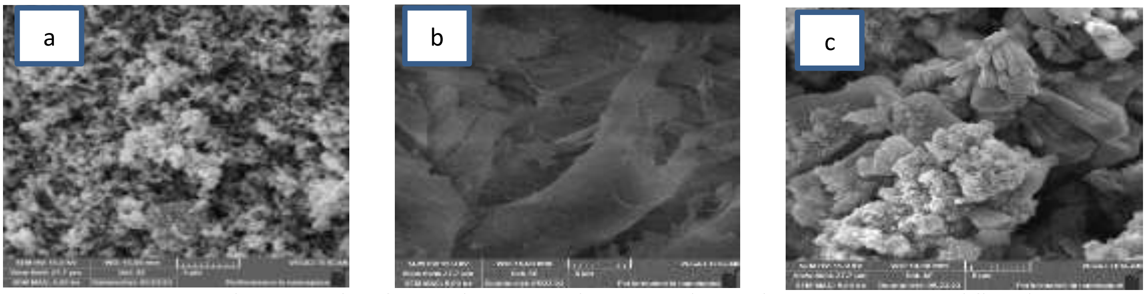


Figure 1 SEM micrograph of **(a)** TiO_2 **(b)** SiO_2 **(c)** SiO_2-TiO_2 at 5K magnification

The elemental composition of the sulfonated TiO_2-SiO_2 solid acid catalyst was determined through SEM-EDX in the **Table 1**. As can be seen in **Figure 2**, elements such as Ti, Si, O, and S have significant peaks, which confirm their presence in structure of catalyst.

Table 1 Elemental analysis of sulfonated TiO_2-SiO_2 catalyst

Element	Weight %
O	50.45
Si	37.88
Ti	7.15
S	4.52

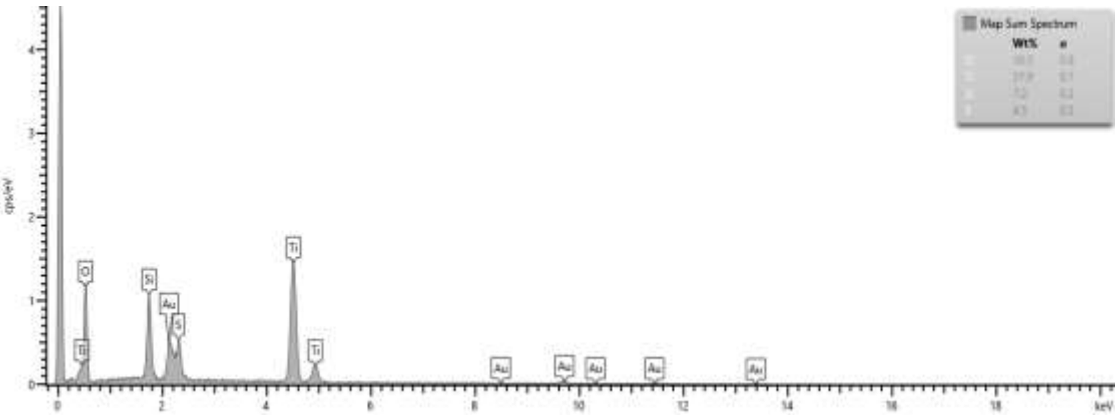
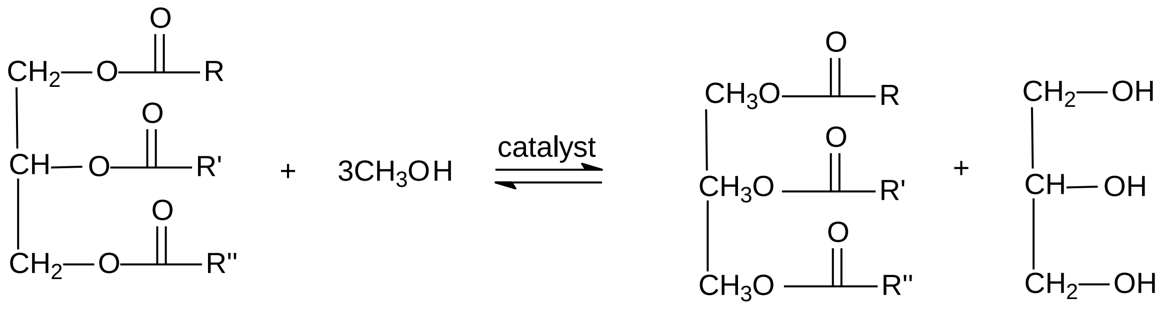


Figure 2 EDX spectrum of sulfonated TiO_2-SiO_2 catalyst

The acid strength of the catalyst was tested using Hammett indicators. The pH range for the sulfonated TiO_2-SiO_2 solid acid catalyst for this study was in the range of pH 3.0-6.3 which indicated moderate acidity ranges. From the previous study by Vargas et al. (2019), the acid strength of the catalyst was determined to be between pH 3.8 to 4.7, which was successful in converting FFA to FAME.

Effect of reaction time on the FAME yield

An analysis was conducted to determine the optimal reaction time to be used, with time reactions of 1, 2, 3, 4, and 5 h, using a 3 wt% catalyst loading and a 9:1 methanol to oil ratio at reaction temperature of 90˚C. As can be seen in the Figure 3, the highest FAME yield obtained was 28.02% with a 4 h reaction time and the lowest was 10.63% with 5 h reaction time, utilizing 3 wt% of sulfonated TiO_2-SiO_2, 9:1 methanol to oil ratio at 90˚C. Increasing reaction time resulted in higher biodiesel yields. The positive effect of reaction time resulted from the reaction having sufficient time to achieve equilibrium (Amenaghawon et al., 2022). However, in longer reaction times, the methyl ester preferred a backward reaction, yielding more glycerol (Leung et al., 2010), hence the FAME yield produced only 10.64% after 5 h. The following reaction occured to form FAME and glycerol



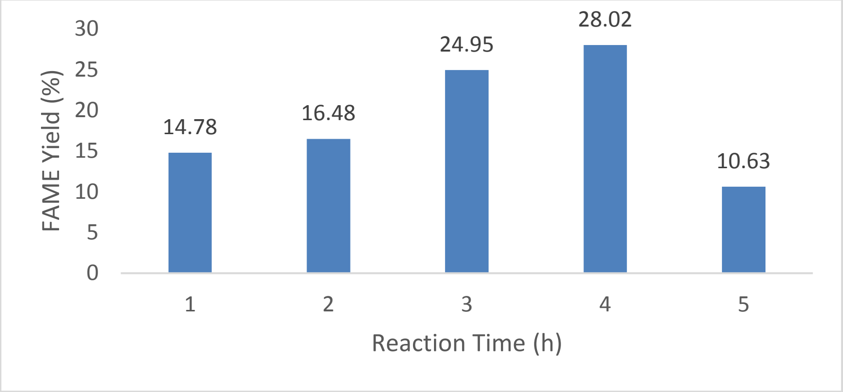


Figure 3 The effect of reaction time on the FAME yield at constant temperature of 90˚C and methanol to oil ratio of 9:1 with 3 wt% of catalyst loading.

Effect of catalyst loading on the FAME yield

As shown in **Figure 4**, FAME yield increased from 48.42% to 67.07% with an increase in catalyst loading from 1 to 3 wt%, respectively, as the total number of active sites available in the reaction increased (Al-Saadi et al., 2020). However, the FAME yield started to decrease from 67.07% to 40.43% when the catalyst loading increased from 3 to 5 wt%. There are two causes for the poor performance of powder catalyst: either the catalyst is easily coated by glycerol as the catalyst and glycerol settle at the bottom of the container, or direct contact between the catalyst and magnetic stirrer deactivates the catalyst (Alonso et al., 2007).

A high molar ratio needed a shorter reaction time since sufficient methanol was present (15:1 methanol-to-oil ratio) to bring the reaction to completion with a high yield (Mohd Shohaimi & Marodzi, 2018). Therefore, 2 h reaction time was chosen as the optimal reaction time due to high FAME yield. Besides, the yield of biodiesel increased rapidly and consistently when the reaction temperature was increased. Higher temperatures are desirable for the efficient dispersion of catalyst particles, the enhancement of mass transfer properties, and the enhancement of the interaction between the catalyst and methanol molecules (Amenaghawon et al., 2022). Additionally, a higher temperature decreases the viscosity of the WCO, increasing the rate of the reaction (Gardy et al., 2016). Hence, a temperature of 150˚C was chosen to maximize FAME yield production (67.07%).

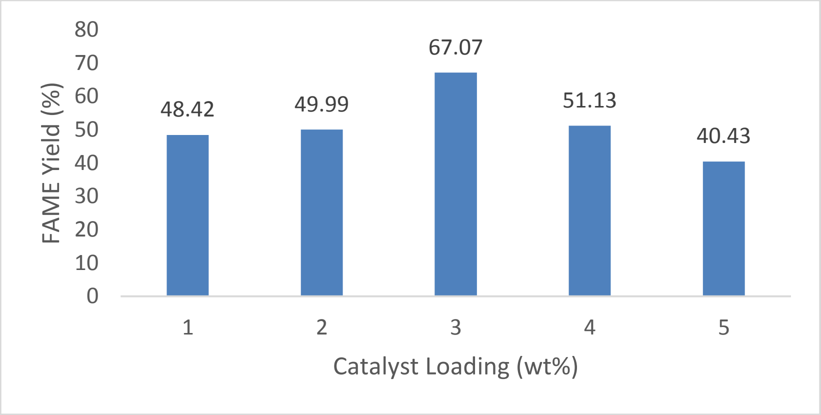


Figure 4 Effect of catalyst loading on the FAME yield at constant temperature of 150 ºC and methanol to oil ratio of 15:1 with reaction time of 2 h

Qualitative analysis of FAME content

Figure 5 showed the GCMS chromatogram of FAME. Table 2 showed eight identified methyl ester peaks. All peaks detected were verified against various esters and confirmed using the mass spectroscopy (MS) library programme.

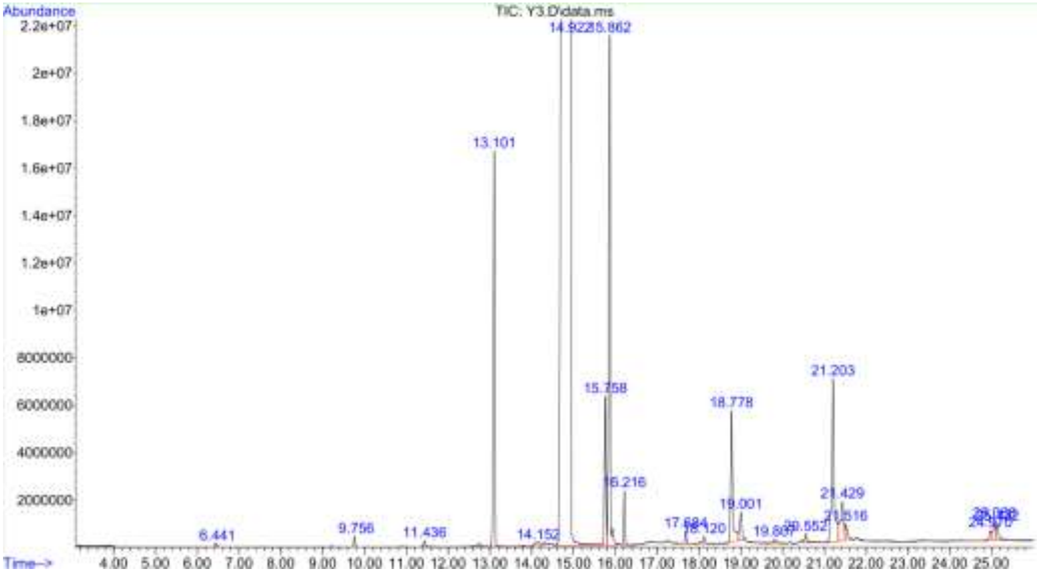


Figure 5 GC-MS chromatogram of FAME

Table 2 FAME composition in biodiesel

Retention Time (min)	Methyl Ester Compound	Common Name	Chemical Formula
6.439	Decanoic acid methyl ester	Methyl decanoate	$C_{11}H_{22}O_2$
9.754	Methyl tetradecanoate	Methyl myristate	$C_{15}H_{30}O_2$
11.435	Pentadecanoic acid methyl ester	Methyl pentadecanoate	$C_{16}H_{32}O_2$
13.101	Hexadecanoic acid methyl ester	Palmitic acid ME	$C_{17}H_{34}O_2$
14.922	Methyl heptadecanoate (Internal standard)	Methyl margarate	$C_{18}H_{36}O_2$
15.758	9,12-Octadecadienoic acid (Z,Z), methyl ester	Linoleic acid ME	$C_{19}H_{34}O_2$
15.861	9-Octadecadienoic, methyl ester, (Z)	Oleic acid ME	$C_{19}H_{36}O_2$
16.214	Octadecanoic acid, methyl ester	Methyl stearate	$C_{19}H_{38}O_2$
17.683	Nonadecanoic acid, methyl ester	Methyl nonadecanoate	$C_{20}H_{40}O_2$

Conclusion

As for conclusion, the highest FAME yield for esterification reaction of waste cooking oil using sulfonated TiO_2-SiO_2 catalyst was 67.07% with optimum conditions of 2 hours reaction time, 3 wt.% catalyst loading refluxed at 150°C and 15:1 methanol to oil ratio. The GCMS result indicated the confirmation of eight methyl ester presence.

Ethic Statement

The research does not require research ethics approval.

Authors' Contribution

Writing - draft preparation, Kamarullah, S.H., Kamilan, N.N.A.N.A, Abdullah, N.A.N; Writing - Review and editing, Khazaii, S. N.K

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Conflict of interests

Author declares no conflict of interest.

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