



Corncob-Derived Sulfonated Magnetic Solid Catalyst Synthesis as Heterogeneous Catalyst in The Esterification of Waste Cooking Oil and Bibliometric Analysis

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ABSTRACT

A corncob-derived magnetic solid acid catalyst was synthesized through the sulfonation method and an impregnation process, respectively. In the sulfonation process, the concentrated H₂SO₄ was utilized as an activation agent to obtain acidic properties. The solution of ferric sulphate-ferrous sulphate was utilized for impregnation to generate the magnetic behaviour of the material. The prepared magnetic acid solid catalyst had a high saturation magnetisation value of 16.48 emu/g and a total acidity of 1.43 mmol/g. The performance of the catalyst was evaluated in the esterification reaction of waste cooking oil. The best result presented 86.12% FFA conversion under reaction conditions of 5% catalyst loading and a 1:15 oil-to-methanol molar ratio at 60°C for 4 h. The catalyst was separated magnetically from the reaction solution and exhibited a good reusability with 61% remaining active after 5 consecutive cycles of reaction. This study resulted in a promising method to obtain magnetic-sulfonated carbon-based catalyst from corncob residue, and it is economical potentially and environmentally friendly for the esterification of low-quality feedstock for biodiesel production.

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1. INTRODUCTION

Biomass, which refers to plant-based material, has abundant lignocellulose. It is composed of 60-80% cellulose and hemicellulose and together with lignin, it can build plant structure. Biomass has been utilized as raw material in the synthesis of carbonaceous materials. Lately, biomass-derived carbonaceous materials become a concern for offering porous carbons. The porous area of a material facilitates efficient mass transfer and provides good accessibility to the active site. For this reason, it is suitable to use as a support in the synthesis of heterogeneous catalysts (Deng *et al.*, 2016). Several studies concerned with the development of biomass-derived heterogeneous catalyst since it offers many advantages in the scope of chemical reactions (Chen *et al.*, 2018; Dechakhumwat *et al.*, 2019; Efiyanti *et al.*, 2020). Akinfalabi *et al.* (2017) demonstrated a synthesis of a solid acid catalyst from soaked palm seed cake employed in the esterification of palm fatty acid distillate to produce biodiesel. The catalytic activity was insignificantly dropped for the first five reaction cycles. Meanwhile, Farabi *et al.* (2019) synthesized sulfonated carbon-based solid catalysts from palm kernel shells and bamboo. The reusability test of both catalysts retained about 70% catalytic activity after 4 cycles. Those results represented that the heterogeneous catalyst could be easily recovered from the reaction mixture, and it could be efficiently re-used in the consecutive multiple reaction cycles.

However, those studies still required filtration and centrifugation to separate the solid catalyst from the reaction mixture. Though in small quantities, the mass loss of solid catalyst during separation could be unavoidable, and bring some disadvantages to the next reaction cycles (Miceli *et al.*, 2021). Seeing that efficient and easy separation are the main features of heterogeneous catalysts, incorporating magnetic properties into biomass-derived solid catalysts is to be considered. It was found that the recovery rate of magnetic solid catalysts was 1.7-fold higher than non-magnetic solid catalysts (Abida *et al.*, 2020; Li *et al.*, 2020; Xie & Wan, 2018). Araujo *et al.* (2021) successfully inserted the magnetic behaviour into acai seed-derived carbon material using the impregnation process followed by carbonization and sulfonation, and red mud was used as the magnetic source. Another synthesis of biomass-based magnetic solid acid catalyst was developed by Krishnan *et al.* (Krishnan *et al.*, 2022), performing a one-step impregnation process with Ferric sulphate - Ferrous sulphate solution mixture as a magnetic source as well as a sulfonation agent. Magnetic solid acid catalysts are very useful for chemical reactions specifically in esterification reactions for biodiesel production (Araujo *et al.*, 2021; Ibrahim *et al.*, 2019; Jenie *et al.*, 2020; Krishnan *et al.*, 2022).

Biodiesel is a renewable fuel, which is offered as a biodegradable and environmentally friendly fuel. It is produced through esterification/transesterification of edible or non-edible oils. A problem comes out when the low quality of feedstock with high free fatty acid (FFA) is employed in reaction for biodiesel production (Bashir *et al.*, 2022; Daryono & Dewi, 2022; Mathew *et al.*, 2021; Mohiddin *et al.*, 2021). The high FFA feedstock requires a heterogeneous catalyst to avoid any difficulty in product separation and purification. The heterogeneous acid catalysts have been proven more effective, environmentally friendly and easier for recovery. Recent studies have reported the utilization of carbon-based catalysts in esterification reactions for biodiesel synthesis and yielded a high conversion of FFA (Tang *et al.*, 2018).

Corncob is one example of lignocellulosic biomass with great application because of its structure and composition. Sulfonated solid catalyst, supercapacitor and adsorbent have been synthesized from corncob (Haryanto *et al.*, 2023; Karnan *et al.*, 2017; Rocha *et al.*, 2019). A previous study showed that the main cell wall of corn cob is composed of cellulose (31.34%), hemicellulose (39.62%) and lignin (14.4%). Moreover, corncob had a carbon content of about

23.34% (Mardina *et al.*, 2023) exactly has been in accordance as a carbon precursor in solid catalyst synthesis.

In turn, this study aims to synthesize and characterize a corncob-derived magnetic solid acid catalyst for biodiesel production. The synthesized catalyst was characterized by Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy with Electron Dispersive X-ray Spectroscopy, X-ray diffraction, Thermogravimetry, Vibration Sample Magnetometry, and total acidity. The catalytic performance of a corncob-derived magnetic solid acid catalyst was investigated in the esterification of waste cooking oil to produce biodiesel. The effect of catalyst loading, reaction time, oil-to-methanol molar ratio, and reaction temperature on free fatty acid conversion was evaluated as well. Furthermore, the reusability test of a corncob-derived magnetic solid acid catalyst was performed to identify its potential as an efficient reusable catalyst for chemical reactions. This study offers an efficient and rapid method to synthesize magnetic solid acid catalyst by chemically and physically modifying the surface of corncob particles. To the best of our knowledge, there is no study or research to utilize corncob residue as the carbon precursor of magnetic solid acid catalyst synthesis. With a two-step process; sulfonation and impregnation were conducted to insert the acid and magnet behaviour into corncob particles. It was proven that this type of catalyst has great technical and economic efficiency in esterification reactions.

2. METHODS

2.1. Materials

Corncob and waste cooking oil were purchased from traditional agricultural areas in South Kalimantan, Indonesia. Sulphuric acid, ferric sulphate, ferrous sulphate heptahydrate, sodium hydroxide, and methanol were supplied from Tunggal Jaya Kimia, Indonesia.

2.2. Catalyst Preparation

The two-step sulfonation-impregnation approach was used to synthesize the corncob-magnetic solid acid catalyst. Corncob particles were pre-treated with 10 %wt NaOH solution for 3 h at 50 °C with a solid-to-liquid ratio of 1:10. The treated corncob was then washed with distilled water to eliminate the remaining NaOH, and continued to oven-dried at 100 °C overnight. The dried particles of treated corncob were sulfonated hydrothermally in the Teflon-lined autoclave using H₂SO₄ 98% at 200 °C for 10 h. The sulfonated corncob was filtered and washed several times with distilled water until the wasted water reached pH 7.0. The magnetic sulfonated solid catalyst was synthesized using an impregnation method. The material was loaded into a solution of ferric sulphate and ferrous sulphate heptahydrate with a solid-to-liquid ratio of 1:10 through stirring at 60 °C for 4 h. A mol ratio of ferric sulphate to ferrous sulphate heptahydrate of 1:2 was conducted to generate the magnetic behaviour of a solid catalyst. Then, the impregnated sample was oven-dried for 10 hours at 80 °C. Following the drying, the material was subjected to calcine in a vacuum furnace at 500°C for 2 h with a heating rate increase of 10 °C/min. The obtained catalyst was named CO-SO₃H-Fe, and the untreated corncob as a controller was named CO.

2.3. Characterization of the Catalysts

The presence of functional groups on the surface of the magnetic solid catalyst was identified by Fourier transform infrared spectroscopy (FTIR; Bio-rad, Digilab FTS-3500) and the analysis was conducted at 400-4000 cm⁻¹. The surface morphology of the catalyst was determined using Scanning Electron Microscopy (SEM) with Electron Dispersive X-ray Spectroscopy (EDX). The chemical and structural composition of the catalyst, meanwhile,

were analysed using X-ray Diffraction (XRD) (Rikagu D/MAX-B X-ray diffractometer) equipped with a copper K-alpha (Cu K α) radiation sources with 2θ in the range of 5 to 50 °C at a scan rate of 2°/min at a voltage of 40 kV and current of 30 mA. Magnetic characterization was conducted with Vibrating Sample Magnetometry (VSM) and the analysis was performed at room temperature. Furthermore, the total acidity of the catalyst was determined by the acid-base titration mentioned somewhere (Zhu et al., 2017).

2.4. Esterification of Waste Cooking Oil

The esterification reaction of waste cooking oil and methanol over the corncob-derived magnetic acid catalyst was performed by using a 250 mL rounded bottom three neck-flask equipped with a conventional reflux system. The different quantities of the synthesized catalyst (1–5%), and waste cooking oil to methanol ratio of 1:12 were mixed followed by heating at varied temperatures (40–120°C) with the reaction times (1–5 h). After the reaction, the used catalyst was recovered magnetically, washed with methanol and oven-dried for 8–10 h at 80°C. The recovered catalyst was ready to be used for consecutive esterification reactions to analyse the reusability of the catalyst.

The acid values (AV) of biodiesel were determined according to SNI 01-3555-1998, and it is calculated by Equation (1). Furthermore, the FFA conversion was calculated using Equation (2). The composition of biodiesel was determined using a GC-MS Shimadzu QP 2010 SE equipped with a Rtx-5MS and Carbowax column. Nitrogen was used as the carrier gas.

$$\text{Acid value (AV)} = \frac{V_{\text{KOH}} \times N \times MR}{w} \quad (1)$$

where V_{KOH} refers to the used volume of KOH (mL) in the titration method, N is the normality of KOH, MR is the molecular weight of KOH (56.11 g/mol), and w is the mass of the sample (gram).

$$\text{FFA conversion (\%)} = \left(\frac{AV_i - AV_t}{AV_i} \right) \times 100\% \quad (2)$$

where AV_i and AV_t represent the acid values before (i) and after (t) the esterification process, respectively.

3. RESULTS AND DISCUSSION

3.1. Bibliometric Analysis of Corncob-Derived Sulfonated Solid Catalyst for Esterification Process

The bibliometric study here analysed the research development in the esterification process for biodiesel production using heterogeneous catalysts. Hence, the interaction of topics of research, the new specific field of research, and tracing of the development of future research can be explored for better strategic planning of the research (Nandiyanto et al., 2021, Nandiyanto et al., 2022).

The bibliometric analysis of this research used the reference data in the range of 2014–2022. Huge numbers of biodiesel publications using heterogeneous catalysts are observed during the range of years. The biodiesel production using the esterification process is also one of the concerns in the production of biodiesel with a lot of publications, though the transesterification process has more articles published. Furthermore, the development of corncob catalysts in the esterification process for biodiesel production also significantly increased during three ranges of years (2014–2016; 2017–2019; 2020–2022). Based on the data in ScienceDirect, there are 17 articles in the first range (2014–2016), 41 articles in the

second range (2017-2019), and 96 articles in the third range (2020-2022). However, there are few research developments in the corncob-derived sulfonated solid catalyst for biodiesel production using the esterification process with several articles of 7, 14, and 37 for each range. It indicates that the development of the research topic is interesting as a significant increase in the third range was observed.

Figure 1 shows the visualization of the network mapping on the corncob-derived sulfonated magnetic solid catalyst. The research on biodiesel production with the esterification process using the catalyst and the correlations on the methods and materials used are a lot of numbers as indicated with big size of colour circles and thick lines, though the biodiesel production using the transesterification process is higher amounts of work compared to that using the esterification process.

The utilization of biomass for raw materials as catalysts or oils is also massively developed. On the other hand, the research on corncob use for catalyst development is still minimal, hence it is interesting to be developed in the future. However, based on the near lines' relation, the correlations between keywords of biomass, hydrolysis, cellulose, starch, and corncob are very close, indicating that the method for the synthesis of solid catalysts based on corncob is similar for the majority of the works. It was also observed that there is no research on magnetic processes in the synthesis of corncob-derived sulfonated solid catalysts. Therefore, this research potentially contributes to the scientific research of the field.

Table 1 shows the publication of corncob-derived sulfonated solid catalysts used in the esterification process for the most cited articles in 2022. The presented data is the five top citations as the most impact article has a citation of 75. Though the publication date is less than one year, the articles are cited with many works. It indicates that the topic of corncob-derived sulfonated solid catalyst using the esterification process is interesting and gives a real contribution to the scientific work.

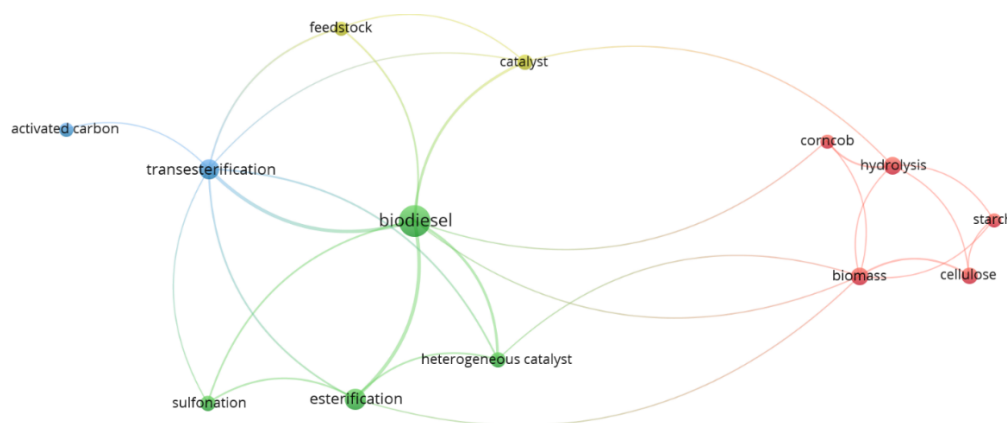


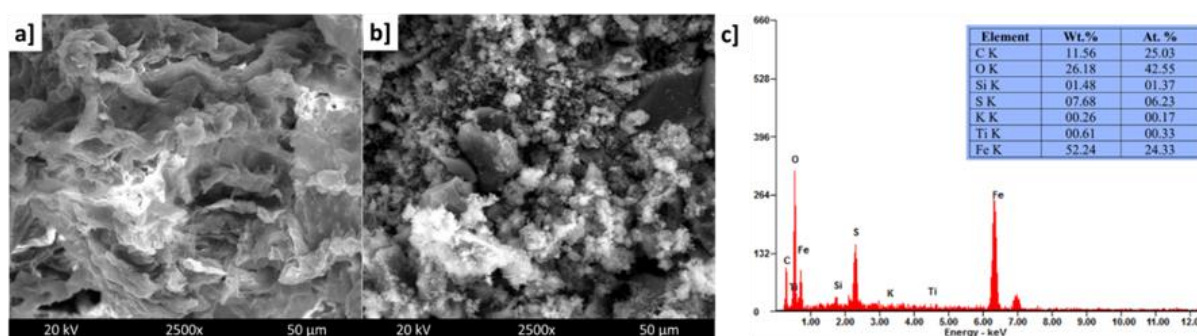
Figure 1. Network visualization of corncob solid catalyst for biodiesel production.

3.2. Catalyst Characterization

The morphology and element composition of CO and CO-SO₃H-Fe are presented in **Figure 2**. Due to the lignocellulose as the major component of CO, the surface was smooth and arranged by the irregular shape of larger aggregates (**Figure 2a**). After further modification using sulphonation and Fe impregnation, the surface became rougher and the size of aggregates became smaller which were distributed uniformly on the surface (**Figure 2b**). The elemental analysis of CO-SO₃H-Fe exhibited the chemical composition of carbon (11.56%), oxygen (26.18%), silicon (1.48%), sulphur (7.68%), potassium (0.26%), titanium (0.61%) and iron (52,24%).

Table 1. Data of publication of corncob solid catalyst for the most cited articles in 2022.

Author	Title	Journal	Citations
Muhammad Aamir Bashir <i>et al.</i>	Recent development of advanced processing technologies for biodiesel production: A critical review	Fuel Processing Technology	75
Akintomiwa O. Esan, Siwaporn M. Smith, Shangeetha Ganesan	A non-conventional sustainable process route via methyl acetate esterification for glycerol-free biodiesel production from palm oil industry wastes	Process Safety and Environmental Protection	64
Joshua Iseoluwa Orege <i>et al.</i>	Recent advances in heterogeneous catalysis for green biodiesel production by transesterification.	Energy Conversion and Management	56
P.R. Yaashikaa, P. Senthil Kumar, S. Karishma	Bio-derived catalysts for production of biodiesel: A review on feedstock, oil extraction methodologies, reactors and lifecycle assessment of biodiesel.	Fuel	48
Samah Zaki Najji, Ching Thian Tye	A review of the synthesis of activated carbon for biodiesel production: Precursor, preparation, and modification.	Energy Conversion and Management: X	42

**Figure 2.** SEM images of before and after sulphonation-impregnation process, a) CO and b) CO-SO₃H-Fe; c) EDS spectra of CO-SO₃H-Fe.

FT-IR was used to identify the functional groups on the surface of CO and CO-SO₃H-Fe particles (**Figure 3a**). The vibrational mode of O-H, C-H, C=O (carboxylic acid), and C=C (aromatic carbon) was detected at 3328, 2924, 1710, and 1533 cm⁻¹, respectively (Araujo *et al.*, 2021; Ibrahim *et al.*, 2019; Krishnan *et al.*, 2022). Furthermore, the bands at 1230 and 1020 cm⁻¹ were attributed to the stretching vibration of cellulose and pyranose ring skeletal (Krishnan *et al.*, 2022). The presence of the -SO₃H group on the surface of CO-SO₃H-Fe appeared at two vibration bands, i.e. 1113 and 1030 cm⁻¹ (Ibrahim *et al.*, 2020). Furthermore, the successful Fe attachment by impregnation was indicated at 540 cm⁻¹ (Krishnan *et al.*, 2022). This result revealed that the acidity behaviour of CO-SO₃H-Fe was related to the presence of -OH, -COOH and -SO₃H, and the quantitative measurement is shown in **Table 2**. Moreover, the existence of Fe as the magnetic carrier was supported by the XRD pattern of CO-SO₃H-Fe (**Figure 3b**).

The XRD pattern of CO indicated a peak of cellulose at $2\theta = 16.22^\circ$ with an amorphous structure (Nata *et al.*, 2017). The peak at $2\theta = 22.47^\circ$ showed a graphitic structure that attributed to the carbon planes of (002) (Ibrahim *et al.*, 2020). The amorphous carbon was assigned to diffraction broad at 20-70°. The main XRD diffraction peaks at $2\theta = 30.3, 35.6, 57.55, \text{ and } 62.96^\circ$ were attributed to (220), (311), (511) and (440), indicating the formation

of magnetite (Fe_3O_4) (Araujo *et al.*, 2021). Meanwhile, the formation of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) was assigned at $2\theta = 33.23$, 49.97 , and 54.3° and attributed to (310), (421) and (430) (Figure 3b) (Krishnan *et al.*, 2022). It confirmed that the components of iron oxide were successfully attached to the CO through the impregnation process.

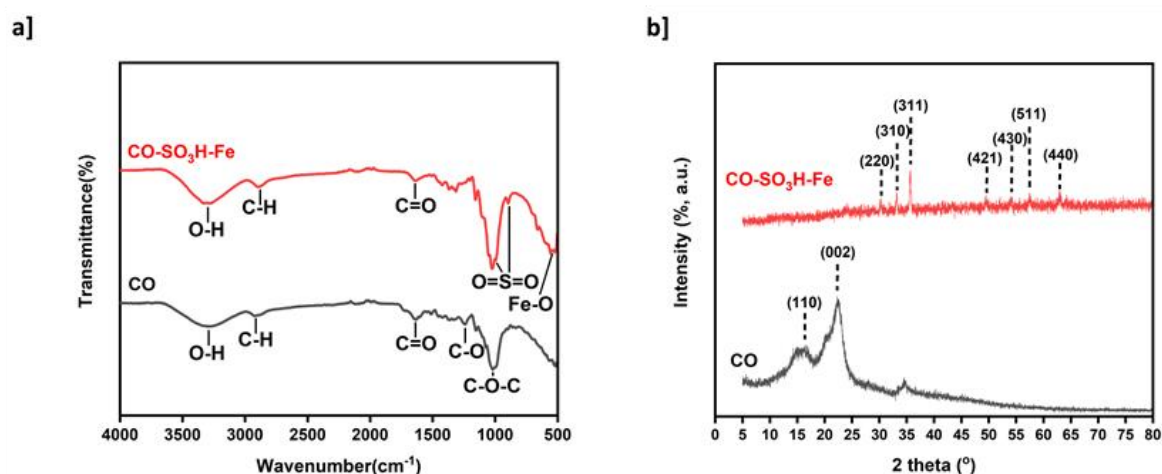


Figure 3. The qualitative characterization of corncob before and after the sulphonation-impregnation process, a) The FT-IR spectra of CO and CO-SO₃H-Fe, and b) XRD patterns of CO and CO-SO₃H-Fe.

Table 2. The densities of acidic groups

Materials	Total acid (mmol/g)	-SO ₃ H (mmol/g)	-OH (mmol/g)	-COOH (mmol/g)
CO	0.66	-	0.55	0.11
CO-SO ₃ H-Fe	1.43	0.74	0.57	0.12

Thermogravimetric (TGA) analysis was performed to evaluate the thermal stability of the catalyst, CO-SO₃H-Fe, and raw feedstock, CO (Figure 4). The CO particle exhibited two mass loss events. The first mass loss was due to the water evaporation. It was around 9.5% of mass loss and occurred from 40-100°C. Meanwhile, the second mass loss (78.9%) at the temperature range of 300-400°C was related to the decomposition of cellulose (da Luz Corrêa *et al.*, 2020). After the treatment (sulfonation-impregnation), the CO-SO₃H-Fe particle showed three mass loss regions.

The first region was at a temperature in the range of 40-100°C with 4.09% mass loss that was associated with water evaporation. The second one was at the temperature in the range of 250-300°C with 11.62% mass loss related to the decomposition of -SO₃H (Chellappan *et al.*, 2018), and the last region was at the temperature in the range of 780-900°C with 27.51% mass loss related to the decomposition of the catalyst (Dehkhoda *et al.*, 2010; Shu *et al.*, 2009). It suggested that the -SO₃H group in the catalyst was stable until 450°C, and should not be utilized for reaction at a temperature over 450°C.

Vibrating sample magnetometry (VSM) was utilized to detect the magnetic hysteresis curves (Figure 5). The CO-SO₃H-Fe particle had a high saturation magnetisation value of 16.48 emu/g after the impregnation process. The value was not found in the CO particle because no magnetic behaviour was inserted into the particle. The same result was also revealed by Chellapan *et al.* (2018) that synthesized a cassava peel-derived magnetic acid catalyst with a magnetization value of 11.16 emu/g.

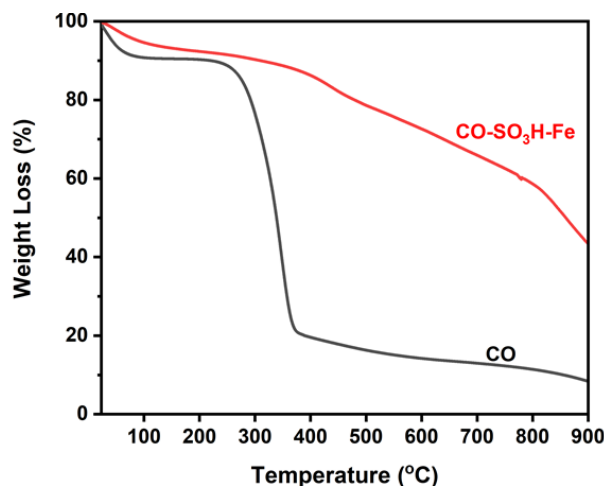


Figure 4. TGA analysis of corncob before and after sulphonation-impregnation process.

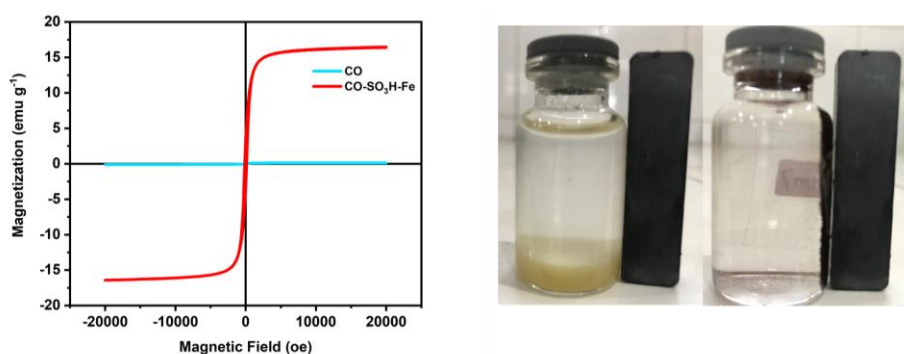


Figure 5. VSM analysis of corncob before and after the sulphonation-impregnation process. Separation of CO and CO-SO₃H-Fe particle from solution.

3.3. Esterification Reaction of Waste Cooking Oil

The evaluation of catalyst loading and reaction time on the esterification reaction of WCO is described in **Figure 6**. The esterification reaction was performed by using different amounts of catalyst (1-5 wt%) and different ranges of reaction time (1-5 h) at 60°C and a molar ratio of 15:1 of methanol to WCO. The results exhibited that the FFA conversion increased from 61.65±2.6% to 86.12±2.1% as the amount of catalyst was increased from 1 to 5 wt%. The greater amount of catalyst could increase FFA conversion effectively; however, the amount of catalyst beyond 4wt% did not have any significant impact on FFA conversion. It was only a few increases in FFA conversion after the 5wt% catalyst was added to the reaction solution. According to [Araujo et al. \(2021\)](#), an increase in the amount of solid acid catalyst was observed followed by an increase in the number of active sites providing H⁺ during an esterification reaction. Nevertheless, the excess solid catalyst could lead to the mass transfer problem ([Zhou et al., 2016](#)). The excessive solid catalyst particles in reaction solution show a tendency of self-agglomeration that inhibits the accessibility of reactant into the active site of catalyst ([Thushari & Babel, 2017](#)). To provide sufficient mass transfer between solid catalyst and liquid reactants, the reaction time should be longer than liquid phase reaction system. The duration of esterification reaction is determined by an interaction between reactant and catalyst to generate the target product ([Araujo et al., 2021](#)). The conversion of FFA increased slowly until 2 h of reaction. A significant enhancement in the FFA conversion started from 3 to 4 h. Thereafter, the conversion remained constant at 5 h.

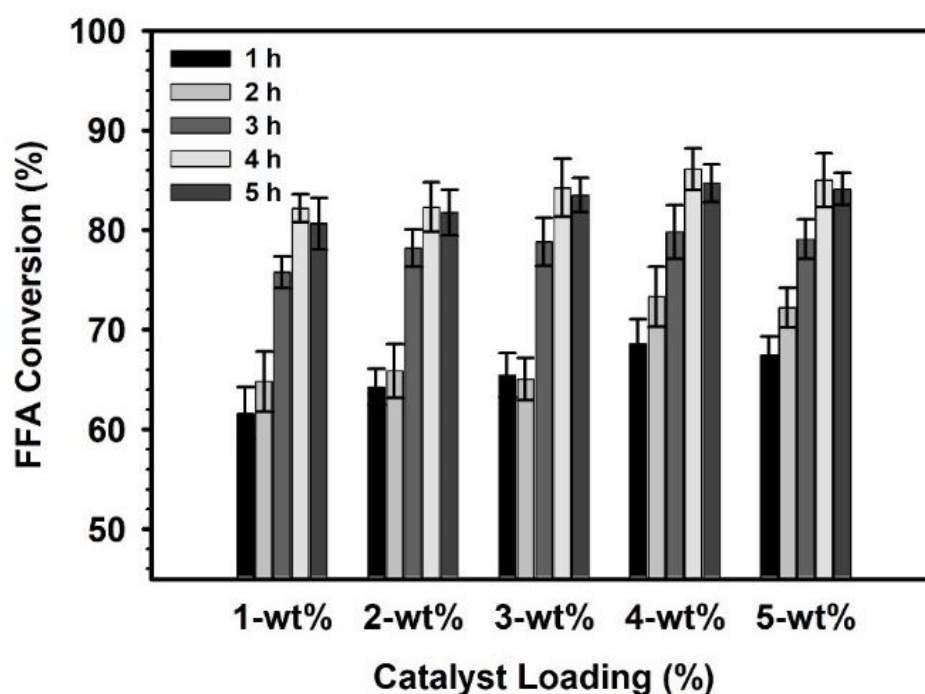


Figure 6. Effect of catalyst concentration and reaction time on esterification of WCO. The reaction was conducted at methanol to WCO mol ratio of 15:1 and 60°C reaction temperature.

It could be concluded that prolonged reaction time could lead to a shift in the reaction toward the reactant (Farabi *et al.*, 2019). For this reaction with the range amount of catalyst loading between 1% and 5%, the optimum reaction time was selected to be 4 h generating 86.12±2.1% conversion of FFA.

Theoretically, 1mol of alcohol is required for 1mol of FFA in esterification as a reversible reaction system. As a way to shift the reaction toward the product, excess alcohol is added to the reaction system (Hussain & Kumar, 2018; Ma *et al.*, 2014). This study also evaluated the effect of the molar ratio of WCO on methanol (Figure 7a). The molar ratio of WCO on methanol was varied to 1:1, 1:3, 1:6, 1:9, 1:12, 1:15 and 1:18. The experiment was conducted at 5wt% catalyst loading, and at 60°C for 4 h. FFA conversion gradually increased from 65.43±2.5% to 86.12±2.1% after mole of methanol increased from 1 to 15. An insignificant enhancement of FFA conversion (85.29±3.2%) was identified after 18 moles of methanol were added to the reaction system. The excess of alcohol in the esterification system at a particular point could dilute the reaction system (Mardina *et al.*, 2021). It could hinder the mass transfer between solid catalysts and reactants. Furthermore, it could lead to a low reaction rate (Ibrahim *et al.*, 2019).

The effect of reaction temperature of esterification catalysed by CO-SO₃H-Fe was investigated. The reaction temperature was varied into 40, 60, 80, 100, and 120°C. The experiment was conducted at 5wt% catalyst loading, 1:15 of WCO to methanol molar ratio for 4 h. The FFA conversion remained constant after 60 °C. It tended to decrease after 100 °C (Figure 7b). Here, a high temperature could have a positive effect on the esterification reaction. According to Ibrahim *et al.* (2020), the miscibility of methanol and oil could increase as soon as the temperature of the reaction increases. However, a further increase in temperature could evaporate the alcohol, particularly methanol. The reaction rate became slow due to the decrease in mole of methanol that shifted the reaction into the reactant (Abusweireh *et al.*, 2022; Correa *et al.*, 2020; Verma & Sharma, 2016).

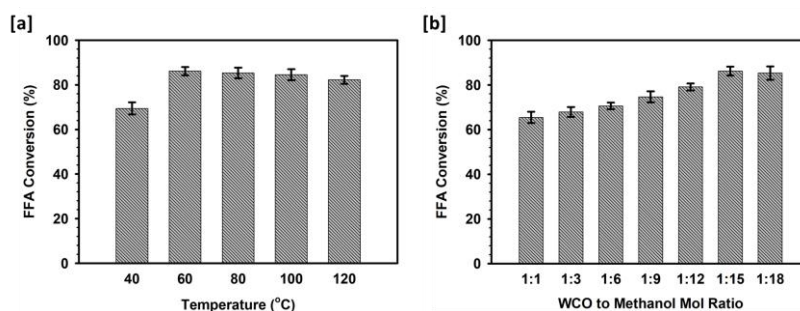


Figure 7. (a) Effect of reaction temperature on FFA conversion of WCO esterification, the reaction was conducted at 5-wt% catalyst loading, methanol to WCO mol ratio of 15:1 and 4 h. (b) Effect of WCO to methanol mol ratio on FFA conversion of WCO esterification, the reaction was conducted at 5-wt% catalyst loading, 4 h and 60°C reaction temperature.

In **Figure 8**, the catalytic performance of CO, CO-SO₃H-Fe and concentrated H₂SO₄ was observed for the esterification reaction of WCO and methanol under optimum conditions. The results indicated that the FFA conversion was enhanced by the existence of high acidity. The conventional catalyst (H₂SO₄ 98%) exhibited the highest FFA conversion (89.33±1.8%) followed by CO-SO₃H-Fe (86.12±2.1%), and the lowest value was yielded by CO (3.99±1.9%). Chromatograms peak for the produced biodiesel for the best result is illustrated in **Figure 9**. The effectiveness of the utilization of CO-SO₃H-Fe was confirmed by the formation of six intense peaks which belong to Lauric acid methyl ester (C12:0), myristic acid methyl ester (C14:0), palmitic acid methyl ester (C16:0), stearic acid methyl ester (C18:0), oleic acid methyl ester (C18:1), and arachidic acid methyl ester (C20:0) (**Table 3**).

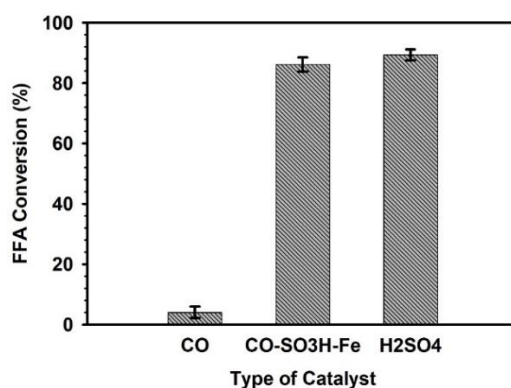


Figure 8. Effect of the type of catalyst on FFA conversion of WCO esterification. The reaction was conducted at 5-wt catalyst loading, methanol to WCO mol ratio of 15:1, 4 h and 60°C.

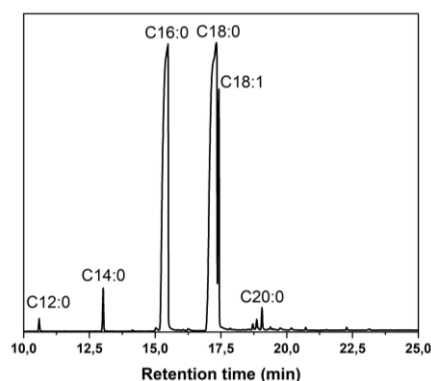


Figure 9. Chromatogram peak of produced biodiesel.

Table 3. Components of the produced biodiesel.

Compounds	Retention time (min)	Area %
Lauric acid methyl ester (C12:0)	10.589	0.32
Myristic acid methyl ester (C14:0)	13.024	1.10
Palmitic acid methyl ester (C16:0)	15,484	38.89
Stearic acid methyl ester (C18:0)	17.326	50.03
Oleic acid methyl ester (C18:1)	17.419	7.58
Arachidic acid methyl ester (C20:0)	19.062	0.61

3.4. Catalyst Reusability

High recovery rate and high reusability are the main targets of magnetic solid acid catalyst synthesis. The reusability of the synthesized catalyst was evaluated in five esterification cycles under an optimum condition. After each cycle, the catalyst was recovered by the external magnetic field and was washed with methanol to remove any impurities. The retained catalytic performance of each cycle is described in **Figure 10**.

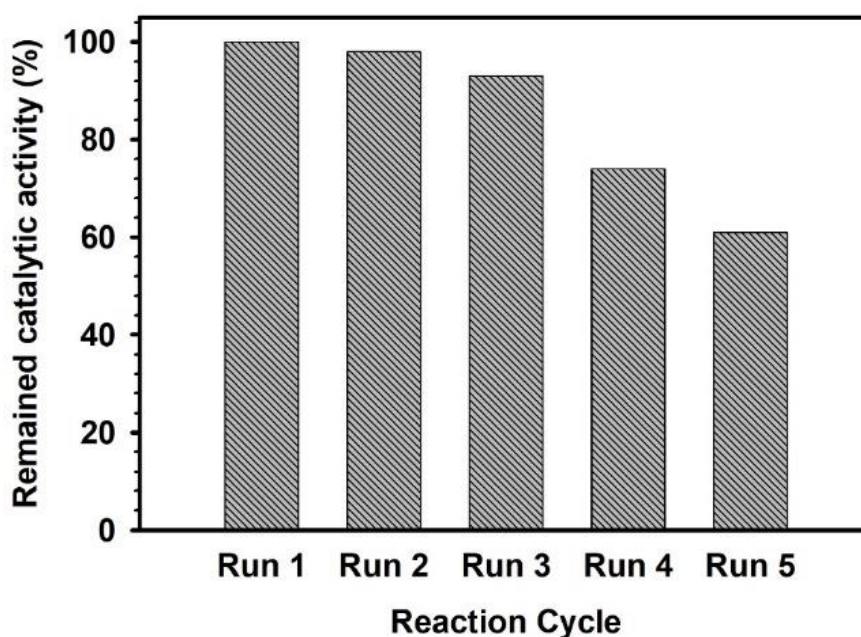


Figure 10. Reusability study of CO-SO₃H-Fe in the esterification of WCO. The reaction was conducted at 5 wt% catalyst loading, methanol to WCO mol ratio of 15:1, 4 h and 60°C.

The performance insignificantly decreased after the third cycle, but it started to decrease around 26 and 39% in the fourth and fifth cycles, respectively. The reduction of catalytic performance suggested that it might be due to the leaching of the -SO₃H groups during the reaction (Farabi *et al.*, 2019). It was proven by -SO₃H density and FT-IR analysis of reused particles after five cycles (Fu *et al.*, 2012; Mardina *et al.*, 2023). The concentration of -SO₃H decreased from 0,74mmol/g to 0,32mmol/g (Table 4).

Table 4. The acidity of CO-SO₃H-Fe before and after 5 consecutive cycles in esterification of WCO.

Particles	Acidity properties (mmol/g)		FFA Conversion (%)
	-SO ₃ H	Total acidity	
CO-SO ₃ H-Fe	0.74	1.43	86.12
CO-SO ₃ H-Fe-Reused	0.32	1.01	52.53

Correlated with that value, the FT-IR data obtained for the reused catalyst showed that the bands related to $\text{-SO}_3\text{H}$ groups at 1113 cm^{-1} and 1030 cm^{-1} were weaker after five consecutive cycles (**Figure 11**).

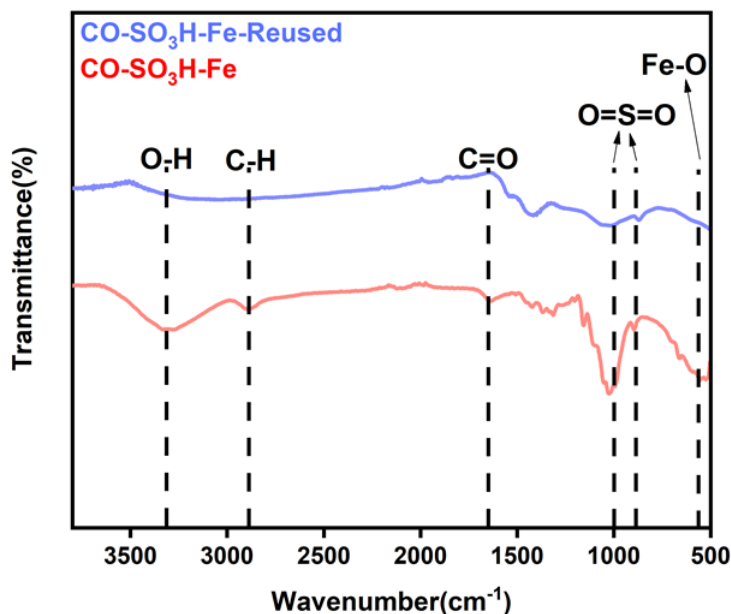


Figure 11. FTIR spectra of $\text{CO-SO}_3\text{H-Fe}$ and reused catalyst, $\text{CO-SO}_3\text{H-Fe-Reused}$, to provide evidence of $\text{-SO}_3\text{H}$ group leaching after 5 cycles reactions.

3.5. Comparison with Previous Literature

The catalytic performance of the $\text{CO-SO}_3\text{H-Fe}$ was comparable to previous similar studies, which synthesized the biomass-derived solid acid catalyst with magnetic behaviour and the obtained catalysts was evaluated in esterification reaction (**Table 5**). Many methods have been employed to synthesize high performance catalyst with good recovery rate.

Table 5. The comparison studies of biomass-derived magnetic solid acid catalysts for biodiesel production.

Biomass	Method	Total Acidity (mmol/g)	Application	Results	References
Jatropha hulls	Hydrothermal precipitation, pyrolysis and sulfonation.	2.96	Biodiesel production from Jatropha oil.	Yield of biodiesel 96% (cycle 1), 90% (cycle 2) and 86% (cycle 3)	Zhang et al. (2017)
Palm Empty Fruit Bunch	Sulfonation, carbonation, and impregnation.	-	Esterification of PFAD	FFA conversion 98,65%	Ibrahim et al., (2019)
Acai seeds	Impregnation with red mud followed by sulfonation.	3.40	Esterification of oleic acid.	Oleic acid conversion 93%	Araujo et al., (2021)
Corncob residue	Sulfonation-Impregnation	1.43	Esterification of WCO	FFA conversion 86.12±%	This Study

Generally, carbonization, impregnation and sulfonation are conducted sequentially to generate acid and magnetic properties on the surface of particles. For this study, the maximum reaction conversion was $86.12 \pm 2.1\%$ with a 5% catalyst loading, a methanol to oil molar ratio of 15:1, and a reaction temperature of 60°C within 4 h. The $\text{CO-SO}_3\text{H-Fe}$ had an ability to reuse for five cycles with the FFA conversion of $52.53 \pm 1.7\%$. The modification and development on synthesis process are required to more enhance catalytic performance and the recovery rate of catalyst for efficient esterification reaction.

4. CONCLUSION

The corncob-derived magnetic acid solid catalyst was synthesized through 2-step processes; i.e., sulfonation-impregnation. The sulfonation of the corncob resulted in acid particles which consisted of strong acid groups; $-\text{SO}_3\text{H}$ and $-\text{COOH}$ and weak acid group; $-\text{OH}$. Furthermore, the sulfonated particles were impregnated using ferric sulphate and ferrous sulphate heptahydrate solution (chemical ratio of 1:2). The magnetic-sulfonated solid catalyst was applied in the esterification of WCO, and yielded $86.12 \pm 2.1\%$ FFA conversion under optimum reaction conditions with 5wt% catalyst for 4 h reaction at 60°C and 15:1 methanol-to-WCO molar ratio. The used catalyst was separated magnetically from the reaction solution and exhibited comparable reusability up to the fifth reaction cycle with 61% remaining activity. This study successfully synthesized the magnetic sulfonated solid catalyst from corncob residue. These results could be expanded to utilize other biomass as its carbon precursor.

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper was free of plagiarism.

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