

1        **Waste sugarcane bagasse derived nano catalyst for microwave assisted**  
2        **transesterification: Thermal, kinetic and optimization study**

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## 1 **Abstract**

2 Production of biodiesel has been increased globally during the last decade to overcome the  
3 problems of increasing prices of petro-diesel and depletion of fossil fuels. The present study  
4 aims to utilize agro-waste sugarcane bagasse (SCB) to synthesize heterogeneous acid catalyst  
5 for biodiesel production using waste cooking oil. Waste sugarcane bagasse was converted into  
6 biochar through partial carbonization and activated via sulfonation by using 1M, 3M, 5M and  
7 concentrated sulfuric acid at a sulfonation temperature of 180 °C for 5 h. The prepared catalysts  
8 were characterized by using Fourier transform infrared spectroscopy (FT-IR),  
9 thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Brunauer–Emmett–  
10 Teller (BET), X-ray diffraction (XRD), and CHNS analyzer. The prepared catalyst exhibited  
11 an excellent surface area of 20.78 m<sup>2</sup>/gm and a total acid density of 3.94 mmol/gm. The yield  
12 of biodiesel was optimized over the influence of four process parameters in the range of  
13 reaction temperature (40-70 °C), methanol to oil molar ratio (5:1-20:1), catalyst loading (1-7  
14 wt.%) for 5-25 min using microwave reactor. The maximum conversion of 95.45% and yield  
15 of 92.12% was obtained under optimum conditions; catalyst loading 5 wt.%, methanol to oil  
16 molar ratio (15:1), temperature (60 °C) after 15 min. The results of experiments were validated  
17 by using response surface methodology which validated the predicted model. Kinetic study of  
18 experiments depicted that the use of sulfonated catalyst lowered the activation energy (10.5  
19 kJ/mol) and reactants attained equilibrium point after a short interval of time under microwave  
20 heating. Moreover, reusability of catalyst up to seven cycles with 77.34% yield of biodiesel  
21 using low-grade feedstock showed that the catalyst is stable and can be used for sustainable  
22 biodiesel production. The utilization of wastes for catalyst synthesis as well as for biodiesel  
23 production can help us to minimize the overall production cost of biodiesel.

24 **Keywords:** Renewable energy; Biodiesel synthesis; Process optimization; Biofuels; Waste  
25 cooking oil and Sugarcane bagasse.

# 1 Introduction

2 The unexceptional situations have created in the past few years to replace petroleum-based  
3 materials with bio-based alternatives because of the increasing prices of the fuels and rapid  
4 depletion of fossil fuels [1, 2]. Therefore, attention has been given to biomass resources to  
5 diminish the challenges of the global environment and increasing prices of crude petroleum  
6 [3]. Biodiesel is considered the most promising alternative to petro-diesel. It is renewable,  
7 biodegradable, environment friendly, greater lubricity causes less emissions of toxic  
8 compounds [4, 5]. The 75% price of biodiesel is mainly dependent on the feedstock used. Many  
9 types of oils (edible, non-edible, and plant), as well as animal fats, are utilized as a substrate  
10 for biodiesel synthesis, but due to limited resources for feedstock, the focus is to turn to utilize  
11 the waste materials to overcome the food crisis as well as to reduce the price of biodiesel [6,  
12 7].

13  
14 Numerous types of waste feedstocks like waste cooking oil [8], waste frying oil [9], waste palm  
15 oil [10], oils and fats extracted from different resources [11, 12] have been used for biodiesel  
16 production. Biodiesel is generally produced by transesterification of fat or oil by using a solvent  
17 like methanol or ethanol and catalyst. Catalysts such as NaOH and KOH are not favourable  
18 because of some disadvantages e.g. saponification and catalyst separation [13]. Homogeneous  
19 acid catalysts are also not suitable due to their corrosive nature and difficult recovery of the  
20 catalyst from the reaction mixture and large volume of water for purification [14]. Therefore,  
21 attention has been diverted towards heterogeneous solid acid catalysts as they can perform  
22 esterification and transesterification simultaneously [15]. Moreover, these are environmentally  
23 benign, less corrosive and reusable without further modification [16].

24

1 Agricultural residues are rich sources of cellulose, hemicellulose, and lignin [17]. They can be  
2 used to produce various valuable products by different methods [18]. The major components  
3 of sugarcane bagasse are mainly cellulose, hemicellulose, lignin and a minor quantity of ash  
4 and volatile matter. The 2<sup>nd</sup> most abundant polymer on earth followed by cellulosic biomass is  
5 lignin. Sugarcane is mainly produced in northwest states (Perlis and Kedah) of peninsular  
6 Malaysia. About 700,000 tons of sugarcane is obtained from 22,000 hectares annually. In  
7 general, one tone of sugarcane generates 0.3 ton of waste sugarcane bagasse, which can be a  
8 promising feedstock for the synthesis of carbon-based nanocatalyst [19].

9  
10 The materials derived from different wastes e.g. waste chicken eggshells [20], sodium silicate  
11 obtained from rice husk [21], chicken and fish bones [22], orange peels [23], palm fruit bunch  
12 derived catalyst [24], used coffee beans [25] and many other bio-waste materials based  
13 catalysts have been applied for biodiesel synthesis as the available in bulk quantity and can be  
14 prepared easily. Different studies have been carried out to synthesize solid acid catalysts. There  
15 are different process parameters of sulfonation (sulfonation time, sulfonation temperature,  
16 carbonization time and carbonization temperature) that have been previously described in the  
17 literature [26]. The influence of acid concentration on sulfonation of biomass-derived catalysts  
18 is hardly reported in the literature. The catalyst obtained from yeast residue gave 94.8%  
19 biodiesel yield using a low-grade feedstock at 70 °C with a methanol to oil ratio 10:1 and 4  
20 wt.% of catalyst [27]. Kenaf seed-based catalyst showed 97.9% FAME yield at 65 °C with 2  
21 wt.% of catalyst, 10:1 of methanol to feedstock after 1.5 h [28].

22  
23 A.O. Etim et al. [29] synthesized a biocatalyst from *Carica papaya* peels and achieved 97.5%  
24 yield of biodiesel using waste vegetable oil under optimum conditions. Heterogeneous catalyst  
25 synthesized from red banana peels used to produce biodiesel approximately 98.73% conversion

1 with 2.68 wt.% catalyst using 11.26:1 to methanol to oil after 1.8 h [30]. A biodiesel yield of  
2 92.7% was obtained using a catalyst synthesized from coconut meal residue and waste palm  
3 oil under optimum conditions [31]. Anietie et al. [29] developed a heterogeneous catalyst from  
4 banana peels and utilized it in the transesterification of marula seed oil. They claimed 96.45  
5 wt.% yield of methyl esters in their study. The use of waste cork based catalyst for  
6 transesterification of waste cooking oil under optimized reaction parameters gave 98% yield of  
7 biodiesel [32].

8  
9 Rice husk based catalyst produced 98.6% yield of biodiesel at 75 °C, 12:1 of methanol to used  
10 cooking oil with 4wt.% catalyst after 240 min [33]. A solid acid catalyst synthesized from palm  
11 fruit bunch was utilized in the transesterification of low-grade feedstock and gave 88.5% yield  
12 of biodiesel over-optimized reaction parameters [34]. Bamboo and palm kernel shell derived  
13 acid catalysts were used in biodiesel production and reported for 94.2% and 95.8% FAME  
14 yield respectively [35]. Catalyst derived from sugarcane leaf ash at 64 °C, catalyst  
15 concentration of 5 wt.%, and 19:1 of methanol to oil gave 97% yield of biodiesel [36].  
16 Sulfonated catalyst derived from cow-dung gave 96.5% conversion of palm fatty acid distillate  
17 under optimized reaction conditions [37]. Furthermore Hassan et al. [38] and Varol et al. [39]  
18 synthesized biodiesel by using a microwave reactor and commercially available catalyst  
19 (KOH). They claimed 93% yield and 97% conversion, respectively. The disadvantage of this  
20 study was to pre-treat the oil and longer reaction time due to the use of homogeneous base  
21 catalyst.

22  
23 Ngaosuwan et al. [40] achieved 71.5% FFA conversion using biomass-derived catalyst  
24 obtained from the coffee residue after 4 h of transesterification. The time required to complete  
25 the transesterification process was noted to be quite higher under conventional heating. Bureros

1 et al. [41] achieved 94% FFA conversion from oleic acid using cacao shell derived catalyst  
2 after 24 h. In most of the previous studies of microwave-assisted transesterification of different  
3 feedstocks, commercially available homogeneous catalysts were used which are not suitable  
4 for low-grade feedstocks. Therefore, pre-treatment of feedstocks was required to achieve  
5 maximum yield of biodiesel which in result increased the time as well as overall production  
6 cost of biodiesel [42, 43].

7

8 The kinetic and optimization study of microwave-assisted transesterification using waste  
9 sugarcane bagasse derived nanocatalyst is hardly reported in the literature. Moreover, 92.12%  
10 yield of biodiesel achieved in this study after 15 min by using a modified microwave reactor is  
11 comparably higher than previous studies. In the present work, sugarcane bagasse is utilized to  
12 develop heterogeneous acid catalyst to produce biodiesel WCO under the influence of  
13 microwave heating. The process optimization and kinetic studies of biodiesel synthesis using  
14 WCO and biomass waste derived catalyst via microwave irradiation is hardly reported in the  
15 literature. Therefore, there is a dire need of developing a biomass waste derived catalyst and  
16 investigating its effect on biodiesel production. The prepared catalyst from waste sugarcane  
17 bagasse in this study would decrease an overall production cost of biodiesel and making its  
18 implementation possible to commercial scale.

19

20 The catalysts were synthesized by partially carbonization, activation and varying the  
21 concentration of sulfuric acid (1M, 3M, 5M and conc.  $H_2SO_4$ ), at given conditions and effect  
22 of acid concentration on sulfonation of catalyst was investigated. The process of  
23 transesterification was optimized by using the prepared catalyst in a modified microwave  
24 reactor. The interaction between the parameters affecting the transesterification process and  
25 biodiesel yield was investigated using mathematical modelling developed by response surface

1 methodology. The active surface area and pore size of catalyst under this study was higher  
2 enough to support the transesterification process giving maximum yield of biodiesel with  
3 minimum reaction time. The utilization of waste material for catalyst preparation as well as for  
4 biodiesel production using microwave reactor will save energy and minimize biodiesel  
5 production cost.

## 6 **2 Material and methods**

### 7 **2.1 Materials**

8 Sugarcane Bagasse was purchased from a juice stall in Batu Gajah, Malaysia. Sulfuric acid  
9 (95-97%), Sodium Hydroxide (NaOH), n-hexane, phosphoric acid, sodium chloride,  
10 phenolphthalein and methanol were ordered from Sigma Aldrich Malaysia. The chemicals used  
11 in experiments were of analytical grade and their CAS number, mass fraction purity and boiling  
12 temperature is given in Table 1. WCO was obtained from a cafeteria located in Universiti  
13 Teknologi PETRONAS, Malaysia.

### 14 **2.2 Preparation of catalyst**

15 Waste sugarcane bagasse was washed using deionized water to separate from impurities. After  
16 washing it was dried at 105 °C for 24 h until its weight became constant. After drying, SCB  
17 was cut into small pieces (1-2 cm), then it was ground in a granulator to produce a powder.  
18 Afterwards, the fine powder was obtained (1 mm) using a biomass grinder. Raw SCB was  
19 impregnated by using phosphoric acid (85 wt.%) at 25 °C for 12 h [44]. Excess moisture was  
20 removed by drying the material at 105 °C. Chemically treated powdered SCB was filled in the  
21 porcelain crucible and placed in a tube furnace for the partial carbonization of SCB to produce  
22 a carbon structure. Carbonization was done at 300-800 °C (heating rate of 10 °C/min) for 60-  
23 120 min using nitrogen (50 mL/min) to study the effect of carbonization time and temperature  
24 on char yield and surface area [45]. Nitrogen gas was used to obtain the higher carbon content  
25 during carbonization because it is an inert and stable gas that degrades material without

1 oxidation [46]. The char produced at 400 °C after 60 min showed the highest surface area  
2 (25.32 m<sup>2</sup>/gm), therefore, 400 °C and 60 min were selected as an optimum carbonization  
3 temperature and time, respectively. The yield of char was calculated using Eq. (1).

$$4 \quad \text{Char yield (\%)} = \frac{\text{Mass of char produced}}{\text{Mass of SCB}} \times 100 \quad (1)$$

6  
7 The extracted char was washed with hot water (85 °C) and the final product was dried at 105  
8 °C to remove moisture. Four samples of catalyst were prepared by fixing the sulfonation time  
9 (5 h), sulfonation temperature (180 °C) and varying the acid concentration from concentrated  
10 acid (95-97%) to 1M, 3M and 5M. In most of the previous studies, heterogeneous acid catalyst  
11 from waste biomass was prepared by using concentrated acid and sulfonation using dilute  
12 acidic solutions is hardly reported in the literature. Therefore, in the present study, the strength  
13 of acid solution was varied to study the effect of acid strength on catalytic activity, acid density  
14 as well as the attachment of different functional groups on char surface during sulfonation.  
15 Sulfonation was done in a 2-neck flask having a condenser by placing it in an oil bath at a  
16 constant stirring of 400 rpm. After sulfonation mixtures were cooled down, filtered, and  
17 washed to remove extra acid until a filtrate of pH 7 was obtained then dried at 105 °C to remove  
18 the remaining moisture and kept in glass containers labelled as A, B, C and D.

### 19 **2.3 Characterization of waste sugarcane bagasse and prepared catalysts**

20 The thermogravimetric analysis of waste biomass and prepared catalysts was done using a  
21 PerkinElmer thermal analyzer in the temperature range of 25-800 °C (10 °C/min) using  
22 nitrogen at a flow rate of 50 mL/min [47]. Fourier transform infrared spectroscopy analysis  
23 (FT-IR) was performed from 400-4000 cm<sup>-1</sup> in order to study functional groups of biomass and  
24 biomass active catalysts [48]. Spectroscopic analysis of waste biomass and biomass derived  
25 catalyst to study the morphological behaviour before and after activation was performed



1 through the scanning electron microscope. The surface area of waste SCB and prepared  
2 catalysts was determined by using a surface area analyzer (SAP). The samples were degassed  
3 overnight at 120 °C before analysis [49]. The CHNS analyzer was used for the elemental  
4 analysis of waste biomass and catalysts to determine the amount of C, H, N and S before and  
5 after activation. X-RAY diffraction (XRD) was done by using Philips X' Pert MPD X-ray  
6 diffractometer under the following operating parameters;  $\lambda = 0.15$  nm, 5–70° 2 $\theta$  range, 0.05°  
7 step size, 2.990 s step time [50].

## 8 **2.4 Catalytic activity**

9 The sulfonic acid groups density attached to the catalyst surface after sulfonation was measured  
10 by a method stated by Sani et al. [51] and total acid density (sulfonic group, hydroxyl group  
11 and carboxyl group) was calculated by the procedure stated by Lee [52]. For total acidic  
12 density, 0.5 gm of the sample was mixed with 50 mL sodium chloride (NaCl, 2 N) solution at  
13 200 rpm. The solid was removed through vacuum filtration. 15 mL of filtrate was taken, and  
14 three drops of universal indicator were mixed in the solution. Then, this filtrate was titrated  
15 against 0.01 M standard sodium hydroxide (NaOH) solution until the final point was achieved.  
16 Total acid density was determined from Eq. (2).

$$17 \quad \text{Total acid density} = \frac{(V_{NaCl} \times \text{normality of NaCl}) - (V_{NaOH} \times N_{NaOH})}{\text{mass of catalyst}} \quad (2)$$

18 where  $V_{NaCl}$  (mL) is the volume of NaCl,  $N_{NaOH}$  is the normality of NaOH solution and  $V_{NaOH}$   
19 (mL) is the volume of NaOH used during titration. Total acid density (3.94 mmol/gm) was  
20 found in catalyst prepared by concentrated H<sub>2</sub>SO<sub>4</sub>. Proximate analysis of the raw sample was  
21 done by putting 3 gm of powdered bagasse was put into a 50 mL crucible and it was placed in  
22 an oven at 105 °C until the weight became constant. The moisture content of the waste  
23 sugarcane bagasse was 6.22%. To calculate volatile matter, the covered crucible was placed in  
24 a muffle furnace at 900 °C for five min reaction time with the open door and 3 min by closing

1 the door of the furnace. After that, the sample was taken out and allowed to cool in a desiccator  
2 for 60 min before weighing. Volatile content was determined using Eq. (3).

$$3 \quad \text{Volatile matter (\%)} = \frac{m_{105^{\circ}\text{C}} - m_{900^{\circ}\text{C}}}{m_i} \times 100 \quad (3)$$

4 where  $m_i$  is the initial weight and  $m_{900^{\circ}\text{C}}$  is the weight of the crucible after heating at  $900^{\circ}\text{C}$ .  
5 For determining ash and fixed carbon content the uncovered crucibles were heated at  $750^{\circ}\text{C}$   
6 for 180 min and then cooled for 1h in a desiccator before weighing. The percentage of ash  
7 content and fixed carbon content were calculated by using Eq. (4) and Eq. (5) respectively.

$$8 \quad \text{Ash content (\%)} = (m_{750^{\circ}\text{C}} - \frac{m_s}{m_i}) \times 100 \quad (4)$$

$$9 \quad \text{Fixed Carbon (\%)} = 100 - (\text{Moisture content} + \text{Volatile content} + \text{Ash content}) \quad (5)$$

10 where  $m_{750^{\circ}\text{C}}$  is the weight of the crucible after heating to  $750^{\circ}\text{C}$ .

## 11 **2.5 Microwave-assisted transesterification**

12 The selection of a suitable catalyst was done based on their initial performance after different  
13 time intervals by keeping other reaction variables to be constant. The further reaction cycles  
14 were determined by using that catalyst. The transesterification was done in a microwave of  
15 1000 W. The process was carried out by varying four parameters: temperature of the reaction,  
16 catalyst loading, reaction duration and oil to methanol ratio. To maximize the conversion of  
17 transesterification reaction, SCB-SO<sub>3</sub>H catalyst 1-7wt.% was selected based on initial  
18 screening, methanol: oil ratio 5:1 to 15:1, reaction temperature 40-70 °C and for a time interval  
19 of 5-25 min. The transesterification process is an endothermic reaction and the yield of  
20 biodiesel increases by increasing temperature. Moreover, high-temperature shifts the reaction  
21 equilibrium toward the product side, therefore, the temperature was varied to study the effect  
22 of temperature on biodiesel yield [53].

23

1 The desired amount of WCO having a higher value of FFA content (4.68%) was taken in a  
 2 flask and heated up to 60 °C. The measured amount of catalyst and solvent were added to the  
 3 reaction mixture at 400 rpm. Each experiment was performed three times to ensure the accuracy  
 4 of each run. The standard deviation ( $\pm 3\%$ ) of each input parameter was accommodated to  
 5 express overall biodiesel yield. After transesterification, the catalyst was removed by filtration  
 6 and FAME was washed twice using hot water (80 °C) and dried at 100 °C for 60 min to remove  
 7 moisture. Gas chromatography-mass spectrometry (GC-MS) was used to quantify the product  
 8 by using a capillary column in a heating range of 120-300 °C (10 °C/min) and an injector  
 9 temperature of 200 °C. The FFA conversion was obtained by using Eq. (6) [54].

$$10 \quad X_A(\%) = \left(1 - \frac{C_A}{C_{AO}}\right) \times 100 \quad (6)$$

11 where  $X_A$  is the triglycerides conversion,  $C_A$  (mol/L) is the concentration of un-reacted oil and  
 12  $C_{AO}$  (mol/L) is the initial concentration of oil.

## 13 **2.6 Optimization of biodiesel synthesis**

14 Central composite design (CCD) and response surface methodology (RSM) was used to  
 15 validate experimental data. The influence of alcohol to oil molar ratio, catalyst loading, reaction  
 16 time, and the temperature was investigated on biodiesel yield. The biodiesel yield was the  
 17 response variable. The model equations were generated for all significant variables to optimize  
 18 the values. The relation between input and output variables by coded and uncoded model  
 19 equation was presented. The effect of one input parameter was investigated on biodiesel yield  
 20 using OFAT method due to the limited number of trials available in this study. A second-order  
 21 mathematical model as shown in Eq. (7) was used to determine the adjusted values.

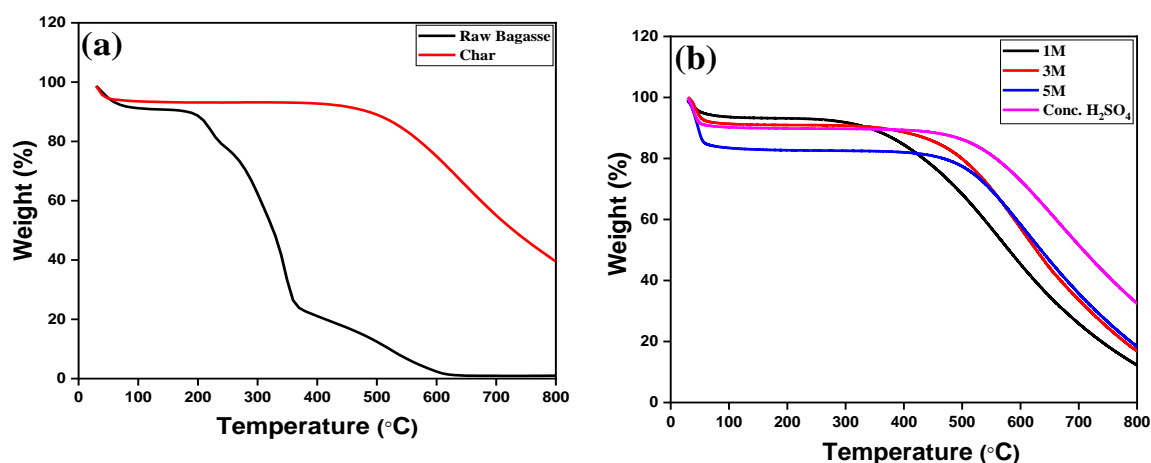
$$22 \quad Y = \beta_o + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^4 \beta_{ij} X_i X_j + \sum_{i=1}^4 \beta_{iii} X_i^3 \quad (7)$$

23 where  $Y$  is yield,  $\beta_o$  is offset factor,  $\beta_i$  is a linear effect,  $\beta_{ii}$  is the square effect,  $\beta_{ij}$  is interaction  
 24 effect,  $X_i$  is  $i$ th independent variable and  $X_j$  is  $j$ th independent variable.

### 3 Results and discussions

#### 3.1 Thermal stability analysis of waste biomass and prepared catalysts

Thermal stability of raw SCB, carbonized SCB and catalysts was done by using thermogravimetric analysis (TGA). Fig. 1 (a, b) shows the thermogravimetric analysis of raw-SCB, char and prepared catalysts. It can be observed from Fig. 1, that raw samples and prepared catalysts were decomposed gradually at different points due to the degradation of various compounds. The mass loss occurred in three stages during combustion. In the 1<sup>st</sup> stage (30-100 °C) water is removed and from (100-200 °C) removal of bound moisture and some volatile matter took place. In the 2<sup>nd</sup> stage (200-350 °C), maximum weight loss (53%) occurred due to devolatilization and degradation of cellulose and hemicellulose because SCB mainly consists of lignocellulose which starts burning above 270 °C. Above 350 °C remaining cellulose and lignin degraded by releasing a huge amount of volatile matters which indicated a significant combustion reaction at this stage [55].



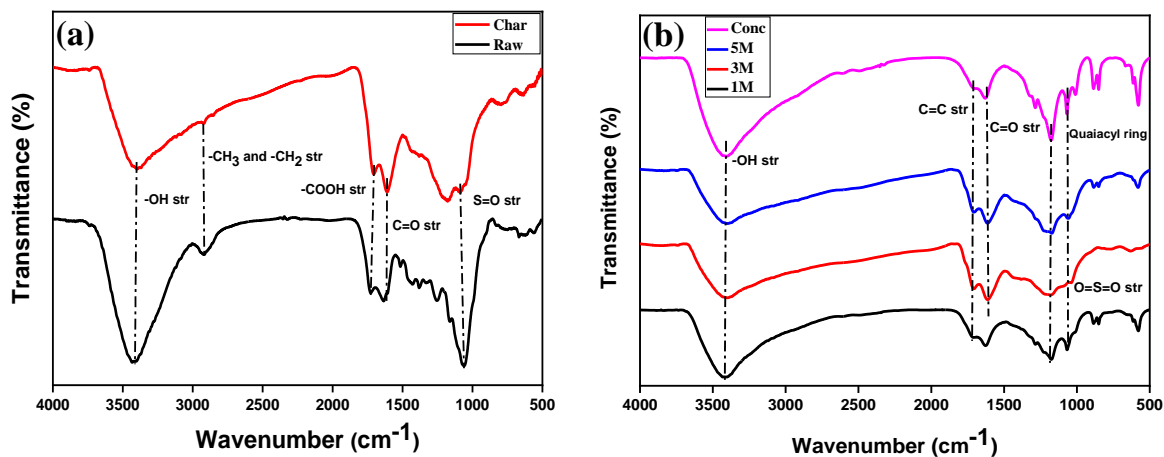
**Fig 1.** Thermal stability analysis of waste biomass, char, and prepared catalysts; (a) Raw SCB and Char and (b) Prepared catalysts with different strength of acid solutions.

This is also called an active pyrolysis zone. At 600 °C the combustion process was almost completed. Above 500 °C the de-sulfonation and decarboxylation occur, but it was noted that

1 even after de-sulfonation and decarboxylation, catalyst retained its activity because of the  
2 strong covalent attachment of sulfonic (-SO<sub>3</sub>H) and carboxyl (-COOH) group on the catalyst  
3 surface. The comparison of raw SCB and the char produced showed that the char is thermally  
4 more stable as compared to the raw bagasse which can be possible due to chemical activation  
5 with H<sub>3</sub>PO<sub>4</sub> and the presence of a large amount of total and stable carbon because of the  
6 removal of volatile matter [56]. Similar results were obtained from Subramaniyan et al. [57]  
7 study where they have reported the thermal stability of catalyst up to 400 °C.

### 8 **3.2 Surface chemistry analysis**

9 Fig. 2 (a, b) shows the FT-IR spectrums of waste SCB, char, and prepared catalysts,  
10 respectively. The comparison of raw sugarcane bagasse and the char produced showed that  
11 most of the peaks had been vanished in the char after partial carbonization due to the  
12 dehydration and degradation of biomass at higher temperatures. The char produced is rich in  
13 polycyclic compounds and the quantity of methyl and ethyl groups had been reduced due to  
14 the elimination of hydrogen during carbonization. Different vibrational stretching was recorded  
15 in the prepared catalysts. Bands at 1292 cm<sup>-1</sup> and 881 cm<sup>-1</sup> showed quaiacyl ring of lignin. The  
16 bands at 1467 cm<sup>-1</sup> showed stretching of bonds in cellulose and hemicellulose, respectively.  
17 The vibrational band at 1610 cm<sup>-1</sup> showed bond stretching of carbonyl and ester functional  
18 groups. The vibrational band at 1179 cm<sup>-1</sup> shows (-S=O) and the band at 1070 cm<sup>-1</sup> shows the  
19 presence of a functional group of sulphur (O=S=O). The band at 1503 cm<sup>-1</sup> presented an  
20 aromatic region.



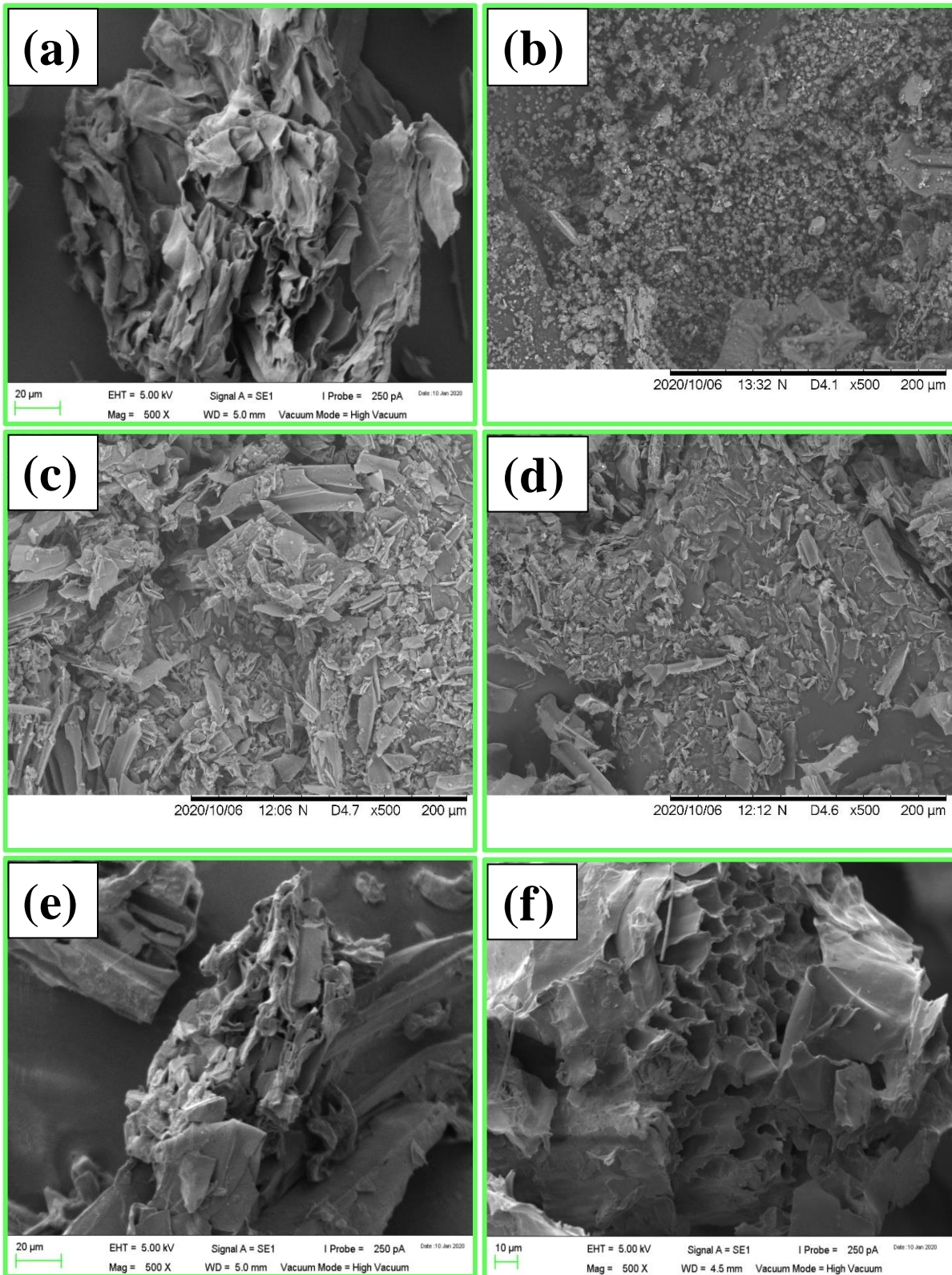
**Fig. 2.** Surface chemistry analysis of waste biomass and biomass derived catalysts; (a) Raw SCB and char and (b) Prepared catalysts with different acid concentrations.

The band at  $1697\text{ cm}^{-1}$  showed the stretching of C-H bond of aliphatic carbon. The band at  $1672\text{ cm}^{-1}$  showed stretching of C=C. The band at  $1617\text{ cm}^{-1}$  showed stretching in C=O bond. The band at  $576\text{ cm}^{-1}$  showed ring deformation of cycloalkanes [58, 59]. These bands are present in almost all the catalysts, but the intensity is different due to the strength of acid solutions indicating that the sulfonation has been taken place successfully. The intensity of bands of the sulfonic acid group in the catalyst prepared with concentrated acid is much higher as compared to the others. The vibrational bands in raw SCB and SCB-char at  $3450\text{ cm}^{-1}$  shows the availability of -OH group [60]. The bands at  $1750\text{ cm}^{-1}$  and  $1840\text{ cm}^{-1}$  shows C=O stretching confirming the presence of carboxyl group (-COOH) in char and prepared catalysts. Similar behaviour of bands stretching was discussed by Gao, Z et al. [61].

### 3.3 Surface morphology analysis

The catalyst surface plays a significant role in catalytic activity as it provides active sites for transesterification to take place giving maximum biodiesel yield [62]. The morphological structure of waste SCB, char and catalysts were analyzed by SEM. Sulfonation does not change the surface morphology drastically, particles retain some of their original shapes before and after sulfonation in an irregular way. Raw SCB appears as flakes of irregular dimension having

1 no porous structure as shown in Fig. 3(a), but after partial carbonization, sugarcane bagasse  
2 derived char has a porous structure as shown in Fig. 3(b). The spongy like structure of the char  
3 was due to the removal of hemicellulose from the lignocellulose biomass during carbonization.  
4 The presence of small pores on the surface of char has increased the chances of the penetration  
5 of the sulfonic group on the surface. As a result of sulfonation of sugarcane bagasse derived  
6 pre-treated char to acid-activated catalysts the porosity has been increased. The catalysts  
7 prepared with different acid strength solutions showed different structural morphology as  
8 shown in Fig. 3(c, d, e).



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2  
3  
4  
5  
6

**Fig. 3.** Surface morphology analysis of waste biomass, char, and prepared catalysts; (a) Raw, (b) Char, (c) Catalyst prepared with 1M acid, (d) Catalyst prepared with 3M acid, (e) Catalyst prepared with 5M acid and (f) Catalyst prepared with concentrated sulfuric acid.



1 The catalysts prepared with 1M, 3M and 5M acid solutions have needle-like structures with  
2 very less pores on the surface when compare with the SCB-char. The preparation of  
3 heterogeneous solid acid catalysts for biodiesel production with dilute acid solutions is hardly  
4 reported in the literature. Meanwhile, the catalyst prepared with concentrated acid showed a  
5 less porous bulk structure with less surface area and pore size of irregular dimension due to  
6 penetration of sulfonic groups on the surface and the deformation of small pores as shown in  
7 Fig. 3(f) during sulfonation of carbon-based material which is an indication that the sulfonation  
8 has been successfully taken place in this catalyst [63]. Dehkhoda et al. [64] described the same  
9 results for their prepared catalysts from hardwood char. While in the other samples, catalysts  
10 appear as flakes and needle-like structures having no porous structure which means that  
11 sulfonation with dilute acid has no significant effect on the morphological behaviour of the  
12 catalyst [65].

### 13 **3.4 Textural analysis**

14 Brunauer–Emmett–Teller (BET) technique was used to find the surface area of waste SCB and  
15 catalysts. The surface area of char produced after partial carbonization is much higher as  
16 compared to the waste SCB which is due to the attack of acid on the structure and the  
17 decomposition of oxygenated groups from hemicellulose and cellulose at a higher temperature.  
18 As shown in Table 2, the surface area of char was strongly occupied by sulfonic ( $-\text{SO}_3\text{H}$ ) group.  
19 The surface availability of catalysts decreases after sulfonation due to the existence of acidic  
20 groups on the porous surface of bio-char. The catalysts sulfonated with 1M, 3M, and 5M acidic  
21 solutions show a readily reduction in surface area due to collision of carbon structure, small  
22 number of apertures present on the surface and no significant change in total acid density was  
23 observed [66].

24 On other hand, the sulfonation with concentrated acid showed not too much reduction in  
25 surface area as compared to other prepared catalysts. Moreover, the pore size, pore diameter

1 and total acid density were also higher in the catalyst prepared with concentrated sulfuric acid  
2 due to covalently attached sulfonic group on the surface of biochar as compared to the other  
3 catalysts. The minor reduction in the pore size and pore diameter due to the attack of acid [67].  
4 Based on higher acidic density and surface area, the catalyst prepared with conc. H<sub>2</sub>SO<sub>4</sub> was  
5 selected for further study. Similar results of the prepared catalyst after sulfonation were  
6 reported by Francis et al. and Akinfalabi et al. [68, 69]. Finally, results depicted that the  
7 sugarcane bagasse char sulfonated with concentrated sulfuric acid gave the higher surface area,  
8 pore volume and total acid density as compared to other catalysts in this study.

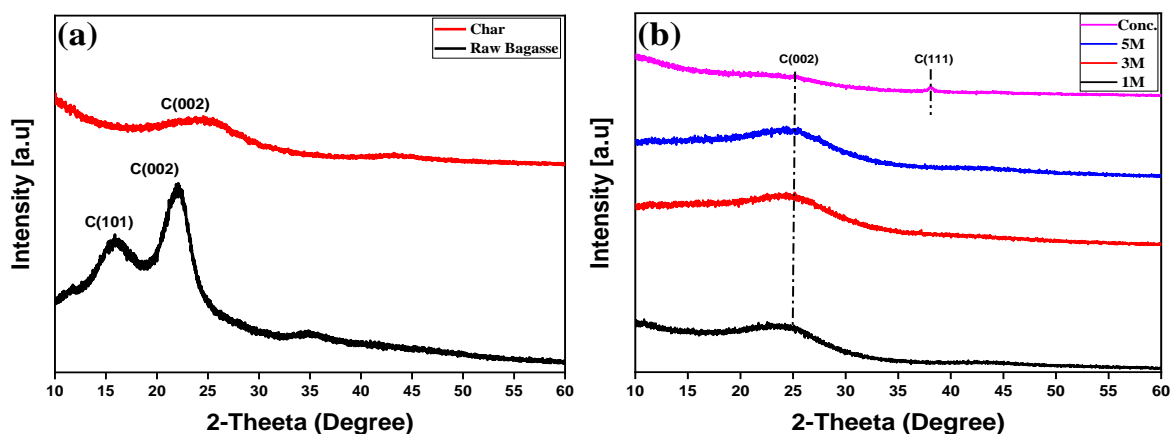
### 9 **3.5 Surface elemental analysis**

10 Ultimate analysis of raw SCB and prepared catalysts was carried out by CHNS analyzer and  
11 it is given below in Table 3. The percentage of oxygen was calculated by the difference. The  
12 ultimate analysis showed that the quantity of carbon has been enhanced after partial  
13 carbonization of waste SCB, however, a decreasing trend in the amount of H and O is because  
14 of the dihydroxylation of hydroxyl group, decarboxylation of the carboxyl group and  
15 decarbonylation of carbonyl group, respectively.

16 Firstly, the elements of hydrogen and oxygen were converted to carbon monoxide, carbon  
17 dioxide, water and methane having lower molecular weight [70]. The other parts of H and O  
18 were converted to bio-oil compounds (aldehydes, phenols, acids, ketones etc.) by the breakage  
19 of ring structure of glucan present in hemicellulose and cellulose and phenylpropane unit of  
20 lignin [71]. The quantity of carbon in char was mainly increased due to the formation of  
21 polyaromatic carbon structure like graphite at elevated carbonization temperature [72].  
22 Ultimate analysis of waste sugarcane bagasse, char and prepared catalysts is given below in  
23 Table 3. The results of ultimate analysis were almost similar as stated by Xie, W., et al. [73].

### 1 3.6 Amorphous nature analysis

2 The XRD analysis of raw SCB, char and catalysts is shown in Fig. 4 (a, b) respectively. Two  
3 sharp peaks in raw sugarcane bagasse at  $2\theta=10^{\circ}$ - $30^{\circ}$  as shown in Fig. 4(a) is due to the crystalline  
4 structure of cellulose present in raw sugarcane bagasse. Meanwhile, these peaks were  
5 diminished after partial carbonization and the char produced showed a strong broad peak at  
6  $2\theta=20^{\circ}$ - $30^{\circ}$  and a weak peak at  $2\theta=40$ - $50$  attributed to C (002) and C (101) respectively [74].  
7 Broad peaks also indicate the stable carbonaceous material and favourable for the attachment  
8 of sulfonic group on char surface which can enhance catalytic activity [75]. It shows a typical  
9 behaviour of amorphous carbon which consists of aromatic carbon sheets [76]. During  
10 carbonization, breakage of C-O-C bond takes place which causes a more rigid and amorphous  
11 structure due to an increase in disorder of carbon framework [35].



13 **Fig. 4.** XRD patterns of waste SCB, char, and catalysts; (a) Waste SCB and char and (b)  
14 Prepared catalysts with different acid concentrations.

15  
16 This structural deformation in the prepared catalyst may play an important role in catalytic  
17 activity during the transesterification process. All prepared catalysts showed a broad peak at  
18  $2\theta=20$ - $30$  except the catalyst prepared with concentrated sulfuric acid showed a weak  
19 diffraction peak at  $2\theta=40$ - $50$  and  $10$ - $20$  as shown in Fig. 4(b). However, there was no  
20 significant correlation with the activity of the catalyst. The prepared catalysts are amorphous

1 in nature while the raw sugarcane bagasse has a crystalline structure due to the presence of  
2 cellulose. The decrease in the intensity of sharp peaks after carbonization and sulfonation is  
3 due to the attachment of sulfonic groups.

### 4 **3.7 Optimization of transesterification reaction**

#### 6 3.7.1 *Effect of catalyst loading*

7 The effect of catalyst loading in transesterification reaction is very significant as it decreases  
8 activation energy to start transesterification reaction and helps to attain the equilibrium in the  
9 minimum possible time. In addition, the increased amount of catalyst activates the carbonyl  
10 groups of triglycerides which precede a nucleophilic attack of methanol [77]. The graphical  
11 relation between catalyst concentration and FAME yield is given in Fig. 5(a). Four different  
12 weight % of catalyst (1:1, 1:3, 1:5 and 1:7) to feedstock were taken by keeping other variables  
13 constant e.g., temperature 60 °C, methanol: oil 15:1, time 15 min. As shown in Fig. 5(a), yields  
14 were 55.13, 72.17, 92.05 and 93.87% with 1, 3, 5 and 7 wt.% respectively. Since there is no  
15 significant difference between the yields of 5 wt.% and 7 wt.% of catalysts.

16 This can be due to the rate of mass transfer, rate of contact between feedstock, catalyst and  
17 solvent achieved the equilibrium point, therefore further increase in catalyst dosage did not  
18 affect biodiesel yield [35]. Therefore, 5 wt.% catalyst loading was selected as an optimum  
19 concentration. A maximum 88.7% yield of biodiesel was achieved by using carbon-based  
20 catalyst derived from corn cobs after 20 min and 20 wt.% of the catalyst under microwave  
21 heating system as stated by Rocha et al. [78]. This study indicates that approximately 92-95%  
22 biodiesel yield can be achieved with 5 wt.% of the catalyst after 15 min. The catalyst  
23 concentration required to complete the Alcoholysis process in this study is significantly lesser  
24 as compared to previous studies. Therefore, considerable overall process cost can be saved by  
25 implementing the microwave heating process using sugarcane bagasse derived catalyst.

### 1 3.7.2 *Effect of oil to methanol molar ratio*

2 Solvent plays an important role in shifting reaction equilibrium towards the product side as  
3 well as increases FAME conversion [79]. Since the process of transesterification is reversible,  
4 therefore, the excess quantity of methanol is required to shift the equilibrium towards the  
5 product side. Experiments were carried out by using different molar ratios of methanol to oil  
6 i.e., 5:1, 10:1, 15:1 and 20:1 by keeping the other parameters constant i.e., 5 wt.% catalyst for  
7 15 min at 60 °C. The effect of time on all the molar ratios was studied separately to select a  
8 suitable quantity of methanol at that time. As shown in Fig. 5b, yields were 55.58%, 72.2%,  
9 92.18% and 89.61% with 5:1, 10:1, 15:1 and 20:1 after 15 min, and 5 wt.% catalyst loading,  
10 respectively. The yield of biodiesel increases from 5:1 to 15:1 but it decreases when the molar  
11 ratio increased up to 20:1 as shown in Fig. 5(b).

12  
13 This is due to the more production of water. The large quantity of water produced caused the  
14 poisoning of an acidic hydroxyl group (-OH) due to dehydration. Furthermore, more methanol  
15 causes hindrance in the adsorption of oil on active sites of catalyst and increases dispersibility  
16 of catalyst [80]. Thus, methanol in excess quantity is not suitable for transesterification  
17 reaction. Therefore, 15:1 molar ratio was kept as an optimum value. Zhang et al. [81] claimed  
18 87% yield of biodiesel by using 20:1 of methanol to oil under optimum conditions. The catalyst  
19 used in this study can achieve the reaction equilibrium using a molar ratio of 15:1, giving  
20 92.18% yield of biodiesel. Hence, sugarcane bagasse-based catalyst proves its suitability to  
21 transesterifying triglycerides.

### 22 3.7.3 *Effect of temperature*

23 The transesterification process is an endothermic reaction and normally takes place between  
24 25-60 °C. The increase in temperature increases biodiesel yield by shifting the reaction towards  
25 the product side. This is because at higher temperature reactants attain sufficient kinetic energy

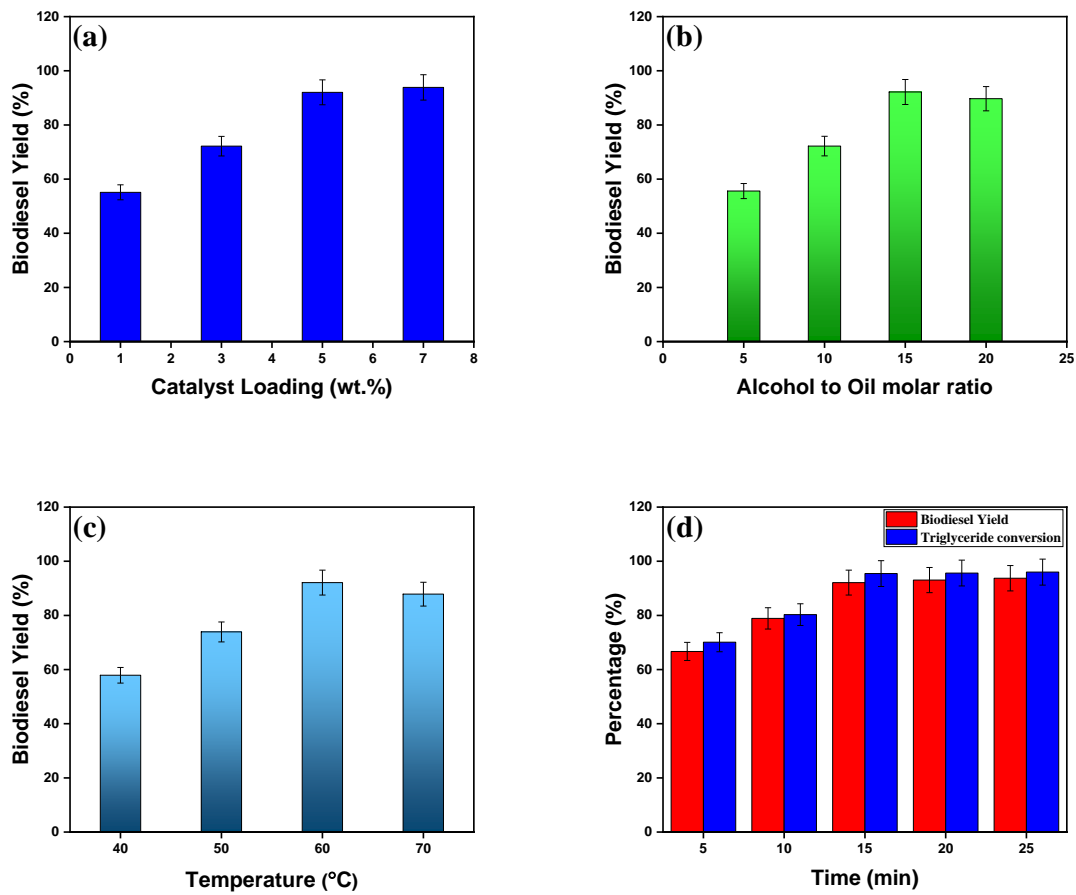
1 to enhance the rate of mass transfer between reactants and catalyst resulting in maximum  
2 conversion [35]. The effect of temperature on the transesterification process is given in Fig.  
3 5(c). The reaction temperature was maintained by placing a thermocouple inside the reactor  
4 and temperature was monitored on screen.

5  
6 The reaction was run at different temperatures (40, 50, 60 and 70 °C) by keeping other variables  
7 constant i.e., catalyst concentration of 5 wt.%, the molar ratio of methanol to oil 15:1 and 15  
8 min. As shown in Fig. 5(c), the yields were 57.89, 73.90, 92.12 and 87.85% at 40, 50, 60 and  
9 70 °C, respectively. Hence, 60 °C was selected as an optimum temperature. By increasing  
10 temperature from 60 to 70 °C, a decrease in biodiesel yield was observed due to reversible  
11 reaction and conversion of methanol into vapours above its boiling point [82]. Li et al. [83]  
12 achieved 87.57% biodiesel yield using rice husk derived catalyst at 155 °C. Overall, the present  
13 work indicated that the use of sugarcane bagasse derived nanocatalyst achieved maximum yield  
14 (92.12%) of biodiesel at 60 °C.

#### 15 3.7.4 *Effect of time*

16 The duration of reaction was also a major parameter discussed in this study. Four samples were  
17 taken from the reaction mixture after 5, 10, 15, 20 and 25 min by keeping other parameters  
18 constant i.e., catalyst loading of 5 wt.%, 15:1 of methanol to oil at 60 °C. As shown in Fig.  
19 5(d), yields were 66.70, 78.90, 92.12, 93.06 and 93.72% after 5, 10, 15, 20 and 25 min,  
20 respectively. There was a minor change after 15 to 25 min. At start, the reaction takes place on  
21 the surface due to lower diffusivity but with the passage of time and increasing temperature  
22 miscibility increases. After 15 min the yield became almost constant because after this time the  
23 reaction has achieved the equilibrium point and by further increasing time reactants were not  
24 reacting to produce the biodiesel.

25



1

2

3 **Fig. 5.** Effect of catalyst loading, methanol to oil molar ratio, temperature, and time on  
 4 transesterification process; (a) Catalyst loading (wt.%), (b) MeOH to oil molar ratio, (c)  
 5 Reaction temperature and (d) Time.

6

7 Therefore, 15 minutes was selected as the optimum time duration for the reaction. Fig. 5(d)  
 8 also shows the yield vs conversion graph during different time intervals. Flores et al. [84]  
 9 described biodiesel production from oleic acid using waste SCB derived catalyst and claimed  
 10 87% conversion of FFA after 8 h. Babel et al. [85] claimed 91% yield of biodiesel in their work  
 11 via microwave-assisted transesterification of WCO after 40 min. However, in this study  
 12 95.45% FFA conversion was achieved after 15 min under the influence of microwave heating.  
 13 Thus, the time required to complete the transesterification was quite lesser than conventional  
 14 heating (2.5-8 h). Therefore, the use of microwave heating can save a lot of energy and time  
 15 resulting in the minimized overall cost of the biodiesel production process.

### 1 **3.8 Product analysis using GC-MS technique**

2 By selecting all the optimum parameters together to obtain the highest yield (92.12%) i.e.,  
3 reaction duration (15 min), catalyst loading (5 wt.%), at 60 °C and (15:1) of methanol to oil.  
4 The three major constituents (oleic acid 53.94%, linoleic acid 28.55% and palmitic acid 9.63%)  
5 of the product were detected by GC-MS technique at a retention time of 19.18, 19.59 and 17.13  
6 s, respectively. The product was analysed by conducting different tests to check the chemical  
7 characteristics of the FAME produced to meet the requirement of standard biodiesel given by  
8 the USA and European chemical societies. The different physicochemical properties of  
9 synthesized biodiesel are presented in Table 4.

10

### 11 **3.9 Optimization of experimental data using RSM**

12 The interaction of input and output parameters for microwave-assisted transesterification for  
13 the synthesized catalyst was determined by choosing the best mathematical model. The  
14 interaction of the process variables are given in Eq. (8).

$$15 \quad Y = 74.06 + 20.42A + 18.48B + 16.35C + 13.64D - 8.57A^2 - 11.44B^2 - 11.93C^2 - 8.90D^2 \quad (8)$$

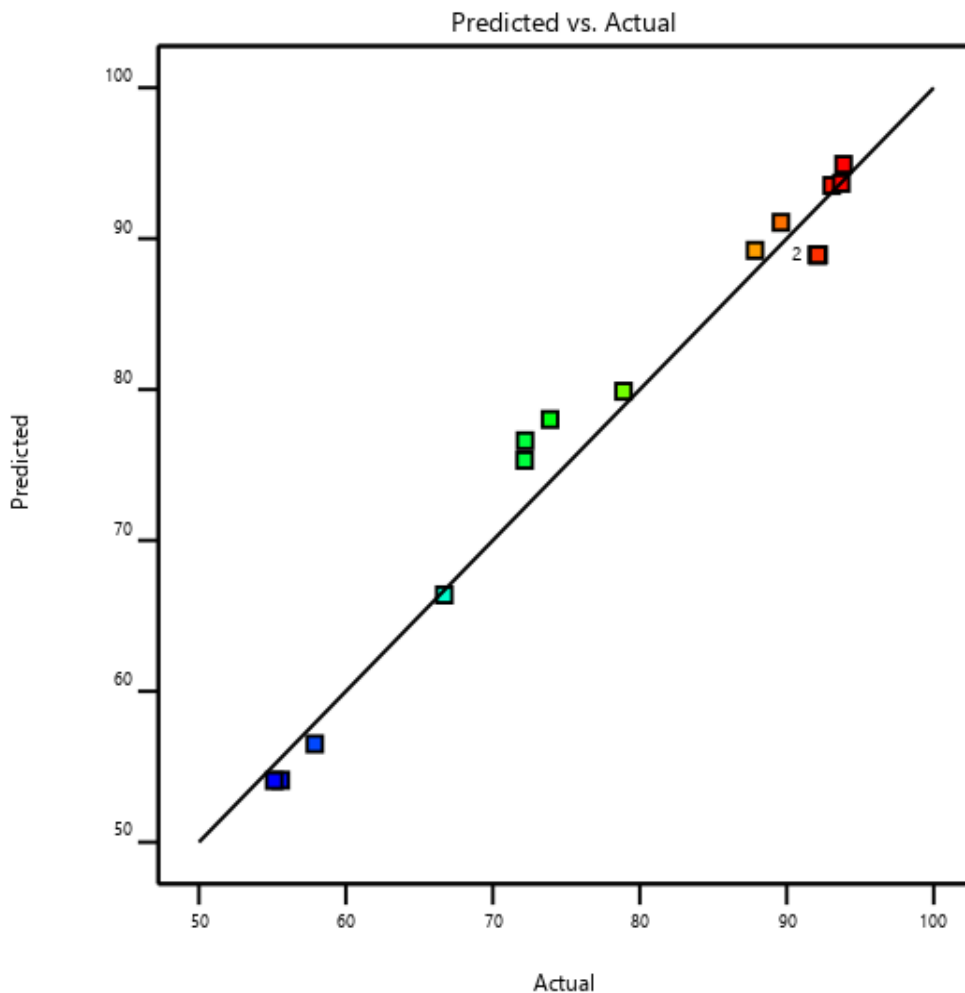
16 where A is catalyst concentration, B; molar ratio, C; reaction temperature and D; time. Eq. 8  
17 fitted most of the experimental data which showed the accuracy of the chosen model. The  
18 quadratic model data is given in Table 5.

19 Analysis of variance (ANOVA) was used to determine optimum conditions for maximum  
20 biodiesel yield. The results of statistical analysis of variance as shown in Table 6 justified the  
21 significance and fitness of the model as well as the individual effect of significant terms and  
22 their interactions on selected responses. F-test was used to control the statistical significance  
23 of chosen design. The values of p i.e., less than 0.05 indicate that the terms of the model are  
24 significant. The smaller values of p show more significance of the corresponding coefficient  
25 [87].



1

2 ANOVA results showed the variables that had a major effect on biodiesel yield were catalyst  
3 concentration (A), molar ratio (B), temperature (C), and time (D). The F-value 19.40  
4 incorporated with p-value < 0.0001 in model indicated that the model is significant at 82%  
5 confidence level. The R<sup>2</sup> value of 0.8214 shows the significance of the model in predicting  
6 response. The model depicted a statistically non-significant lack of fit (p 0.0001), showing that  
7 responses are suitable for employing in this model [87]. Moreover, the model satisfactorily  
8 proved experimental data and the relationship between actual and predicted yield of biodiesel  
9 is shown in Fig 6.

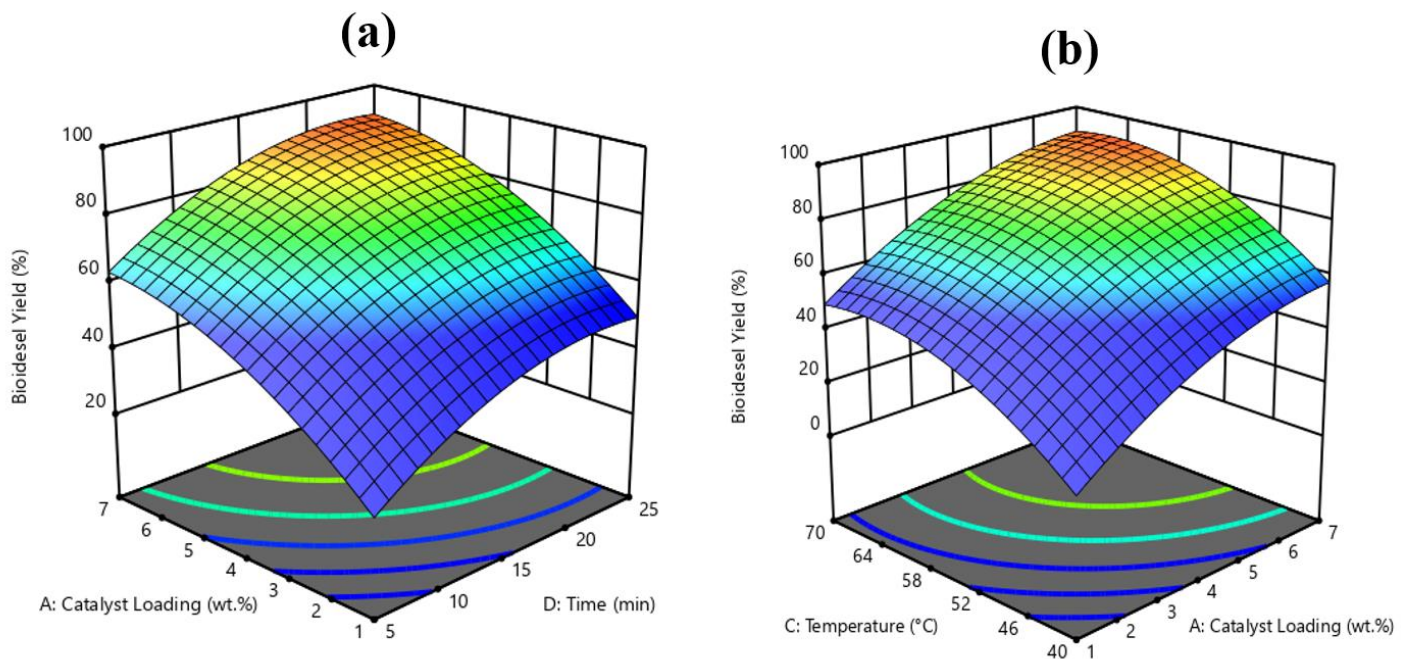


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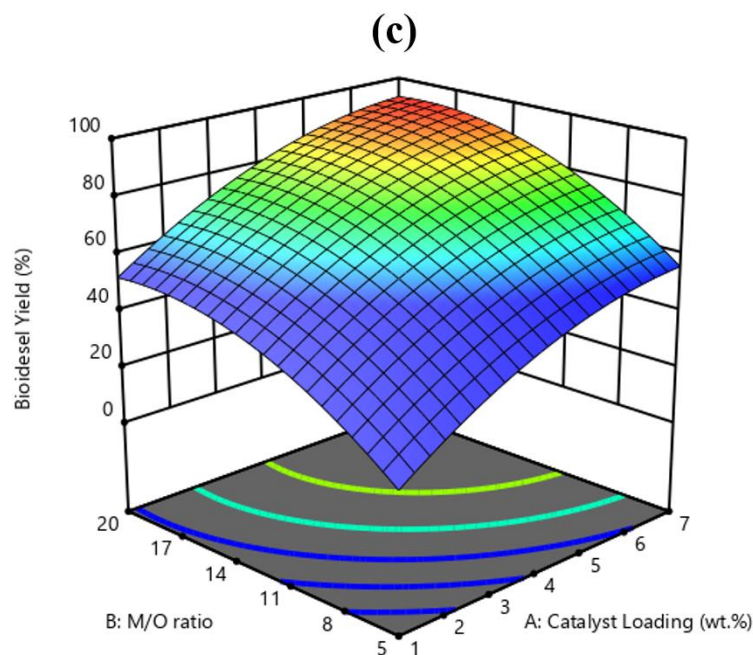
11 **Fig. 6.** Comparison plot of actual yield against the predicted yield of biodiesel.

12

1 Significant lack of fit shows the probability of contribution between regressor-response relation  
2 which is not considered by the model [88]. Fig. 7 shows the combined effect of all four process  
3 parameters on biodiesel yield produced from WCO using a heterogeneous sulfonated acid  
4 catalyst with methanol. The major advantage of these 3-D plots is that with the help of these  
5 graphs, we can find the yield of biodiesel at any value of the process parameters. The interaction  
6 effect of catalyst concentration and temperature on biodiesel yield is given in Fig. 7(a). The  
7 biodiesel yield increases by increasing the amount of catalyst and temperature up to 5 wt.%  
8 and 60 °C respectively but the further increase in temperature up to 70 °C showed a reduction  
9 in yield of biodiesel due to evaporation of methanol above its boiling point and the increment  
10 in catalyst loading up to 7 wt.% did not influence biodiesel yield significantly.



11



1  
 2 **Fig. 7.** Response surface plots showing the effect of some factors on biodiesel yield; (a)  
 3 Catalyst loading against temperature, (b) Catalyst loading against time and (c) Methanol to oil  
 4 molar ratio against catalyst loading.

5 The combined effect of catalyst concentration and time on biodiesel yield is given in Fig. 7(b).  
 6 The yield of biodiesel was increased from 5 to 15 min but not a significant increase in yield of  
 7 biodiesel was observed by further increasing time from 15 to 25 min. The combined effect of  
 8 catalyst concentration and the molar ratio of methanol to oil on biodiesel yield is given in Fig.  
 9 7(c). The biodiesel yield was increased as the amount of catalyst and methanol to oil molar  
 10 ratio was increased up to 15:1 but further increase in the amount of catalyst did not affect  
 11 biodiesel yield. Meanwhile, increasing the oil to methanol molar ratio up to 20:1 reduced  
 12 biodiesel yield by decreasing the rate of contact between oil and catalyst.

13 The results of optimization of microwave-assisted transesterification using response surface  
 14 methodology depicted that the alcohol to oil molar ratio and temperature affected biodiesel  
 15 yield significantly. However, catalyst loading and time moderately affected biodiesel yield.  
 16 Kinetic study of microwave-assisted transesterification. The kinetic study of process was  
 17 conducted to find the rate constant and activation energy for transesterification at 60 °C for 5-

1 25 min. The conversion of triglycerides to biodiesel during different reaction intervals and  
 2 temperatures was calculated through gas chromatography mass spectrometry. The process of  
 3 transesterification is completed in three consecutive reversible steps in which triglycerides are  
 4 converted to diglycerides, monoglycerides and glycerol (by-product) respectively.  
 5 One mole of biodiesel is produced during each reaction step. According to stoichiometry, one  
 6 mole of triglyceride interacts with three moles of methoxy ions of methanol and forms three  
 7 moles of methyl esters and glycerol. To determine the conversion of reactants into products,  
 8 all reaction parameters were kept constant by changing the time from 5 to 25 min. For biodiesel  
 9 production through transesterification reaction is considered as the first-order reaction based  
 10 on assumption as triglyceride is a limiting reactant and due to excess amount of methanol in a  
 11 reaction mixture that will shift reaction equilibrium towards the right, therefore it is not  
 12 considered in rate-determining equation. The rate constant can be calculated by using Eq. (9)  
 13 [89].

$$14 \quad -r_A = kC_A^n \quad (9)$$

15 where  $k$  is rate constant,  $C_A$  (mol/ L) is the concentration of oil and  $n$  is the order of reaction,  
 16 which is supposed to be 1, therefore Eq. (9) can be rearranged as Eq. (10),

$$17 \quad -r_A = kC_A \quad (10)$$

18 The above Eq. (10) can be evaluated as follows Eq. (11).

$$19 \quad \ln \frac{dx}{dt} = \ln C_A + \ln k \quad (11)$$

20 where  $k' = \frac{k}{C_{A0}}$  and  $C_{A0}$  is initial concentration of the triglycerides and  $\frac{dx}{dt}$  shows the conversion  
 21 factor. The rate constant of transesterification reaction after each time interval can be calculated  
 22 using Eq. (12).

$$23 \quad -\ln(1 - X_A) = kt \quad (12)$$

24 To find out the kinetic parameters of the biodiesel synthesis, the rate constant was determined  
 25 from Eq. (12) for each reaction run. The accuracy of the proposed kinetic model was found,

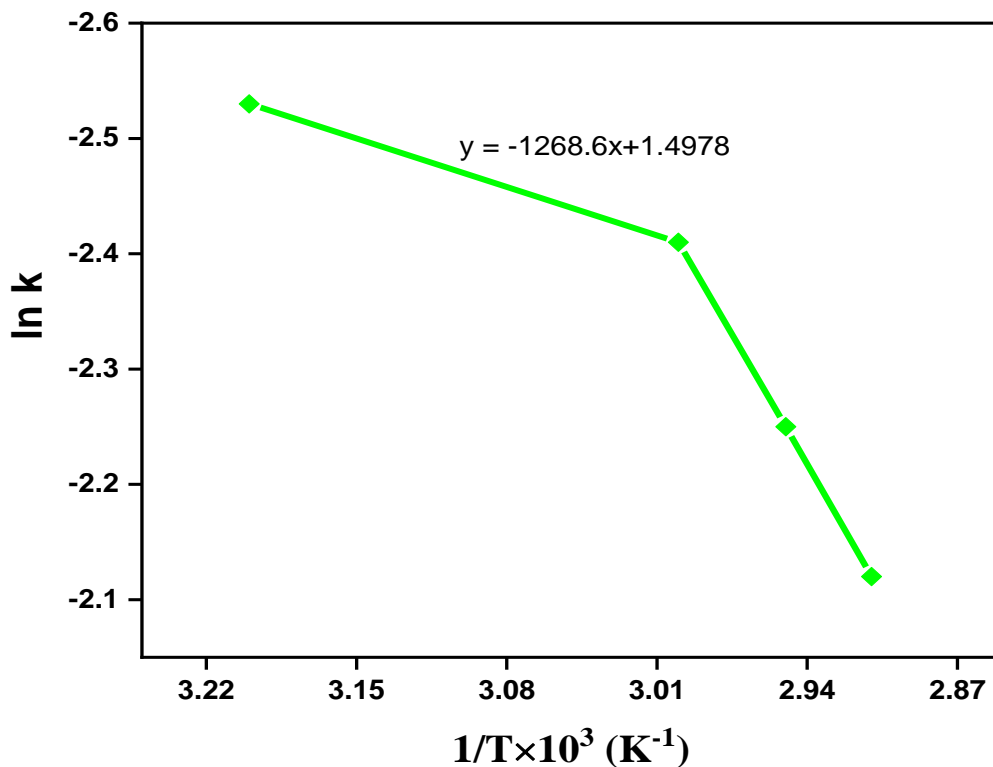
1 and kinetic parameters determined from the proposed kinetic model was in accordance with  
2 experimental data. The rate equation of biodiesel synthesis using a heterogeneous solid acid  
3 catalyst is presented as in Eq. (13).

$$4 \quad -r_A = 0.16 C_A \quad (13)$$

5 Eq. (13) indicates the rate equation for transesterification reaction. The rate constant was  
6 calculated by plotting the graph between  $-\ln(1-X_A)$  and reaction time. The units of rate constant  
7 are  $\text{min}^{-1}$ . The units of concentration are  $\text{mol/L}$ . The activation energy was calculated by using  
8 the Arrhenius equation as presented in Eq. (14).

$$9 \quad k = A e^{\frac{-E_A}{RT}} \quad (14)$$

10 where  $k$  is rate constant,  $A$ ; Arrhenius constant,  $E_A$ ; activation energy,  $R$ ; general gas constant  
11 and  $T$  is temperature. Fig. 8 shows the Arrhenius plot to calculate activation energy and  
12 Arrhenius constant. Kinetic and Arrhenius equation parameters at different temperatures are  
13 given in Table 7.



14

15

**Fig. 8.** Arrhenius parameters for activation energy of the reaction.

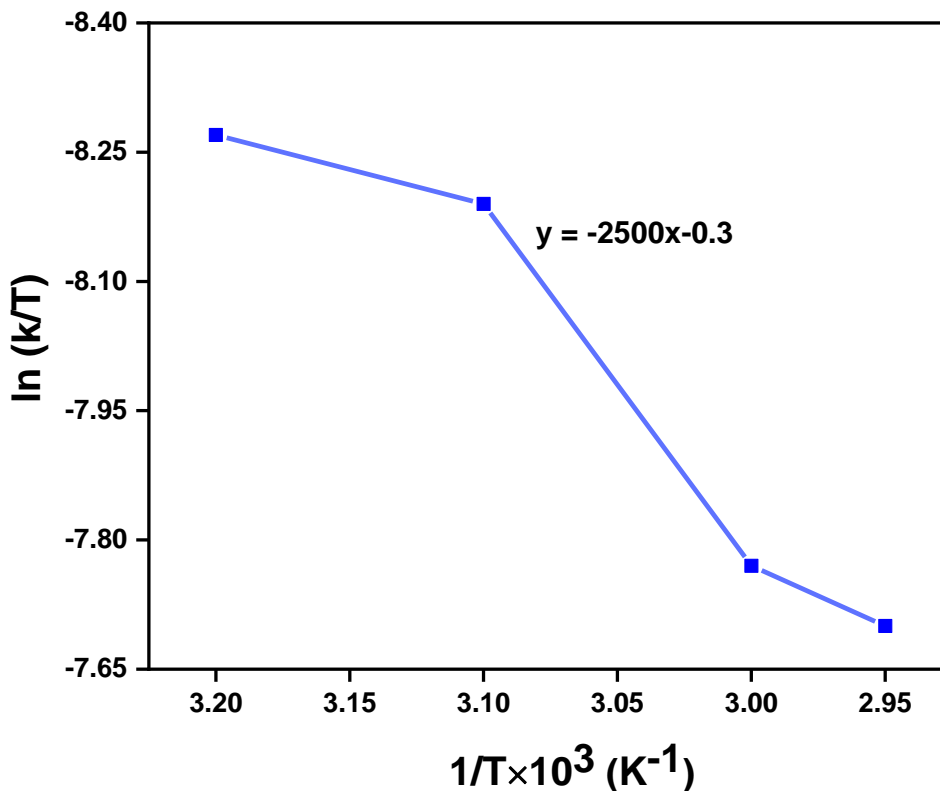
1 The thermodynamic parameters for microwave-assisted transesterification were calculated  
 2 from Eq. (15) [90].

$$k = k^* \frac{k_B}{h} T e^{\frac{-\Delta G}{RT}} \quad (15)$$

3  
 4 where  $k$  is rate constant ( $\text{min}^{-1}$ ),  $k^*$  is transmission co-efficient and generally taken as 1 [91].  $K_B$   
 5 is Stephen-Boltzmann constant ( $1.38 \times 10^{-23} \text{ J/K}$ ), and  $h$  is Planck's constant ( $6.63 \times 10^{-34} \text{ J s}$ ). By  
 6 replacing ( $\Delta G = \Delta H - T \cdot \Delta S$ ) in Eq. 15 resulted in terms of Eq. (16) as shown below,

$$\ln \left( \frac{k}{T} \right) = -\frac{\Delta H}{R} \left( \frac{1}{T} \right) + \left[ \ln k^* + \ln \left( \frac{k_B}{h} \right) + \frac{\Delta S}{R} \right] \quad (16)$$

7  
 8 where  $\Delta H$  and  $\Delta S$  are determined as slope and intercept from graph between  $\ln k/T$  and  $1/T$  as  
 9 shown in Fig. 9. The enthalpy and entropy of the microwave-assisted transesterification process  
 10 was calculated as 16 kJ/mol and -0.19 kJ/mol. K, respectively.



11

12

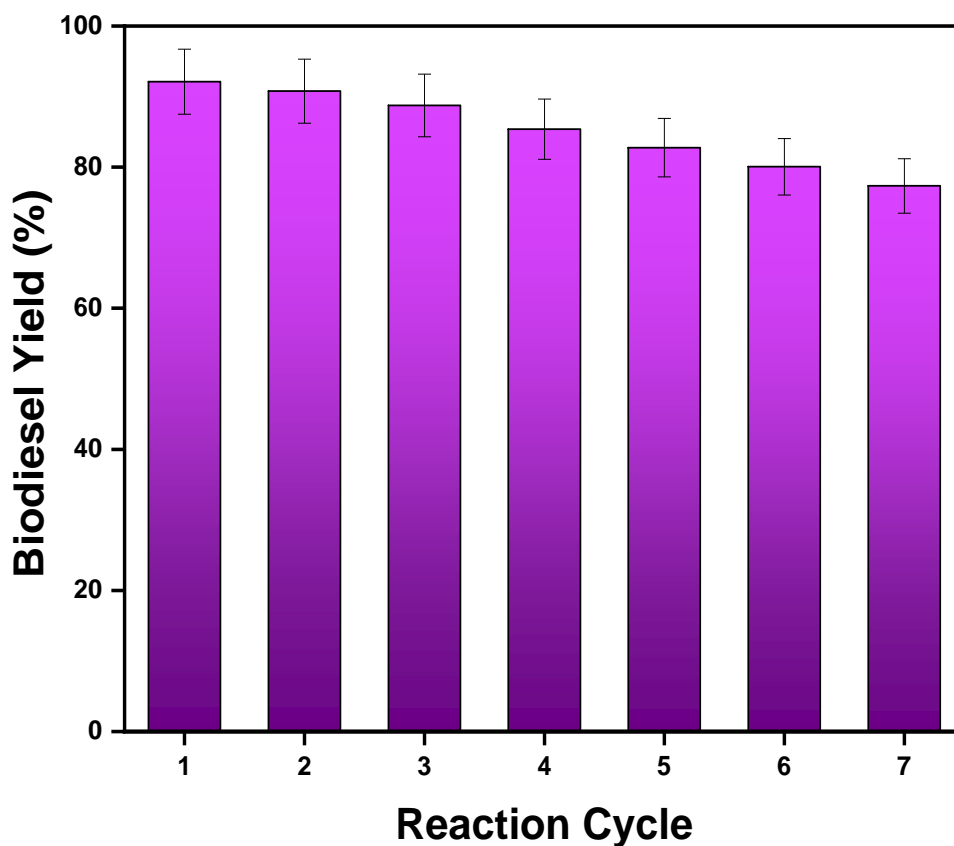
**Fig 9.** Eyring plot to calculate the thermodynamic parameters.

13

1 The results depicted that the use of waste SCB derived catalyst lowered the activation energy  
2 of the transesterification process as compare to the other studies previously described in the  
3 literature [92, 93].

### 4 **3.10 Reusability test of catalyst**

5 The reusability or stability of the solid acid catalyst is an important step to determine its  
6 commercial viability. After complete reaction, the catalyst was recovered from the reaction  
7 mixture through filtration, washed and dried at 105 °C for 2 h prior to use in the next reaction.  
8 The catalyst was used under optimized parameters for seven cycles and gave 92.02, 90.78,  
9 88.75, 85.39, 82.76, 80.05 and 77.34% yield of biodiesel as shown in figure 10. Only 8%  
10 reduction in catalytic activity was observed, whereas the other biomass derived catalysts were  
11 reused for 3 cycles as stated in previous studies [44, 62].



12

13

**Fig 10.** Reusability test for catalyst during different reaction cycles.

1 The reduction in biodiesel yield was mainly because of leaching of active sites, weak  
2 interlinkage of polyaromatic hydrocarbon with  $-S_3OH$  group, production of sulfonate esters  
3 and blockage of catalyst pores by reactants, product, or reaction intermediates caused.  
4 Meanwhile, the catalyst can be effected by oxygen,  $H_2O$  and  $CO_2$  during separation [94]. After  
5 minor pre-treatment i.e., by washing with n-Hexane to remove traces of biodiesel, un-reacted  
6 oil and methanol, the catalyst maintained its activity which shows that waste sugarcane bagasse  
7 derived catalyst can be utilized as a substantial catalyst. Similar deactivation results of carbon-  
8 based catalysts were reported by Alhassan et al. [95] and Kanokwan et al. [40] in the literature.

#### 9 **4 Conclusion**

10 Sugarcane bagasse derived sulfonated catalyst was successfully prepared, characterized, and  
11 used in biodiesel production using WCO as a low-cost substrate under the influence of  
12 microwave heating. The partially carbonization and sulfonation using sulfuric acid of different  
13 concentrations gave an idea to develop a suitable heterogeneous catalyst that gave the highest  
14 yield of biodiesel. The catalyst prepared with concentrated sulfuric acid exhibited the best  
15 catalytic activity in terms of surface area ( $20.78 \text{ m}^2/\text{gm}$ ), pore size (14.98 nm), pore volume  
16 ( $0.02 \text{ cm}^3/\text{gm}$ ), availability of sulfonic acid functional groups, total acid density ( $3.94 \text{ mmol}/$   
17  $\text{gm}$ ), porous structure and gave the maximum yield of biodiesel under optimum conditions i.e.,  
18 reaction time (15 min), reaction temperature ( $60 \text{ }^\circ\text{C}$ ), catalyst loading (5 wt.%) and 15:1 of  
19 methanol to oil at 400 rpm using microwave as a heating source. The maximum yield (92.12%)  
20 of biodiesel and 95.45% conversion of triglycerides was achieved. The catalyst was thermally  
21 stable up to  $500 \text{ }^\circ\text{C}$  with quite a higher surface area and the presence of a covalently bonded  
22 sulfonic group on the catalyst surface increased its efficiency. The results proved that the  
23 environment friendly and green catalyst obtained from waste sugarcane bagasse is a potential  
24 catalyst in the synthesis of biodiesel using waste feedstocks. The main advantage of this  
25 catalyst was its reusability and stability up to seven cycles giving biodiesel yield up to 77.34%



1 from low-grade feedstocks with a slight loss in its activity 8%. Hence, the performance of the  
2 synthesized catalyst was significant for batch transesterification. However, further  
3 investigation for continuous process using the synthesized catalyst might increase the overall  
4 biodiesel yield, minimizing the overall process cost. Moreover, a wide range of  
5 transesterification parameters will also help to further optimize the productivity of the process.

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11

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**List of tables**

**Table 1.** Cas number, mass fraction purity and boiling point ( $T_b$ ) of the chemicals.

Chemical	CAS no.	Supplier	Mass fraction	$T_b$
Sulfuric acid	7664-93-9	Sigma-Aldrich, Malaysia.	0.95-0.97	337
Methanol	67-56-1	Sigma-Aldrich, Malaysia.	$\geq 0.980$	64.70
Sodium hydroxide	1310-73-2	Sigma-Aldrich, Malaysia.	$\geq 0.980$	1388
n-Hexane	110-54-3	Sigma-Aldrich, Malaysia.	$\geq 0.990$	69
Phosphoric acid	7664-38-2	Sigma-Aldrich, Malaysia.	$\geq 0.850$	158
Phenolphthalein	77-09-08	Sigma-Aldrich, Malaysia.	0.1 N	557.80
Sodium Chloride	7647-14-5	Sigma-Aldrich, Malaysia.	$\geq 0.990$	1465

$T_b$ = Standard boiling points of chemicals in degree Celsius.

**Table 2.** Total acid density and textural properties of raw bagasse and bagasse -SO<sub>3</sub>H. catalysts.

Sample Name	Sulfonating agent	BET	Pore volume	Pore diameter	Total acid density
		m <sup>2</sup> /gm	cm <sup>3</sup> / gm	Nm	Mmol/ gm
Raw Bagasse		0.58	0.0007	5.88	0.04
Char		25.32	0.03	15.76	1.09
Sample A	1M	4.21	0.01	7.83	1.95
Sample B	3M	8.59	0.01	9.44	2.12
Sample C	5M	12.15	0.01	12.35	2.76
Sample D	Conc. H <sub>2</sub> SO <sub>4</sub>	20.78	0.02	14.98	3.94



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**Table 3.** Surface elemental analysis of raw bagasse and SCB-SO<sub>3</sub>H catalysts.

Samples	Ultimate analysis				
	C (%)	H (%)	O (%)	N (%)	S (%)
Raw SCB	45.25	6.22	46.86	1.13	0.55
SCB-char	60.75	2.93	33.92	1.41	0.99
Sample A (1M)	59.82	2.28	35.97	1.29	0.64
Sample B (3M)	59.55	2.70	35.56	1.24	0.96
Sample C (5M)	59.46	2.89	34.69	1.80	1.17
Sample D (conc. H <sub>2</sub> SO <sub>4</sub> )	58.82	2.99	33.58	1.39	5.22

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**Table 4.** Comparison of the Biodiesel produced from WCO with Standard biodiesel [86].

Diesel property	WCO biodiesel	Testing technique	ASTM D6751	EN14214
Water content (%)	0.02	ASTM D6304	0.03	
Sulphur content (ppm)	0.003	ASTM D4294	0.001-0.005	
Cloud point (°C)	-1.55	ASTM D2500	-	-
Kinematic viscosity (mm <sup>2</sup> /s)	4.12	ASTM D445	1.9-6.0	3.5-5.0
Density (g/ mL)	0.87	ASTM D50002	0.87-0.90	
Cetane number	50.34	ASTM D613-18a	47	51
Acid value (%)	0.43	ASTM D664	0.80	0.50
Oxidation stability	6.90	ASTM D7462	-	-
Flash point (°C)	130	ASTM D93	-	-

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**Table 5.** The sequential model sum of squares.

Source	Sum of squares	df	Mean square	F-value	p-value	
Mean vs total	1.086E+05	1	1.086E+05			
Linear vs mean	2887.10	4	721.77	19.40	<0.0001	Suggested
2FI vs linear	0.0000	0				
Residual	446.51	12	37.21			
Total	1.120E+05	17	6587.16			

The data is taken by using design of expert (DOE) software.

**Table 6.** Optimization of transesterification parameters by analysis of variance (ANOVA).

Source	Sum of squares	df	Mean square	F-value	p-value	
<b>Model</b>	3235.02	8	404.38	32.81	<0.0001	Significant
A-catalyst loading (wt.%)	995.04	1	995.04	80.74	<0.0001	
B-M/O ratio	815.38	1	815.38	66.16	<0.0001	
C-temperature (°C)	638.39	1	638.39	51.80	<0.0001	
D-time (min)	465.12	1	465.12	37.73	<0.0003	
A <sup>2</sup>	88.62	1	88.62	7.19	0.0279	
B <sup>2</sup>	157.84	1	157.84	12.81	0.0072	
C <sup>2</sup>	171.62	1	171.62	13.93	0.0058	
D <sup>2</sup>	120.92	1	120.92	9.81	0.0140	
<b>Residual</b>	98.59	8	12.32			
Lack of fit	98.58	5	19.72	6979.35	<0.0001	Non-significant
Pure error	0.0085	3	0.0028			
<b>Cor total</b>	3333.61	16				

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2 **Table 7.** Kinetic and Arrhenius parameters for transesterification of waste cooking oil.

<b>Temperature (°C)</b>	<b>k (min<sup>-1</sup>)</b>	<b>E<sub>A</sub> (kJ/mol)</b>	<b>A</b>
<b>40</b>	0.08	10.50	4.48
<b>50</b>	0.09	10.50	4.48
<b>60</b>	0.14	10.50	4.48
<b>70</b>	0.12	10.50	4.48

3 The uncertainty of temperature u (T) was ±3 °C.

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