Scientific Research Journal,
Vol 21, No 1 (2024) 99-116
https://doi.org/10.24191/srj.v21i1.25200

SCIENTIFIC RESEARCH JOURNAL SRJ
ISSN: 1675-7009
e-ISSN: 2289-649X

Effect of Calcination Temperature on Sulfonated Lignin Catalyst Preparation for Glucose Ethanolysis to Ethyl Levulinate

Kamarul Ridwan Zainuddin[1], Muzakkir Mohamad Zainol[1,*], Abdul Hafidz Hassan[1], Mohd Asmadi[2], Syed Shatir Asghrar Syed Hassan[1], Mohd Yazid Yusof[1], Didi Dwi Anggoro[3]

[1]School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA 40450 Shah Alam, Selangor, Malaysia
[2]Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia 81310 UTM Johor Bahru Johor, Malaysia
[3]Department of Chemical Engineering, Diponegoro University, Semarang 50273, Indonesia St. Prof. Soedarto, SH, Tembalang, Semarang, Indonesia

**Corresponding author's E-mail: muzakkir@uitm.edu.my*

Received: 27 December 2023
Accepted: 14 January 2024
Online First: 01 March 2024

ABSTRACT

An abundance of biomass material is generated globally which has the potential to be converted to various bio-based chemicals including ethyl levulinate (EL). EL is well known as a sustainable fuel additive and can be produced from glucose, a biomass derivative in an ethanolysis reaction throughout acidic catalysis. In this study, sulfonated lignin carbon catalysts were used to catalyze the ethanolysis of glucose to synthesize EL. The catalysts were prepared from lignin via calcination at different soaking temperatures (400 to 600 °C) for 1 h to produce carbon material, followed by sulfonation with concentrated sulfuric acid at a 1:10 (carbon-to-acid, g/mL) ratio. The catalysts were tested for glucose ethanolysis reaction in a batch reactor equipped with a thermocouple on selected conditions (0.4 g of glucose, 40 mL of ethanol, 1.2 g of catalyst, and 6 h reaction) at 180 °C and their performance was evaluated according to the EL yield obtained. Then, the catalyst characterization was conducted for the selected catalyst using Fourier transform infrared spectroscopy (FTIR), ion-exchange titration, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), nitrogen sorption analysis, and Thermalgravimetric analysis (TGA). The

PENERBIT PRESS
UNIVERSITI TEKNOLOGI MARA

result showed that the performance of the sulfonated lignin carbon catalysts was reduced, especially at higher soaking calcination temperatures. The catalyst prepared from lignin carbon calcined at 450 °C, (CS450) was able to provide a high EL yield of 22.54 mol% with a good acidity of 1.0 mmol/g, a high surface area of 229.95 m^2/g, and suggested thermal stability at 300 °C. The results indicated that the sulfonated lignin carbon catalyst could be used as a solid acid catalyst for glucose ethanolysis reaction, yet further catalyst modification is required in the future to enhance its performance for higher EL yield.

Keywords: Carbon-based Catalyst; Ethanolysis; Ethyl levulinate; Glucose ; Lignin

INTRODUCTION

The current excessive usage of non-renewable fossil fuels such as petroleum to synthesize chemicals has resulted in reservoir depletion. As the reliance on these resources reaches unsustainable levels, the progress for alternative approaches such as biomass utilization is becoming more extensively established. Biomass is generated excessively around the globe, giving an interesting option as a renewable resource to minimize the dependency on conventional fossil fuels. One of the levulinate esters, EL is a platform chemical that can be produced from direct alcoholysis of biomass and its derivatives under acidic catalysis. EL has broad commercial applications such as the food, fragrance, and polymer sectors, plus it is famed as an octane booster for gasoline fuel [1]. The addition of EL into the fuel can improve fuel properties including flash point, lubricity, and cold flow as well as gas emissions [2]. Several possible reaction routes to the synthesis of EL, and currently, esterification of levulinic acid and ethanolysis of furfuryl alcohol are commonly practiced [3]. The reactions are favorable since they can be conducted in moderate reaction conditions and provide a high EL yield. Even so, the high cost of pure levulinic acid and furfuryl alcohol in the chemical market has given a major challenge to synthesize EL, especially for overall production cost. Hence, the research has mostly aimed toward the cost-effective synthesis of EL.

Glucose, one of the monomer units of cellulose biomass, has been chosen as the raw material for glucose conversion to EL. This six-carbon sugar molecule is considered a promising feedstock because of its high availability, abundance, and inexpensive material of biomass derivative [4]. Many studies have reported the ethanolysis of glucose over an acid catalyst to synthesize EL [5]. An effective acid catalyst is essential in the catalytic conversion to produce high desired product. Homogeneous catalysts such as mineral acids (H_2SO_4) and metal salts were commonly used to catalyze the reaction. Yet, these catalysts possessed major drawbacks such as corrosion, product separation, and catalyst recycling [6]. For these reasons, various solid acid catalysts have been objectively designed and employed in the catalytic synthesis of EL. For instance, modified zeolite [7], zirconia [8], and carbon acid catalyst [5]. Solid acid catalysts offer greater value in terms of easy separation from the reaction mixture and reusability in a few reaction cycles. Sulfonated carbon catalyst has recently been highlighted as an excellent catalyst on account of its performance in the reaction, low-cost carbon material, easy-to-modified catalyst, and can be produced from different sources of carbon precursor [6]. Focusing on lignin, a high abundance and underutilized biomass component is an attractive source of carbon material for sulfonated carbon catalyst production. Lignin can also be obtained as a by-product of pulping and papermaking industries [9]. The upgrading of lignin into a solid acid catalyst is endorsing affordable and sustainable practices for EL synthesis. The glucose conversion to EL via ethanolysis over catalyst from lignin and the effect of calcination temperature of lignin towards the effectiveness of the catalyst in glucose ethanolysis have limited reports in the works of literature. Hence, these research gaps are the opportunity to evaluate the catalyst competency and performance for the particular reaction.

This study aims to produce a sulfonated lignin carbon acid catalyst for the ethanolysis of glucose using the one-pot method to synthesize EL. Different lignin carbons were prepared via calcination at various temperature ranges (400 – 600 °C) for 1 h, followed by hydrothermal sulfonation to produce sulfonated lignin carbon acid catalysts and evaluate their effect on catalytic activities throughout the reaction. A catalyst was selected according to EL yield (mol%) and characterized to study its physiochemical properties and effects on the reaction.

METHODOLOGY

Materials and Chemicals

The sulfonated lignin carbon catalyst preparation: Lignin (Sigma-Aldrich Co.,) and sulfuric acid, H_2SO_4 - 97% (Supelco). The catalyst characterization: Sodium hydroxide, NaOH pallet (Vchem), sodium chloride, NaCl (Fisher Chemical), and phenolphthalein, $C_{20}H_{14}O_4$ - 1% solution (Bendosen). The reaction testing: Glucose, $C6H_{12}O_6$ (R&M Chemicals), ethanol, C_2H_6O - 95% (Vchem). Liquid product analysis: ethyl levulinate standard, $C_7H_{12}O_3$ - 99% (Sigma Aldrich Co.). In this work, all the received chemicals were utilized immediately without any pretreatment.

Catalyst Preparation

Carbon material from lignin preparation was referred from Hassan et al. [10]. To study the effects of calcination temperature, lignin was calcined at different temperatures (X = 400, 450, 500, 550, and 600 °C) for 1 h with a fixed ramp of 10 °C/min in a high-temperature box furnace, model HTBF-17-12L. The outside of the selected calcination temperature range might cause partial carbonation or major degradation of lignin, and moderate ramping temperature ensures the lignin is uniformly calcined. The sample was left to cool at room temperature before being washed with distilled water to eliminate any remaining unknown chemicals from the carbon structure and dried overnight at 100 °C in a universal oven, model UFE 600. Then, the black solid was sulfonated with concentrated H_2SO_4 in a 100 mL Teflon stainless steel auto-clave reactor at 180 °C for 6 h based on 1:10 (carbon to acid ratio, g/mL). Upon completion, the black mixture was diluted with 1 L of distilled water followed by continuous washing and filtering by vacuum filtration until the pH of the filtrate was around 7. Finally, the sample was left to dry overnight at 100 °C and labeled as CSX, where CS is sulfonated lignin carbon and X is the particular temperature.

Catalyst Characterization

The selected sulfonated lignin acid catalyst (CSX) and its lignin carbon (CX) as the control sample were characterized. The presence of chemical bonding and functional groups by the changes in peak spectra of the sample were evaluated using Fourier transform infrared, FTIR spectroscopy in the IR range of 700 - 4000 cm^{-1} (model: Perkin-Elmer Spectrum One spectrometer) with potassium bromide, KBr pellets. The catalyst acidity was determined by ion exchange titration [11]. The sample was added to 10 mL of 2 mol/L NaCl solution at room temperature. To make sure all acid functional groups from the sample were displaced by Na^+ ions, the mixture was stirred at 150 rpm for 24 h. The solid component was removed by filtration and a few drops of phenolphthalein were added to the filtrate before conducting the titration with 0.01 mol/L of NaOH solution. As the mol of NaOH titrated is equivalent to the mol of acid from the catalyst, the catalyst acidity was calculated by using Eq. (1) as follows:

$$\text{Acidity (mmol/g)} = \text{Mol of NaOH used during titration (mmol)} / \text{Mass of catalyst (g)} \quad (1)$$

The physical catalyst morphology was observed using a scanning electron microscope, SEM (model: SU3500), and the elemental mapping on the catalyst surface was detected using energy-dispersive X-ray spectroscopy, EDX (model: Element). The catalyst surface area was analyzed using a Micromeritics 3-Flex instrument, where the sample was degassed in a vacuum at 200 °C for 6 h to eliminate pores blockage, and the standard nitrogen, N_2 adsorption-desorption was performed at -196 °C. The total surface area was calculated using Brunauer Emmett Teller, BET, and pores distribution (mesopore and micropore) using Barrett Joyner Halenda, BJH, and t-plot methods. The catalyst's thermal decomposition and stability were determined using a thermogravimetric analyzer, TGA (model: Mettler Toledo). The sample was heated in an inert condition from 30 to 950 °C with a ramping temperature of 20 °C/min.

Reaction Testing and Liquid Product Analysis

The ethanolysis of glucose was conducted in a batch reactor system. The reactor was equipped with a thermocouple to monitor temperature and pressure and aided with a magnetic stirrer (300 rpm) throughout the reaction. The reaction conditions are referred from Zainol et al. [12] with the adjustment to ensure the conditions are compatible with the reactor capacity. The selected fixed conditions of glucose ethanolysis were as follows: 0.4 g of glucose, 40 mL of ethanol, 1.2 g catalyst loading, and 6 h reaction time at 180 °C. The result of glucose ethanolysis to EL using selected sulfonated lignin carbon catalyst sample was compared with its lignin carbon precursor as a control. After the reaction finished, the mixture was left to cool at room temperature prior filter to separate the solid component from the liquid product. The final volume of the liquid product was recorded.

The liquid product analysis was conducted by gas chromatography-mass spectrometry, GC-MS (model: Varian 450-GC) with a 5MS column. The GC-MS conditions were set as follows; 1.0 mL/min helium flow rate, oven temperature at 40 to 120 °C (3.0 °C/min), temperature up to 280 °C (50.0 °C/min), the coolant fixed at 50 °C, 20 min of coolant timeout, and 0.50 min of coolant stabilization time. The calibration curve was developed using EL standard prior the sample was tested by GC-MS. The EL concentration (mg/L) can be determine by graph extrapolation and EL yield (mol%) was calculated using Eq. (2).

$$\text{EL yield (mol\%)} = ((C_{EL} \text{ X } V_{EL})/(1000))/M_{EL}) \,/\, (W_{GLU}/M_{GLU}) \text{ X } 100 \quad (2)$$

Where, C_{EL} (mg/L) is the final concentration of product, V_{EL} (L) is the final volume of liquid product, M_{EL} (144.17 g/mol) is the molecular weight of EL, W_{GLU} (g), is the initial weight of glucose, and M_{GLU} (180.16 g/mol) is the molecular weight of glucose.

RESULT AND DISCUSSION

Catalyst Performance

The performance of the sulfonated lignin acid catalysts was evaluated in the ethanolysis of glucose to synthesize EL. As presented in Figure 1, the catalysts showed different catalytic activities throughout the reaction based on EL yield. CS450 provides the highest EL yield of 22.54 mol%, and the EL yield trend gradually decreased to 9.25 mol% for CS600. The reduction of EL yield occurred as the calcination temperature of lignin increased. The catalyst performance was greatly influenced by the calcination temperature during carbon preparation. The higher calcination temperature of lignin carbon was not favorable to be used as carbon material in the catalyst preparation for glucose ethanolysis. The degradation of C-H active sites at higher temperatures will prevent the sulfonic functional group, SO_3H attached to the lignin carbon [13]. Similar results were reported by da Luz Corrêa et al. [14] and Cao et al. [15], where the SO_3H functional group placement was hindered at carbon material prepared at a higher temperature. For CS450, the validity of sulfonation could be observed from the EL yield, as the reaction rate was influenced by acid sites. The number of acid sites attached to the catalyst was important for the reaction mechanism to take place [16]. For CS400, the calcination temperature of lignin carbon at 400 °C was less suitable because the EL yield recorded was 18.50 mol%. At this calcination temperature, the degradation of lignin carbon might produce a low catalyst surface area to enhance the reaction. The high calcination temperature indeed produces a high catalyst surface area to improve mass transfer for the reaction, nevertheless further increased calcination temperature will reduce the ability of the anchoring of SO_3H functional groups [10].

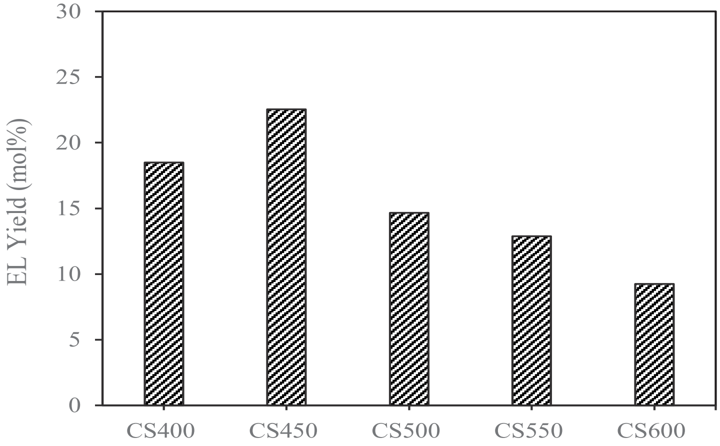


Figure 1: EL yield screening for catalysts prepared at different calcination temperatures. Reaction conditions: 0.4 g of glucose, 1.2 g of catalyst, 6 h and 180 °C.

The effectiveness of CS450 as solid acid catalyst was also proved by comparing the product yield obtained using C450, where the EL yield was 2.14 mol%. This relatively low EL yield explained the importance of sulfonation. The calcination at 450 °C for 1 h was recommended for lignin carbon preparation. Hence, CS450 was chosen for catalyst characterization as well as C450 as carbon precursor to study the physiochemical properties.

FTIR Analysis

The presence of associated functional groups resulting from catalyst preparation was identified at IR peaks as shown in Figure 2. The band spectra for the S=O and S-O absorption bands in the range of 1,300 – 1,000 cm^{-1} were observed to verify the effect of sulfonation. In Figure 2(b), the S=O and S-O stretching were detected approximately at 1,225 cm^{-1} and 1,050 cm^{-1} respectively [17]. As stated by Hassan et al. [18], the detection of peak intensity S=O and S-O was important to indicate the SO_3H functional group which is related to the presence of the acid site on the catalyst. The result indicates that the SO_3H functional group was successfully introduced by the sulfonation process. The C=C and C=O functional groups can be detected around 1,600 – 1,750 cm^{-1} [19]. For C450 and CS450, the C=C stretching was observed approximately at 1,680 cm^{-1} [15]. The C=C functional group shows the existence of aromatic carbon structure for both samples. For CS450, the C=O stretching was observed approximately at 1,700 cm^{-1} [20]. The detection represents the carboxylic acid resulting from oxidation during sulfonation where the sulfonation process can facilitate the occurrence of carboxylic groups on the material surface [21]. The -OH functional group of CS450 which can related to the SO_3H functional group and adsorbed moisture was detected by broad peak stretching at 3000-3500 cm^{-1} [22].

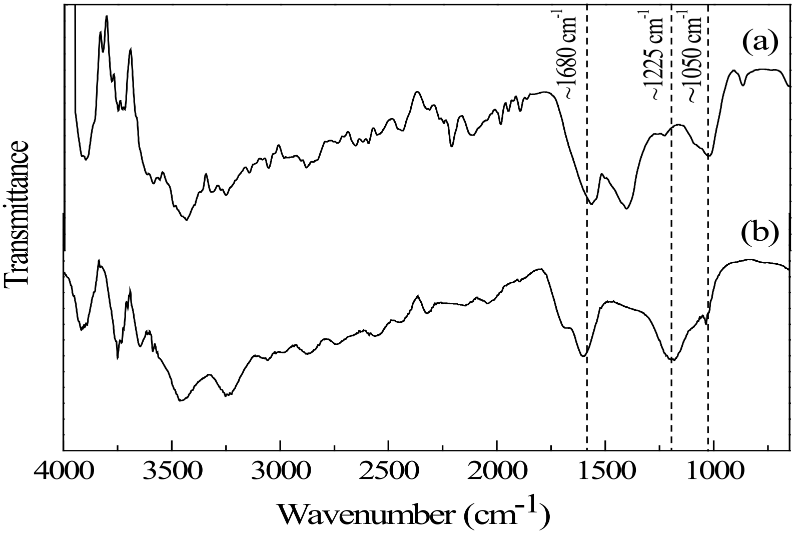


Figure 2: FTIR spectrum of (a) C450 and (b) CS450 catalyst.

Catalyst Acidity

The presence of acid sites on the CS450 resulting from sulfonation can be confirmed by the catalyst acidity and the value of 1.0 mmol/g was recorded. Meanwhile, the acidity of C450 was 0.04 mmol/g since it was a non-sulfonated sample, and its acidity was reflected in the low EL yield as compared to CS450. For CS450, the result demonstrated that the SO_3H functional group was successfully attached to the carbon structure. The aromatic structure of C450 provides placement for the SO_3H functional group. The acidity of the catalyst is also contributed by the carboxylic (COOH) functional group. The COOH formation resulted from the oxidation on the C450 surface by concentrated H_2SO_4 during sulfonation. The acidity result is parallel with the FTIR results. Based on Bosilj et al. [5], the attachment of the SO_3H functional group to the catalyst is the main factor promoting acidity, plus the COOH functional group also has slight effects on it. The catalyst acidity is very important in the ethanolysis of glucose to EL. The active acid sites on the catalyst surface are responsible for glucose etherification during the first step of glucose conversion [7]. Thus, the catalyst acidity plays it significant part in providing higher EL yield from glucose ethanolysis.

SEM-EDX Analysis

Referring to Figure 3, the physical morphology of the C450 and CS450 can be observed through SEM images at x300 and x1000 magnifications. Figures 3(a) and (b) show that the C450 has a low amount of porosity. Calcination of lignin to produce C450 caused the volatile components such as moisture content and low molecular weight components to degrade, eventually leading to pores formation. In Figures 3(c) and (d), the porosity of the CS450 is visible after the sulfonation process was conducted. Further degradation of the C450 surface occurred due to the utilization of concentrated H_2SO_4 and drives the improvement of porous structures. According to Peixoto et al. [23], the use of H_2SO_4 during the sulfonation process caused the breakage structures of the catalyst and produced a higher surface area. Additionally, the application of hydrothermal sulfonation also contributes to the high porosity of CS450. Self-generated pressure in the Teflon autoclave reactor can assist the surface rupture of C450, resulting in various porous structures such as mesopores and micropores.

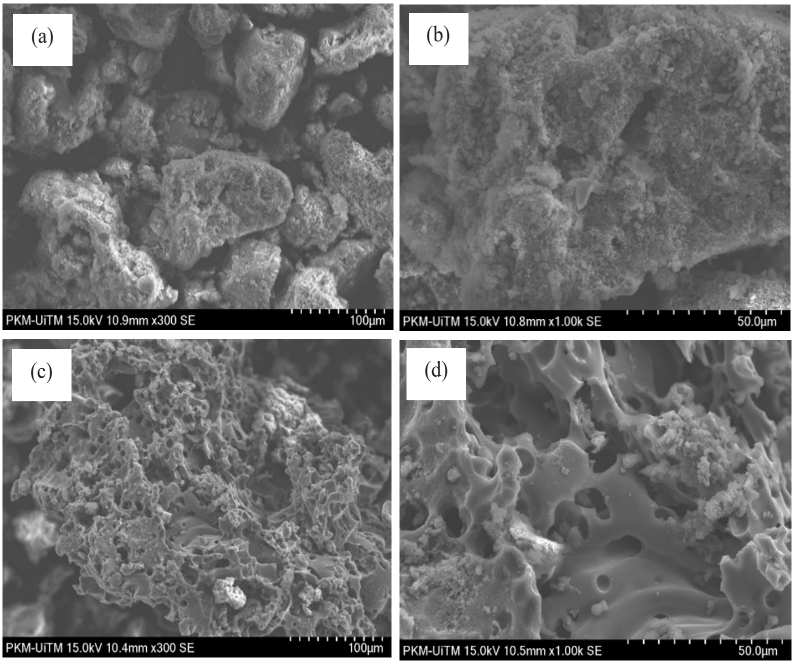
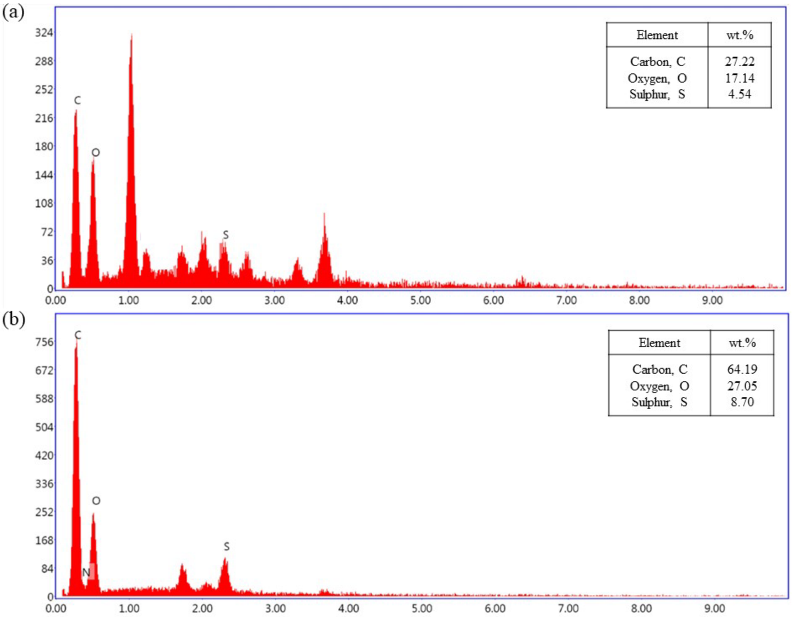


Figure 3: SEM images of C450 at (a) x300, (b) x1000, and CS450 at (c) x300, (d) x1000 magnification.

Figure 4 displays the composition of the elements on the surface of C450 and CS450. There is an increase of S element from 4.54 to 8.70 wt. % and O element from 17.14 to 27.05 wt. %. The increment of these elements proved the sulfonation was successfully conducted by providing the SO_3H functional group. Farabi et al. [24] found that the increased S element of the PKS-SO_3H catalyst may be related to the larger SO_3H functional group present in the catalyst. The EDX results support the acidity and FTIR results. On the other hand, EDX detected that lower C element of C450 (27.22 wt. %) as compared to CS450 (64.19 wt. %). The presence of various unknown elements on the C450 structure resulted in a lower C element. The difference in elemental mapping between samples also could be explained by the deashing experienced by CS450, a process in which the reduction of unknown peaks and unwanted elements. The process occurred due to the use of strong acid during sulfonation. Deashing treatment by strong acid was able to minimize the ash content as well as improve the number of acid functional groups [25]. We also highlight the sulfonation process not only provides the SO_3H functional group, but surface modification can occur simultaneously.



Element	wt.%
Carbon, C	27.22
Oxygen, O	17.14
Sulphur, S	4.54

Element	wt.%
Carbon, C	64.19
Oxygen, O	27.05
Sulphur, S	8.70

Figure 4: EDX results of (a) C450 and (b) CS450 catalysts.

Nitrogen Sorption Analysis

As summarised in Table 1, the mesopore and micropore area of C450 was 7.90 m^2/g and 4.79 m^2/g respectively, which gives a total surface area of 12.69 m^2/g. Meanwhile, the mesopore and micropore area of CS450 were 64.29 m^2/g and 165.66 m^2/g respectively, which give a total surface area of 229.95 m^2/g. The improvement of the total surface area after sulfonation has similar explanations as in SEM results. The high surface area of CS450 helps to provide high physical adsorption of reactants and could minimize the mass transfer limitation. A high surface area together with the micropore and mesopore structure of CS450 is vital for easier access to the acid-active sites to produce the desired EL. Wang et al. [26] stated that the high surface area of the catalyst contributes to more acid site placement as well as increases the accessibility to the acid-active sites.

Table 1: Surface area and pore volume of C450 and CS450.

Catalyst	S_{BET} [a] (m^2/g)	S_{meso} [b] (m^2/g)	S_{micro} [c] (m^2/g)	V_{meso} [d] (cm^3/g)	V_{micro} [e] (cm^3/g)
C450	12.69	7.90	4.79	0.024	0.002
CS450	229.95	64.29	165.66	0.149	0.071

[a] BET surface area from the N_2 adsorption isotherm

[b] Surface area of mesopore from t-Plot method (external area).

[c] Surface area of micropore from t-Plot method.

[d] BJH Adsorption cumulative volume of mesopores.

[e] Volume of micropore from t-Plot method.

TGA Analysis

Figure 5 represents the TGA-DTG curves of C450 and CS450. The high DTG peak below 150 °C for both samples represents high adsorbed volatile materials. The loss of approximately 10 wt.% for C450 and 15 wt.% for CS450 over the sample weight was due to the evaporation of water in the pores structure. The carbon catalyst will experience weight loss due to the loss of water adsorbed on the surface [23]. In the temperature range from 200 – 500 °C, the broad DTG peaks of C450 and CS450 were observed, where the remaining weight for both samples was approximately 80 wt.% and 70 wt.%, respectively. For C450, degradation of the remaining volatile components and low molecular organic compounds has occurred. As compared to CS450, the degradation rate of C450 is lower and thermally stable since the sample was prepared at a temperature of 450 °C. Meanwhile, a higher degradation rate for CS450 showed the degradation of weak acid sites followed by strong acid sites, particularly the SO_3H functional group. Rechnia-Gorący et al. [27] explained this is correlated with the disintegration of oxygenated functional groups that may have been added from the sulfonation process, such as alcohols, phenolic, and carboxylic acids. To maintain the catalyst performance in the reaction, it is suggested that CS450 is thermally stable at 300 °C. Above 600 °C, a major weight loss of C450 was recorded due to high temperatures applied to the samples. This occurrence was due to the deterioration of heavy organic compounds including the aromatic structure of the sample. Babaei et al. [28] stated that the cleavage of carbon structure occurred at high temperatures up to 800 °C. Nevertheless, the trend is contradicted for CS450 at temperature above 600 °C. The decrease of DTG peak above 600 °C explained the continuous high degradation of CS450.

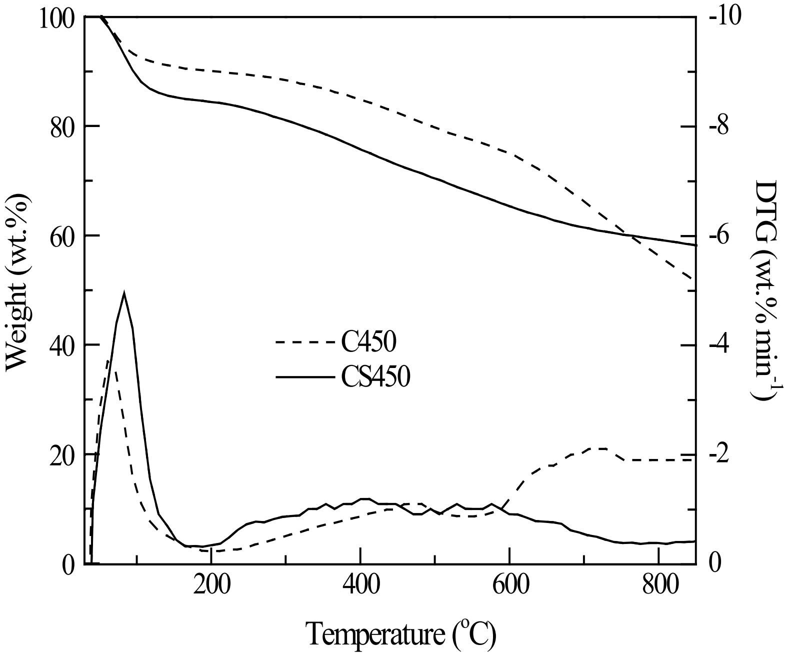


Figure 5: TGA/DTG curve for C450 and CS450.

CONCLUSION

The different calcination temperatures during lignin carbon preparation resulted in the different catalytic activity of sulfonated lignin carbon acid catalysts in glucose ethanolysis. The recommended calcination temperature of lignin carbon for the catalyst preparation was 450 °C, as it showed good catalytic activity in glucose ethanolysis. The CS450 has an acidity of 1.0 mmol/g with a large surface area of 229.95 m^2/g and provides an EL yield of 22.54 mol %. The catalyst has demonstrated its potential to be used as a solid acid catalyst, particularly ethanolysis of glucose to synthesize EL. More catalyst modifications need to be conducted in the future such as introducing Lewis acid to the catalyst, as well as the study of optimum reaction conditions to obtain higher EL yield.

ACKNOWLEDGEMENT

The authors would like to express their sincere gratitude to the Ministry of Higher Education (MOHE), Malaysia and College of Engineering, Universiti Teknologi MARA (UiTM) for the financial support via Fundamental Research Grant Scheme (FRGS/1/2021/TK0/UITM/02/7).

REFERENCES

[1] Z. Weina, C. CHANG, M. Chen, and D. Fengguang, 2014. Kinetics of glucose ethanolysis catalyzed by extremely low sulfuric acid in ethanol medium, *Chinese Journal of Chemical Engineering*, 22(2), 238-242. doi: 10.1016/S1004-9541(14)60049-5.

[2] E. Ahmad, M. I. Alam, K. Pant, and M. A. Haider, 2016. Catalytic and mechanistic insights into the production of ethyl levulinate from biorenewable feedstocks, *Green Chemistry*, 18(18), 4804-4823. doi: 10.1039/C6GC01523A.

[3] Y. W. Tiong, C. L. Yap, S. Gan, and W. S. P. Yap, 2018. Conversion of biomass and its derivatives to levulinic acid and levulinate esters via ionic liquids, *Industrial & Engineering Chemistry Research*, 57(14),

4749-4766.doi: 10.1021/acs.iecr.8b00273.

[4] L. Peng, L. Lin, and H. Li, 2012. Extremely low sulfuric acid catalyst system for synthesis of methyl levulinate from glucose, *Industrial Crops and Products*, 40, 136-144. doi: 10.1016/j.indcrop.2012.03.007

[5] M. Bosilj, J. Schmidt, A. Fischer, and R. J. White, 2019. One pot conversion of glucose to ethyl levulinate over a porous hydrothermal acid catalyst in green solvents, *RSC advances*, 9(35), 20341-20344. doi: 10.1039/C9RA03902C.

[6] J. Zhang and J. Chen, 2016. Modified solid acids derived from biomass based cellulose for one-step conversion of carbohydrates into ethyl levulinate, *Journal of Energy Chemistry*, 25(5), 747-753. doi: 10.1016/j.jechem.2016.06.005.

[7] D. Song, Q. Zhang, Y. Sun, P. Zhang, Y. H. Guo, and J. L. Hu, 2018. Design of ordered mesoporous sulfonic acid functionalized ZrO_2/organosilica bifunctional catalysts for direct catalytic conversion of glucose to ethyl levulinate, *ChemCatChem*, 10(21), 4953-4965. doi: 10.1002/cctc.201801089.

[8] G. Morales, A. Osatiashtiani, B. Hernández, J. Iglesias, J. A. Melero, M. Paniagua, D. R. Brown, M. Granollers, A. F. Lee, and K. Wilson, 2014. Conformal sulfated zirconia monolayer catalysts for the one-pot synthesis of ethyl levulinate from glucose, *Chemical Communications,* 50(79), 11742-11745. doi: 10.1039/C4CC04594G.

[9] C. Huang, J. Ma, W. Zhang, G. Huang, and Q. Yong, 2018. Preparation of lignosulfonates from biorefinery lignins by sulfomethylation and their application as a water reducer for concrete, *Polymers*, 10(8), 841. doi:10.3390/polym10080841.

[10] A. H. Hassan, M. M. Zainol, K. R. Zainuddin, N. Q. Saperi, M. A. M. Yussuf, N. Abd Rahman, and N. A. N. M. N. Azman, 2022. Sulfonated Carbon Catalyst Prepared from Calcination of Lignin for Ethyl Levulinate Synthesis via Ethanolysis of Levulinic Acid, *Chemical*

Engineering Transactions, 97, 307-312. doi: 10.3303/CET2297052.

[11] L. Zhang, G. Xi, J. Zhang, H. Yu, and X. Wang, 2017. Efficient catalytic system for the direct transformation of lignocellulosic biomass to furfural and 5-hydroxymethylfurfural, *Bioresource technology,* 224, 656-661. doi: 10.1016/j.biortech.2016.11.097.

[12] M. M. Zainol, M. Asmadi, N. A. S. Amin, and M. N. F. Roslan, 2022. Glucose-derived bio-fuel additive via ethanolysis catalyzed by zinc modified sulfonated carbon, *Materials Today: Proceedings*, 57, 1008-1013. doi: 10.1016/j.matpr.2021.08.065.

[13] M. Li, Q. Zhang, B. Luo, C. Chen, S. Wang, and D. Min, 2020. Lignin-based carbon solid acid catalyst prepared for selectively converting fructose to 5-hydroxymethylfurfural, *Industrial crops and products*, 145, 111920. doi: 10.1016/j.indcrop.2019.111920.

[14] A. P. da Luz Corrêa, P. M. M. da Silva, M. A. Gonçalves, R. R. C. Bastos, G. N. da Rocha Filho, and L. R. V. da Conceição, 2023. Study of the activity and stability of sulfonated carbon catalyst from agroindustrial waste in biodiesel production: Influence of pyrolysis temperature on functionalization, *Arabian Journal of Chemistry*, 16(8), 104964. doi: 10.1016/j.arabjc.2023.104964

[15] M. Cao, L. Peng, Q. Xie, K. Xing, M. Lu, and J. Ji, 2021. Sulfonated Sargassum horneri carbon as solid acid catalyst to produce biodiesel via esterification, *Bioresource Technology*, 324, 124614. doi: 10.1016/j.biortech.2020.124614.

[16] M. M. Zainol, M. N. F. Roslan, M. Asmadi, and N. A. S. Amin, 2021. Preparation and Characterization of Sulfonated Carbon Cryogel Doped Zinc as a Catalyst for Glucose Ethanolysis to Ethyl Levulinate, *ASEAN Journal of Chemical Engineering,* 21(1), 1-10. doi: 10.22146/ajche.59865.

[17] D. Scholz, O. Kröcher, and F. Vogel, 2018. Deactivation and regeneration of sulfonated carbon catalysts in hydrothermal reaction

environments, *ChemSusChem,* 11(13), 2189-2201. doi: 10.1002/cssc.201800678.

[18] A. H. Hassan, M. M. Zainol, M. A. Samion, M. Asmadi, A. R. M. Daud, I. Saad, and N. A. N. M. N. Azman, 2023. Synthesis of ethyl levulinate over sulfonated lignin-based carbon catalyst as a fuel additive to biodiesel-diesel blends towards engine emissions, *Journal of Cleaner Production*, 418, 138101. doi: 10.1016/j.jclepro.2023.138101.

[19] H. Xiao, Y. Guo, X. Liang, and C. Qi, 2010. One-step synthesis of a novel carbon-based strong acid catalyst through hydrothermal carbonization, *Monatshefte für Chemie-Chemical Monthly,* 141, 929-932. doi: 10.1007/s00706-010-0332-2.

[20] P. D. Rocha, L. S. Oliveira, and A. S. Franca, 2019. Sulfonated activated carbon from corn cobs as heterogeneous catalysts for biodiesel production using microwave-assisted transesterification, Renewable energy, 143, 1710-1716.

[21] B. Zhang, M. Gao, J. Geng, Y. Cheng, X. Wang, C. Wu, Q. Wang, S. Liu, and S. M. Cheung, 2021. Catalytic performance and deactivation mechanism of a one-step sulfonated carbon-based solid-acid catalyst in an esterification reaction, *Renewable Energy*, 164, 824-832. doi: 10.1016/j.renene.2019.05.070.

[22] Z. Chen, S. Zhang, B. Yan, Q. Cai, and S. Zhang, 2022. Lignin-based solid acid catalyst for cellulose residue conversion into levulinic acid in biphasic system, *Industrial Crops and Products,* 178, 114523. doi: 10.1016/j.indcrop.2022.114523.

[23] A. F. Peixoto, R. Ramos, M. M. Moreira, O. S. G. Soares, L. S. Ribeiro, M. F. Pereira, C. Delerue-Matos, and C. Freire, 2021. Production of ethyl levulinate fuel bioadditive from 5-hydroxymethylfurfural over sulfonic acid functionalized biochar catalysts, *Fuel,* 303, 121227. doi: 10.1016/j.fuel.2021.121227.

[24] M. A. Farabi, M. L. Ibrahim, U. Rashid, and Y. H. Taufiq-Yap, 2019. Esterification of palm fatty acid distillate using sulfonated carbon-based catalyst derived from palm kernel shell and bamboo, E*nergy Conversion and Management*, 181, 562-570. doi: 10.1016/j.enconman.2018.12.033

[25] P. Zhang, H. Sun, L. Yu, and T. Sun, 2013. Adsorption and catalytic hydrolysis of carbaryl and atrazine on pig manure-derived biochars: impact of structural properties of biochars, *Journal of hazardous materials*, 244, 217-224. doi: 10.1016/j.jhazmat.2012.11.046.

[26] W. Wang, X. Cao, H. Guo, X. Yang, N. Guo, and Y. Ma, 2022. Carbon-based solid acid derived from lignin and polyvinyl chloride for conversion of xylose and crop wastes to furfural, *Molecular Catalysis,* 524, 112329. doi: 10.1016/j.mcat.2022.112329.

[27] P. Rechnia-Gorący, A. Malaika, and M. Kozłowski, 2018. Acidic activated carbons as catalysts of biodiesel formation, *Diamond and Related Materials*, 87, 124-133. doi: 10.1016/j.diamond.2018.05.015.

[28] Z. Babaei, A. N. Chermahini, and M. Dinari, 2021. Synthesis of n-butyl levulinate as a fuel additive using bimetallic Zr/Al catalysts supported on mesoporous silica: Applying experimental design to optimize the reaction conditions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 625, 126885. doi: 10.1016/j.colsurfa.2021.126885.