

HETEROGENEOUS SOLID ACID CATALYST

Dr. Rupam Patgiri

Assistant Professor, Department of Chemistry

Bajali College, Pathsala

ABSTRACT

In this study, acidic heterogeneous catalysts based on graphene oxide and sulfonated biochar were produced, analysed, and put to use in the formation of ethyl lactate through the process of lactic acid esterification. In order to filter the catalyst from the reactants in a more straightforward manner, graphene oxide was supported on activated carbon (GO/AC). Methods such as XRD, FT-IR, SEM, and BET, in addition to the acid-base titration, were utilised in order to characterise the catalysts. The esterification of lactic acid was used as a test to determine the level of catalytic activity. As a consequence of this, the order in which the activity of the catalysts reduced is as follows: graphene oxide > sulfonated biochar > GO/AC >> activated carbon. In addition, the GO/AC catalyst exhibited high stability, as evidenced by the fact that its yield remained unaltered from the third to the sixth time it was recycled. As a result of these findings, prospective applications for novel acidic heterogeneous catalysts based on graphene oxide and sulfonated biochar have been suggested. These catalysts have the potential to replace homogeneous acids in the future. In order to circumvent the challenges presented by homogeneous catalysts, it is recommended to use heterogeneous acid-based catalysts that are generated from waste biomass and are recyclable. It is more cost-effective to employ agricultural biomass as a catalyst for the transesterification process, which in turn lowers the total cost of producing biodiesel. In the field of biofuels, a significant step forward will be taken once a catalyst that is adequate and effective for transesterification is discovered.

keywords: Heterogeneous , Solid

INTRODUCTION

Biofuels have evolved as a viable alternative energy source to fossil fuels over the course of the past decade, which has helped to alleviate both the energy crisis and environmental degradation. Biodiesel, which is often produced from renewable feedstock such as plant lipids, animal fats or oils, culinary oils or waste, and inedible oils, among other things, is considered to be one of the most promising types of biofuel. The catalytic esterification and transesterification of free fatty acids is the biodiesel production method that is easiest to put into practice and has the lowest production cost (FFAs). The majority of the time, fundamental catalysts like NaOH, KOH, NaOCH₃, and KOCH₃ are utilised. On the other hand, same fundamental catalysts might readily react with fatty acids to produce soap, which would be detrimental to the product separation process. In a similar fashion, acid catalysts such as H₂SO₄, HCl, BF₃, and H₃PO₄ are utilised in order to facilitate the esterification of FFAs. The extreme acidity of the aforementioned acid catalysts, on the other hand, necessitates the use of equipment that is resistant to corrosion. In addition, further separation and neutralisation stages result in a substantial amount of waste water being discharged. As a result, the development of heterogeneous acid catalysts is extremely desirable in order to both reduce the amount of equipment that is required and decrease the negative impact that the process has on the environment.

Numerous solid acid catalysts, such as zeolite heteropolyacids, ion exchange polymer resins, carbon-based solid acids, and zinc lanthanum mixed oxides, have been created up to this point. Because to the use of these solid acid catalysts, the process of esterification may be completed more quickly and at a lower cost per unit of output. However, because these heterogeneous solid acid catalysts have so few active sites, it is impossible to use them in a wide variety of applications. In addition, their comparatively low porosity is not conducive to the mass transfer of reactants by diffusion, which results in a slow reaction rate. This is one of the factors that contributes to the slow reaction rate. As a consequence of this, the production of solid acid catalysts that have a large concentration of acid sites that are simple to reach is something that is sought very much.

ZrP, also known as $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, is a layered molecule that has a high ion exchange capacity and is capable of being exfoliated into single-layer nanosheets. By manipulating the circumstances under which ZrP is synthesised, one may influence both the crystallinity and the size of the material. Because of this, ZrP has found widespread use in the construction of a broad variety of functional materials, including catalysts, polymer nanocomposites, and intercalation compounds, amongst other things. Because of its one-of-a-kind structure, ZrP is able to serve as an outstanding support for the functional groups that are anchored to it. In addition, the single-layer ZrP nanosheets that have been exfoliated may be rapidly and evenly disseminated in a reaction system, which enables a high level of accessibility to the functional groups.

In this study, the solid acid catalyst based on sulfonic acid functionalized ZrP single-layer nanosheets was used as a catalyst for the esterification of oleic acid with methanol. The solid acid catalyst was derived from ZrP single-layer nanosheets. The solid acid demonstrated a catalytic activity that was on par with that of liquid H_2SO_4 and even higher than that of the commercial product known as Amberlyst® 15.

Heterogeneous Solid-Acid Catalytic Transesterification

In spite of their lower activity, heterogeneous solid-acid catalysts have found widespread application in a variety of industrial processes. This is due to the fact that, in comparison to homogenous acid catalysts, they contain a variety of acid sites that exhibit varying degrees of Bronsted or Lewis acidity. Insensitive to FFA content, simultaneous esterification and transesterification, elimination of purification step of biodiesel, easy separation of the catalyst from the reaction products, and reduction of the corrosion problem, even with the presence of acid species are some of the benefits of using solid-acid catalysts [44]. Because of the presence of appropriate acid site strength, heterogeneous solid-acid catalysts such Nafion-NR50, sulfated zirconia, and tungstated zirconia have been used to catalyse the biodiesel-forming transesterification process. Because of its strong acid strength, Nafion showed the highest selectivity among the solid catalysts toward the synthesis of methyl ester and glycerol. Nafion, on the other hand, has a number of drawbacks, including a higher cost and a lower activity level in comparison to liquid acids.

Materials and Methods

Materials

Crushed, screened, and collected sawdust made from pine that was sourced from the Ninh Binh area in Vietnam. The diameters of all sawdust particles fall anywhere between 0.5 and 0.85 millimetres. After that, the sawdust that had been collected was dried at 105 degrees Celsius for two hours. After being rinsed with distilled water, dried at 105 degrees Celsius, and crushed for the last step, activated carbon for commercial use was manufactured from coconut shells in Vietnam. All of these chemicals were acquired from Sigma-Aldrich: expanded graphite powder (45 m, 99.9995%), NaNO_3 (99%), KMnO_4 (99%), H_2O_2 (30%), HCl

(37%), H₂SO₄ (95–98%), lactic acid 85%, and ethanol (99.95%) (Singapore). Deionized water was used in each and every experiment that was carried out.

Synthesis of Graphene Oxide Supported on Activated Carbon (GO/AC)

The process developed by Hummers [27] was adapted in order to carry out the production of graphene oxide. GO, once it has been synthesised, is dissolved in water at a concentration of 5.0 mgxmL¹ and then disseminated. The method of dry impregnation is used to disseminate GO onto an AC support. This process involves stirring 100 mL of the suspension into 5,000 g of 85°C-dried AC in a glass beaker of 250 mL capacity at ambient temperature for five hours. After that, the mixture was left to dry at 85 degrees Celsius for forty-eight hours. After that, it was put into a desiccator to be cooled down. In the end, we were able to collect 5.495 grammes of GO/AC catalyst with a weight ratio of 1:10 between GO and AC. The effectiveness of the supporting procedure reached 99.91% of its potential.

Synthesis of Sulfonated Biochar

There were two steps involved in the synthesis: (i) Carbonation: Forty grammes of pine sawdust were heated in a furnace at a temperature of four hundred degrees Celsius for five hours at a rate of ten degrees Celsius per minute. The end result was referred to as biochar after it was all said and done. (ii) Sulfonation: 15 grammes of produced biochar were mixed with 300 millilitres of a 98% H₂SO₄ solution while being agitated at a temperature of 150 degrees Celsius in a glass flask with three necks for a period of 15 hours. After being chilled, the system for the reaction was gradually diluted with one litre of distilled water. After that, the filtered mixture was washed with hot distilled water at a temperature of 80 degrees Celsius until the sulphate ion was no longer detectable in the 10% BaCl₂ solution. In order to achieve the final product, which was sulfonated biochar catalyst, the solid was allowed to dry out at 105 degrees Celsius for eight hours.

Catalyst Characterization

At a temperature of 82 degrees Celsius, the activity of the catalysts was evaluated by carrying out an esterification reaction with a mole ratio of 1 to 4 involving ethanol and lactic acid with a concentration of 50% lactic acid [29]. The lactic acid was diluted from a solution containing 85% lactic acid. Both the sulfonated charcoal and the GO catalysts have a weight ratio of 5% to the lactic acid, whereas the GO catalyst has a weight ratio of 1%. Because it is difficult to filter, the weight ratio of GO catalyst can't be more than 1%. This is because of the difficulties. The amount of GO that is included within the GO/AC catalyst is identical to the amount that is contained within the GO catalyst. This ensures that the catalytic activity of GO and GO/AC can be compared in an accurate manner.

On an Agilent 7890A gas chromatograph outfitted with a FID, an internal standardisation procedure was used to identify the ethyl lactate product. The following formula was used to determine the amount of ethyl lactate that may be produced:

The following formula may be used to determine the amount of -SO₃H present in 1 gramme of catalyst:

$$N_{-\text{SO}_3\text{H}} = \frac{(0.1 \times V)}{1} \times \frac{50}{20} \left(\text{mmol} \cdot \text{g}^{-1} \right), \quad (1)$$

where V is the volume of used NaOH solution (mL) and $N_{-\text{SO}_3\text{H}}$ is the -SO₃H content per 1 g of catalyst.

Catalytic Tests

The activity of the catalysts was evaluated through the esterification reaction between lactic acid 50% (obtained from 85% lactic acid solution by the dilution) and ethanol (mole ratio 1 : 4) at 82°C [29]. The weight ratios of the sulfonated biochar and GO catalysts to lactic acid are 5% and 1%, respectively. Because of the difficulty in filtering, the weight ratio of GO catalyst cannot be not higher than 1%. To make it easier to compare the catalytic activity between GO and GO/AC, the contents of GO included in the GO/AC catalyst are equal to that of the GO catalyst.

Ethyl lactate product was determined by the internal standardization method on an Agilent 7890A gas chromatograph equipped with an FID. The yield of ethyl lactate was calculated by the following formula:

$$\text{ethyl lactate yield (\%)} = \frac{n_{\text{ethyl lactate}}}{n_{\text{ethyl lactate}}^0} \times 100, \quad (2)$$

where $n_{\text{ethyl lactate}}$ is the real mole of ethyl lactate that is determined by the gas chromatography test and $n_{\text{ethyl lactate}}^0$ is the theory mole of ethyl lactate that is a value with 100% conversion of lactic acid.

2.6. Recycling Catalyst Tests

After the reaction was finished, the GO/AC and sulfonated charcoal catalysts were filtered and washed three times with hot distilled water at a temperature of about 80 degrees Celsius. After that, the catalysts were dried at 105 degrees Celsius for eight hours. The lactic acid esterification process was carried out with the recovered catalysts.

Results and Discussion

Catalyst Characterization

Figure 1 presents the results of an XRD analysis carried out in order to evaluate the structural characteristics of sulfonated biochar, activated carbon, graphene oxide, and GO/AC. These results indicate that the sulfonated biochar catalyst has an amorphous structure [10], since there is a large peak between 20 and 30 degrees on the 2-theta scale. For both graphene oxide and the GO/AC catalysts, there is a distinct peak that can be seen at 11 degrees on the 2-theta scale [22]. This peak corresponds to the crystal structure of graphene oxide. However, the peak has a much diminished degree of prominence when it comes to the GO/AC catalyst. This finding suggested that there was contact between the graphene oxide and activated carbon in the GO/AC catalyst and validated the successful synthesis of graphene oxide from expanded graphite. Graphene oxide was successfully synthesised from expanded graphite.

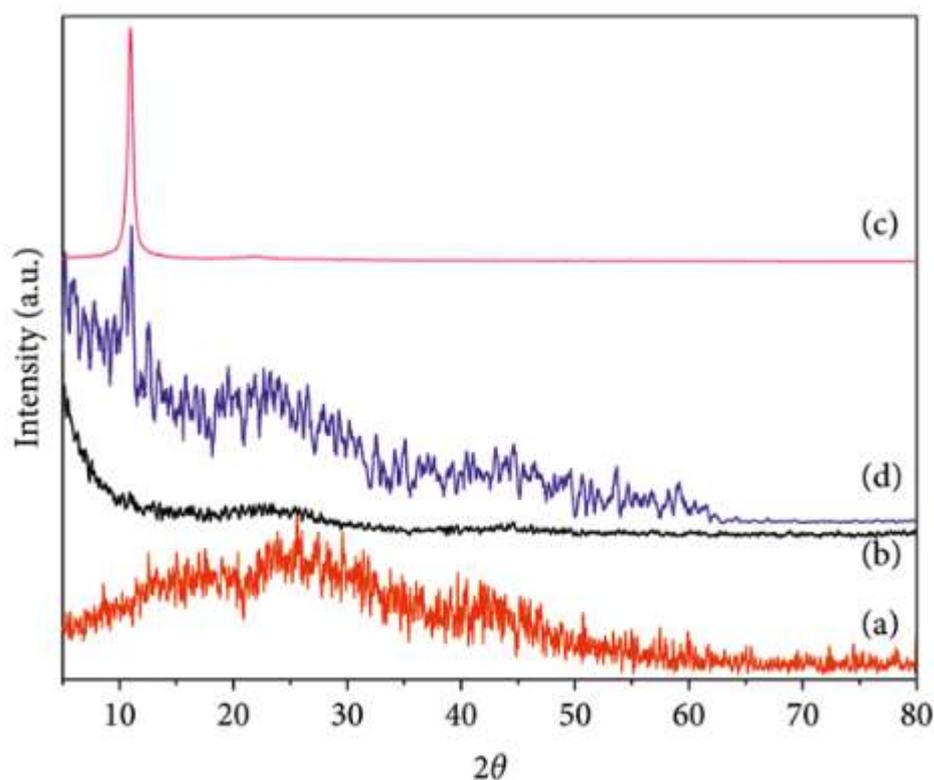
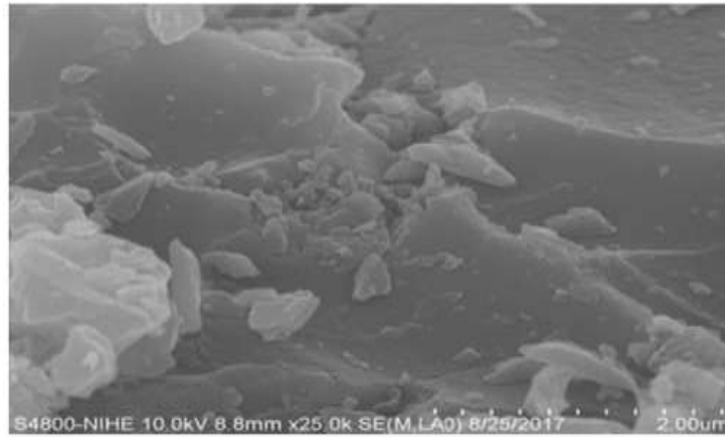


Figure 1 XRD patterns of sulfonated biochar (a), activated carbon (b), graphene oxide (c), and GO/AC (d).

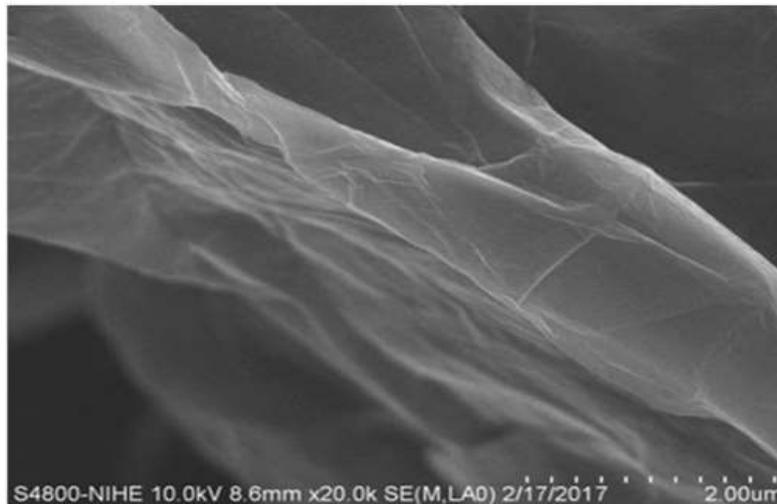
SEM pictures of the sulfonated biochar, activated carbon, graphene oxide, and graphene oxide/activated carbon catalysts are presented in Figure 2. According to the findings, the sulfonated biochar (Figure 2(a)), activated carbon (Figure 2(b)), and graphene oxide (Figure 2(c)) each have a porous structure with extensive capillaries, a solid structure, and a transparently layered structure, respectively. Figure 2(d) demonstrates that the GO/AC catalyst exhibits a "sandwich" shape, which indicates that the GO/AC catalyst was effectively synthesised. This "sandwich" structure depicts the activated carbon as being surrounded by layers of graphene oxide.



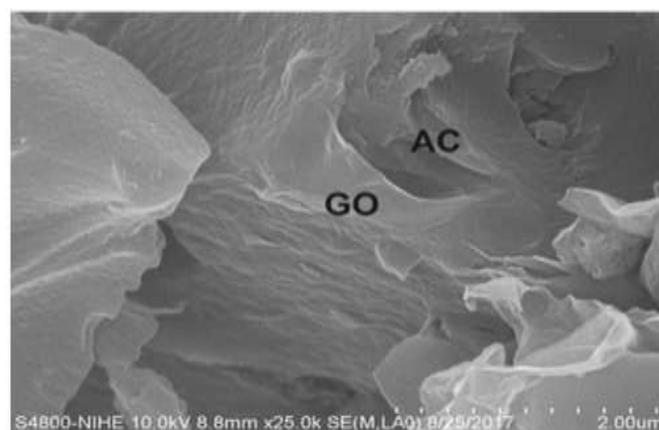
(a)



(b)



(c)



(d)

Figure 2 SEM images of sulfonated biochar (a), activated carbon (b), graphene oxide (c), and GO/AC (d).

Figure 3 presents the FT-IR spectra of the catalysts for your viewing pleasure. In the infrared spectra of sulfonated biochar, graphene oxide, and GO/AC catalysts, there are vibration bands that are characteristic of the -OH bonding and the C=O group, including the -COOH functional group, at 3416, 3387, and 3444 cm^{-1} and 1709, 1698, and 1694 cm^{-1} , respectively. These bands can be found at 3416, 3387, and 3444 cm^{-1} . In addition, the -SO₃H group exhibits valence vibrations associated with the S=O bonding at 1040, 1059, and 1108 cm^{-1} [10, 23]. The absence of valence vibrations of S=O in the case of the activated carbon catalyst is indicative of the absence of -SO₃H groups in the structure of the activated carbon. In the meanwhile.

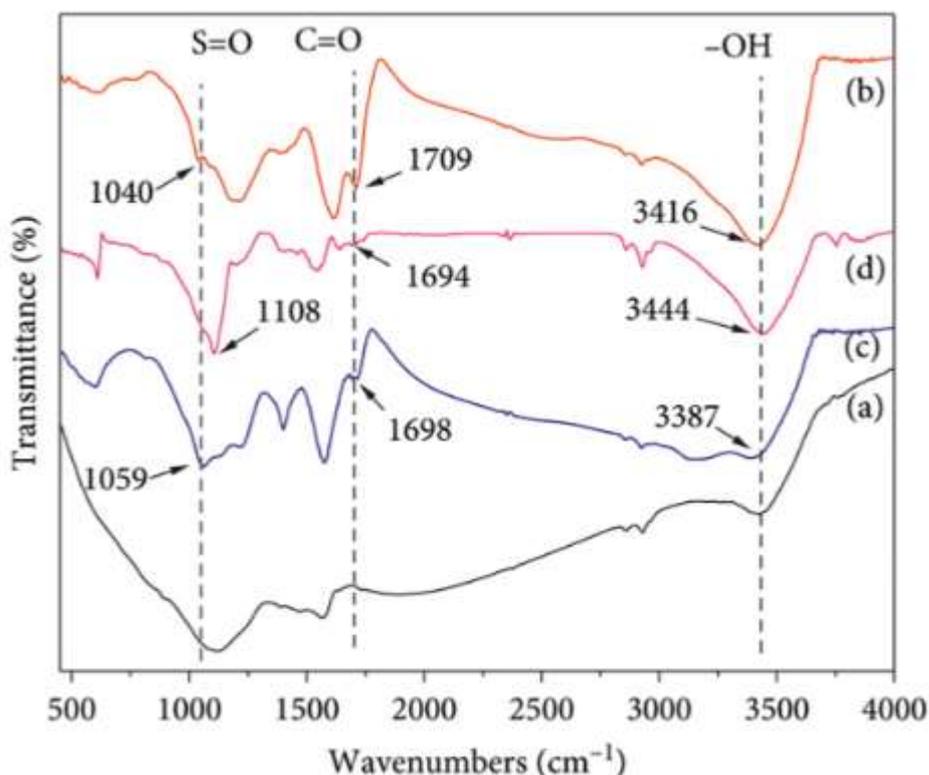


Figure 3 FT-IR spectra of activated carbon (a), sulfonated bio-char (b), graphene oxide (c), and GO/AC (d).

Table 1 contains information on the specific surface areas of the catalysts. According to the findings, the surface areas of the catalysts are relatively large (more than 400 $\text{m}^2 \text{g}^{-1}$). There is a decrease in the specific surface area of the GO/AC in comparison to the initial activated carbon, which may be attributed to the fact that GO particles have filled the micropores of the activated carbon. This reduction in surface area is equal to 150.7 $\text{m}^2 \text{g}^{-1}$. However, as compared to the initial GO/AC, the SBET of GO/AC showed a modest rise after 6 cycles (49 $\text{m}^2 \text{g}^{-1}$ more), indicating that the ratio had been optimised. This can be deduced from a few possible explanations. To begin, it is possible that during the esterification process, trace quantities of GO will be stripped off the surface of the AC and transferred to the reaction liquid. Additionally, the specific surface area of AC is greater than that of GO. GO has a lower specific surface area.

Table 1 Specific surface areas and sulfonic acid group (-SO₃H) content of the catalysts.

Catalysts	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	$-\text{SO}_3\text{H}$ content (mmol g^{-1})
Sulfonated biochar	423.4	1.14
Sulfonated biochar after 4 cycles of reaction	—	0.64
Activated carbon	721.1	0
Graphene oxide	215.9	0.92
GO/AC	570.3	0.35
GO/AC after 6 cycles of reaction	618.9	0.29

In addition, the amounts of sulfonic acid group ($-\text{SO}_3\text{H}$) present in the catalysts are listed in Table 1. According to the findings, the amount of sulfonic acid group included in sulfonated charcoal was 1.14 mmol g⁻¹, whereas the amount contained in GO/AC and GO catalysts was 0.35 mmol g⁻¹ and 0.92 mmol g⁻¹, respectively. The amount of sulfonic acid that was present in GO and sulfonated biochar catalysts was not significantly different from one another.

Catalytic Tests

Figure 4 presents the ethyl lactate yield related to the reaction time for all the catalysts. All the tests were carried out under the same conditions.

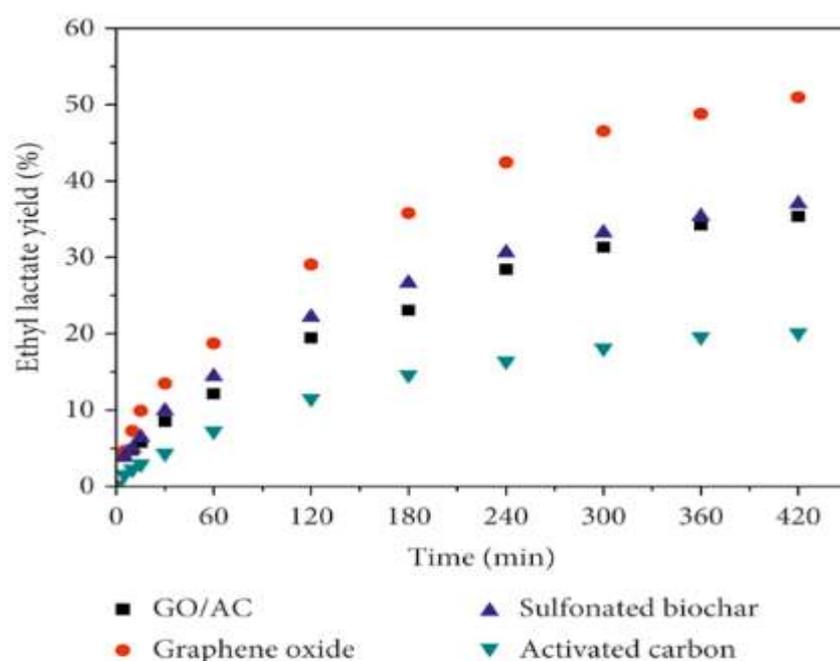


Figure 4 Ethyl lactate yield versus reaction time.

After 420 minutes of reaction time, the findings are displayed in Figure 4, and it is possible to see that the catalytic activity declines in the following order: graphene oxide (51.0%) > sulfonated bio-char (37.0%) > GO/AC (35.4%) >> activated carbon (20.0%). This ranking appears to have some connection to the amount of sulfonic acid contained in each catalyst as well as its dispersion capabilities. Graphene oxide catalysts showed much higher activity than the sulfonated biochar catalysts, which may be due to the higher dispersion of graphene oxide in aqueous medium compared to sulfonated biochar. Even though the sulfonic acid content of sulfonated biochar and graphene oxide is similar (1.14 mmol•g⁻¹ and 0.92 mmol•g⁻¹, respectively), graphene oxide catalysts showed much higher activity. Because its structure contains a great number of hydrophilic functional groups, such as -COOH, -OH, and -CHO, the dispersion of graphene oxide was high as a "pseudo-homogeneous" catalyst. This was discussed before. As a consequence of this, it is not difficult for the "accessible sulfonic groups" of the graphene oxide catalyst to be active in the reaction that causes an increase in the amount of ethyl lactate that is produced. However, one of its drawbacks is that it is difficult to filter or remove the catalyst from the reactants once it has been mixed in. In light of this, the amount of graphene oxide that we utilised in our gas chromatography investigation of ethyl lactate was just one percent by weight.

Although the -SO₃H content of the GO/AC catalyst is only 0.35 mmol•g⁻¹, which is three times lower than that of the sulfonated biochar catalyst, their catalytic activities are comparable. This is due to the fact that the sulfonated biochar catalyst has a higher total amount of sulfonated biochar in its structure. The discovery that a favourable mixture of graphene oxide and activated carbon can function as a catalyst for the esterification of lactic acid is supported by the findings of this study. The fact that the structure of activated carbon does not contain a -SO₃H group, as seen in Table 1, is the explanation for why this catalyst exhibited the lowest level of catalytic activity.

Recycling Tests of Catalysts

The GO/AC catalyst was recycled a total of six times, whereas the sulfonated charcoal catalyst was recycled a total of four times. Figure 5 depicts the amount of ethyl lactate that was produced from each recycling test. Figure 5(a) shows that the activity of the GO/AC catalyst gradually decreased from the 1st to the 3rd cycle, respectively, from 35.4% to 30.3% after a reaction time of 420 min. This represents a decrease of 14.4%, and it appears to be unchanged from the 3rd to the 6th cycle, with only a 3.3% decrease in percentage. In a similar fashion, the activity was reduced with sulfonated biochar as the catalyst (see Figure 5(b)), and it went from 37.0% in the first cycle to 26.1% in the fourth cycle, which is equivalent to a reduction of 29.5%. As a result, the stability of the GO/AC catalyst is significantly greater than that of the sulfonated charcoal catalyst.

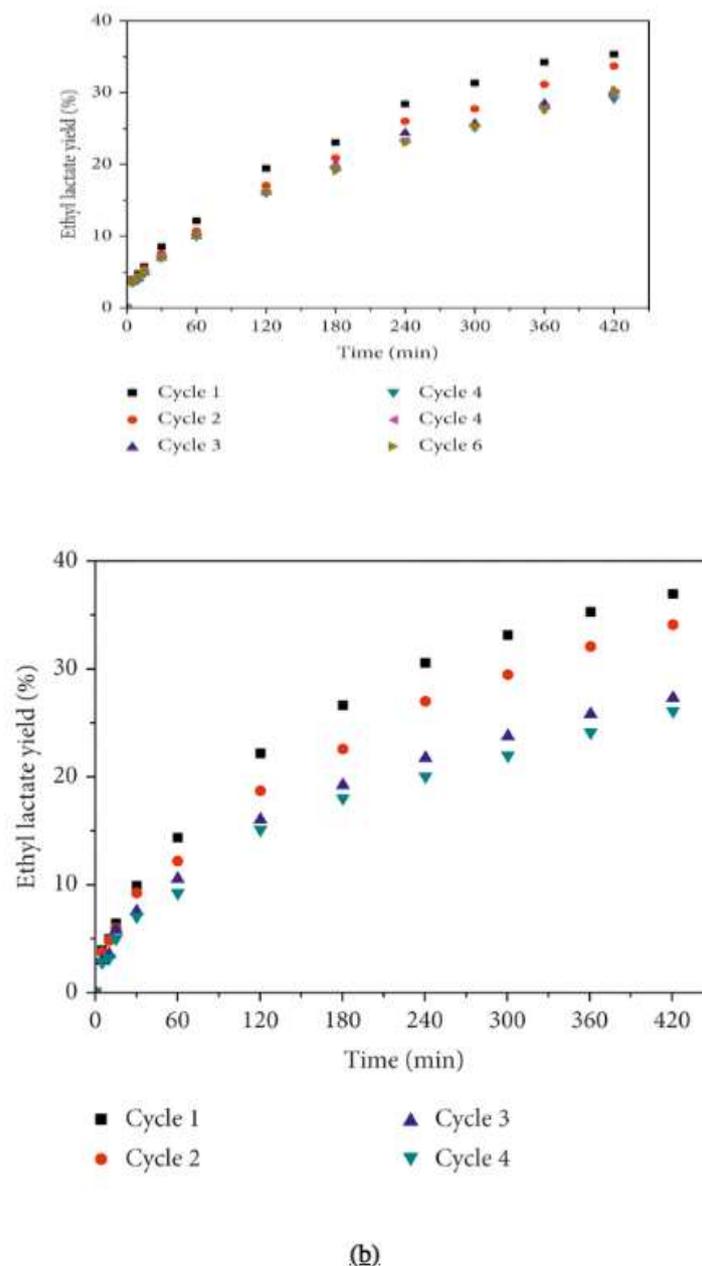


Figure 5 Test of recycled GO/AC (a) and sulfonated biochar (b) catalysts.

The $-\text{SO}_3\text{H}$ contents presented in Table 1 confirm that the durability of GO/AC is higher than sulfonated biochar catalyst. In details, the functional group in GO/AC reduced from $0.35 \text{ mmol}\cdot\text{g}^{-1}$ to $0.29 \text{ mmol}\cdot\text{g}^{-1}$ that means 17.1% of decrease after 6 cycles. However, the value of sulfonated biochar is near 2.6 times higher, 43.9%, after 4 cycles. The result also confirms that in the active phase, GO was well dispersed and attached onto the support, activated carbon. In addition to the strong attachment of graphene oxide onto activated carbon, it seems that the sulfonic group $-\text{SO}_3\text{H}$ of the GO/AC catalyst was more stable than that of the sulfonated bio-char. To explain this phenomenon, FT-IR spectra of 6-times recycled graphene oxide catalyst are presented in Figure 6. The FT-IR spectra of the GO/AC after 6 cycles of reaction also showed vibrations at 3423 cm^{-1} , 1705 cm^{-1} , and 1080 cm^{-1} corresponding to the presence of the $-\text{OH}$, $-\text{COOH}$, and $-\text{SO}_3\text{H}$ groups, respectively.

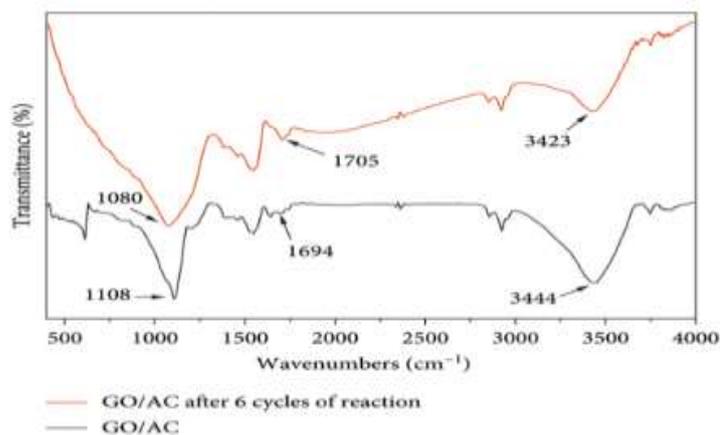


Figure 6 FT-IR spectra of GO/AC and GO/AC after 6 reaction cycles.

According to our current understanding, there are a few different factors that contribute to the close relationship that exists between GO and AC support. To begin, the link that occurs as a result of the esterification of functional groups that are analogous to one another, such as carboxyl (-COOH) and hydroxyl (-OH) (see Figure 7), which are found on the surfaces of both GO and AC [30], can help the combination grow more powerful. In addition, Ai and Jiang [31] provided still another theory which states that both GO and AC have aromatic rings present within their structures. It indicates the possibility of π - π interactions occurring when GO is coated on the surface of AC. As a direct consequence of this, the combination improves.

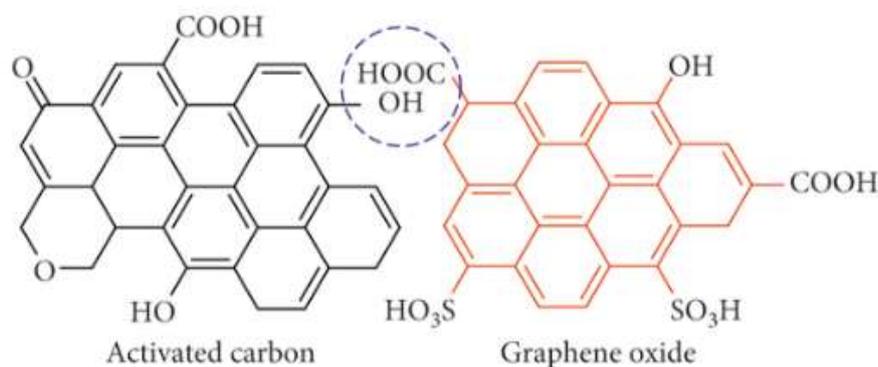


Figure 7 Self-esterification of activated carbon and graphene oxide.

In light of the findings presented above, the GO/AC catalyst demonstrates not only superior catalytic activity but also higher stability than sulfonated charcoal in the process of lactic acid esterification, which culminates in the formation of ethyl lactate. This catalyst displays a combination of "solubility" of the active-phase graphene oxide and a large surface area, in addition to an ease of separation of the activated carbon. Both of these characteristics contribute to the catalyst's overall performance.

Conclusions

In order to produce ethyl lactate through the process of lactic acid esterification, graphene oxide, graphene oxide that has been supported on activated carbon (GO/AC), and sulfonated biochar catalysts were all

produced and examined as potential acidic heterogeneous catalysts. In order of increasing catalytic activity, the catalysts are as follows: graphene oxide > sulfonated bio-char > GO/AC > activated carbon. It would appear that catalytic activities are connected to the -SO₃H content, and more specifically the -SO₃H content that is accessible. After 420 minutes of reaction time, the GO/AC catalyst and the sulfonated charcoal catalyst both showed comparable activity, with an estimated yield of 35% ethyl lactate being produced from the reaction. The high catalytic activity of GO/AC can be attributed to the fact that the active phase contains just 1% of the total weight of GO. In addition, the findings of the experiments performed with recycled catalyst demonstrated that the catalytic activity of the GO/AC catalyst remained unchanged after the third cycle, and the reaction produced a yield of 30.3% ethyl lactate after 420 minutes of reaction time had elapsed. After four cycles of recycling under the same circumstances, the catalytic activity of sulfonated biochar saw a significant decline, which was accompanied by a drop in the output of ethyl lactate from 37.0% to 26.1%. An excellent dispersion, the stability of partial esterification, and the strong contacts between active-phase graphene oxide and activated carbon are responsible for the extraordinary catalytic activity and stability of the GO/AC catalyst. It has been determined that the GO/AC catalyst had a high potential for use as a catalyst for the esterification of lactic acid. This was determined by looking at the application of the catalyst.

References

1. P. G. Jessop, "Searching for green solvents," *Green Chemistry*, vol. 13, no. 6, pp. 1391–1398, 2011. View at: [Publisher Site](#) | [Google Scholar](#)
2. F. F. Bamoharram, M. M. Heravi, P. Ardalani, and T. Ardalani, "A kinetic study of the esterification of lactic acid by ethanol in the presence of Preyssler acid an eco-friendly solid acid catalyst," *Reaction Kinetics, Mechanisms and Catalysis*, vol. 100, no. 1, pp. 71–78, 2010. View at: [Publisher Site](#) | [Google Scholar](#)
3. T. H. T. Vu, H. T. Au, T. H. T. Nguyen et al., "Esterification of lactic acid by catalytic extractive reaction: an efficient way to produce a biosolvent composition," *Catalysis Letters*, vol. 143, no. 9, pp. 950–956, 2013. View at: [Publisher Site](#) | [Google Scholar](#)
4. Y. Zhang, L. Ma, and J. Yang, "Kinetics of esterification of lactic acid with ethanol catalyzed by cation-exchange resins," *Reactive and Functional Polymers*, vol. 61, no. 1, pp. 101–114, 2004. View at: [Publisher Site](#) | [Google Scholar](#)
5. P. Delgado, M. T. Sanz, and S. Beltrán, "Kinetic study for esterification of lactic acid with ethanol and hydrolysis of ethyl lactate using an ion-exchange resin catalyst," *Chemical Engineering Journal*, vol. 126, no. 2-3, pp. 111–118, 2007. View at: [Publisher Site](#) | [Google Scholar](#)
6. C. S. M. Pereira, S. P. Pinho, V. M. T. M. Silva, and A. E. Rodrigues, "Thermodynamic equilibrium and reaction kinetics for the esterification of lactic acid with ethanol catalyzed by acid ion-exchange resin," *Industrial & Engineering Chemistry Research*, vol. 47, no. 5, pp. 1453–1463, 2008. View at: [Publisher Site](#) | [Google Scholar](#)
7. O. Edidiong, S. Habiba, and E. Gobina, "Batch process esterification of lactic acid catalysed by cation-exchange resins for the production of environmental-friendly solvent," in *Proceedings of the World Congress on Engineering and Computer Science. Lecture Notes in Engineering and Computer Science 2015*, vol. II, pp. 623–628, WCECS, San Francisco, CA, USA, October 2015. View at: [Google Scholar](#)
8. S. Kang, J. Ye, and J. Chang, "Recent advances in carbon-based sulfonated catalyst: preparation and application," *International Review of Chemical Engineering*, vol. 5, no. 2, pp. 133–145, 2013. View at: [Google Scholar](#)

9. T. Liu, Z. Li, W. Li, C. Shi, and Y. Wang, "Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol," *Bioresource Technology*, vol. 133, pp. 618–621, 2013. View at: [Publisher Site](#) | [Google Scholar](#)
10. W.-Y. Lou, Q. Guo, W.-J. Chen, M.-H. Zong, H. Wu, and T. J. Smith, "A highly active bagasse-derived solid acid catalyst with properties suitable for production of biodiesel," *ChemSusChem*, vol. 5, no. 8, pp. 1533–1541, 2012. View at: [Publisher Site](#) | [Google Scholar](#)
11. M.-L. Tao, H.-Y. Guan, X.-H. Wang, Y.-C. Liu, and R.-F. Louh, "Fabrication of sulfonated carbon catalyst from biomass waste and its use for glycerol esterification," *Fuel Processing Technology*, vol. 138, pp. 355–360, 2015. View at: [Publisher Site](#) | [Google Scholar](#)
12. M. Zhang, A. Sun, Y. Meng, L. Wang, H. Jiang, and G. Li, "Catalytic performance of biomass carbon-based solid acid catalyst for esterification of free fatty acids in waste cooking oil," *Catalysis Surveys from Asia*, vol. 19, no. 2, pp. 61–67, 2014. View at: [Publisher Site](#) | [Google Scholar](#)