Preparation of Pineapple Peel Activated Carbon Supported by Graphene Oxide as a Potential Catalyst for Biodiesel Production

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Abstract: ***A novel catalyst was synthesized to produce biodiesel or also known as fatty acid methyl ester (FAME) via transesterification reaction of castor oil. Conventional carbon activation method was used in producing activated carbon (AC) from waste pineapple peel (PP). Pineapple peel activated carbon (PPAC) was impregnated into graphene oxide (GO) to prepare a supported catalyst. Fourier Transform-InfraRed (FT-IR) revealed significant peaks to confirm activation of PP and impregnation of GO to PPAC. This was further supported by Scanning Electron Microscope (SEM) images which showed a difference in textural morphology. Differential Thermal Analysis (DTA) analysis was done to reveal a high melting temperature for the supported catalyst. Among the values investigated, the best mass ratio of GO-PPAC and the catalyst loading for transesterification of castor oil were1: 3 and 3% by weight, respectively.***

Keywords: catalyst, graphene oxide, biodiesel, fatty acid methyl ester

1. Introduction

One of the major concerns the world is experiencing today is the scarcity of supply of fuel and the environmental impact brought about by the transportation of fuel. The cost of fossil-based fuels is expected to continuously increase as the supply of petroleum is limited and the need to meet the demand for energy is also rising due to the growth of economy and population. Besides, fossil fuels contribute to environmental problems, such as global warming caused by the emission of greenhouse gas CO_2 and acid rain related with NO_x and SO_x emissions which violates the Kyoto Protocol 1997 that aimed to reduce greenhouse gas emission. These arising problems have led to exploration of potential substitutes or alternative solutions such as high-quality renewable biofuels. (*1*)

One of the efficient ways to overcome environmental concerns on fuels is the biomass conversion into hydrocarbon fuel, or biofuel. Biodiesel, as a renewable energy source, is classified as a cleaner alternative to petroleum fuel. Current researches are focused on looking for high-functioning, environment-friendly, and alternative second-generation biofuels and are without greenhouse gas emissions. Vegetable oil is a promising resource in the production of biofuel via transesterification reaction. Transesterification is a reaction of converting triglyceride into Fatty Acid Methyl Ester (FAME) or also known as biodiesel with the use of catalyst and methanol. In this study, the focus was on the synthesis of a catalyst from pineapple (*Ananas comosus)* peel derived activated carbon (PPAC) supported by graphene oxide (GO) for the transesterification of castor oil.

Recently, preparing activated carbon from fruit peels has been considered as one of the useful options to develop wastes from fruit peels. Producing activated carbon from solid waste like pineapple peels (PP) could be very significant in the field of green chemistry catalysis, solid waste utilization and renewable energy applications *(2).* The PP was chosen for this study because of its high amount of carbon components such as lignin, cellulose and hemicellulose, making it an excellent source of carbon *(3).*

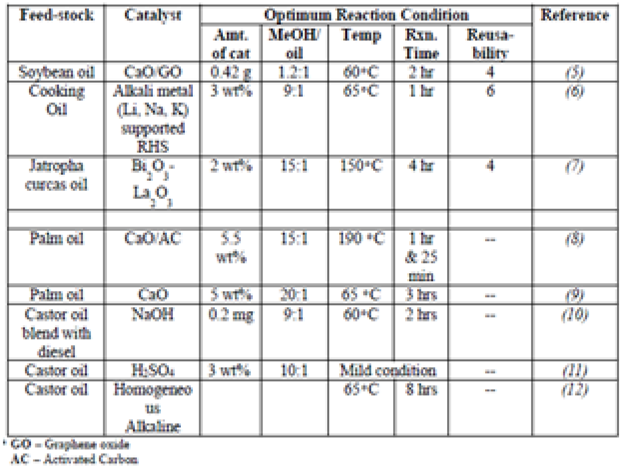
The main novelty of this research was the use of graphene oxide as a catalytic support to the pineapple peel activated carbon. Most heterogeneous catalyst for transesterification either do not use a support or it is chemically derived. To the best knowledge of the authors, this is the first report on the impregnation of GO with PPAC. Thus, this research was an initial investigation exploring a potential novel catalyst for transesterification.

2. Literature Review

In a transesterification process, catalysts have an important role in the yield of FAME in the process. Use of catalytic supports such as porous inorganic substances such as silica, zeolites and other mesoporous materials are one of the possible routes to enhance the low activities of conventional heterogeneous catalysts. The relatively low activities of these catalysts are due to the restricted exposure of the active sites and with the integration of a support; catalysts are expected to increase their sensitivity towards acid and base conditions. A material that supports the catalyst establishes a high dispersion of the active site phase in the catalystwhich renders the catalyst with a high surface area and porosity in relation to the total catalyst loading. With an increased surface area, pores become accessible, and this is essential for obtaining highly dispersed and active catalyst. Surface chemical properties determine the catalytic behavior of a carbon supported catalyst system. Presence and number of heteroatoms (O, N, H) in the form of functional groups in the carbon surface can determine hydrophilic character and acidity/basicity of the carbon surface. *(4).*

Several studies of biodiesel production via transesterification using supported heterogeneous catalyst were conducted and the summaries of results of the studies were tabulated in **Table 1.** All of the catalysts listed on the are table are chemically derived. Not one in the list utilized fruit peel wastes activated carbon.

Table 1: Biodiesel production under optimum reaction conditions using different types of supported heterogeneous catalysts



Feed-stock	Catalyst	Optimum Reaction Condition					Reference
		Amt. of cat	MeOH/ oil	Temp	Rxn. Time	Reusa-bility	
Soybean oil	CaO/GO	0.42 g	1.2:1	60°C	2 hr	4	*(5)*
Cooking Oil	Alkali metal (Li, Na, K) supported RHS	3 wt%	9:1	65°C	1 hr	6	*(6)*
Jatropha curcas oil	Bi_2O_3-La_2O_3	2 wt%	15:1	150°C	4 hr	4	*(7)*
Palm oil	CaO/AC	5.5 wt%	15:1	190 °C	1 hr & 25 min	--	*(8)*
Palm oil	CaO	5 wt%	20:1	65 °C	3 hrs	--	*(9)*
Castor oil blend with diesel	NaOH	0.2 mg	9:1	60°C	2 hrs	--	*(10)*
Castor oil	H_2SO_4	3 wt%	10:1	Mild condition		--	*(11)*
Castor oil	Homogeneous Alkaline			65°C	8 hrs	--	*(12)*

* GO – Graphene oxide
AC – Activated Carbon

Development of activated carbon from fruit peel wastes has been studied as a way to utilize the peel wastes. Fruit peels from durian, orange, rambutan, mangosteen and pineapple have been converted into AC for dye adsorption studies. AC from fruit peels is considered as a versatile carbon for applications such as super capacitor, alternative fuel in cement production, catalyst, and catalyst support *(13).*

In this current study, the peels used were from pineapple (*Ananas comosus Merr.)* Which is a plant commonly found in Asia especially in the Philippines. It is an herbaceous plant, and it has a height of 1.0–1.5 meters. It has 30 or more trough-shaped and pointed leaves surrounding a bushy stem. Pineapple fruit is mainly consumed as fresh or as commercially sold in can food processing industries. However, due to the large-scale cultivation and operations by the food manufacturing industries, there is a massive generation of peel and stem waste. This caused a probable risk towards the environmental pollution to the ecosystems (*14*). This is the reason why the focus of this study is to utilize the waste from pineapple peel by using it as a catalyst in the form of activated carbon. The physical and chemical composition of pineapple peel is shown in **Table 2. (***15)*

Table 2: Chemical composition of pineapple peel

Properties	Composition in g/100g
Total protein	0.75
Ash	1.5
Crude fat	2.0
Crude fibre	65
Insoluble dietary fibre	42.92
Soluble dietary fibre	21.27
Total dietary fibre	64.19
Hemicellulose	28.53
Cellulose	24.53
Lignin	5.78
Pectin	1.58

3. Methods and Materials

3.1 Materials

Pineapple (*Ananas comosus)* peels used in this study were collected from Divisoria, Cagayan de Oro City. Graphene oxide was provided by Juliet Q. Dalagan, PhD.

3.2 Supported Catalyst Preparation

Carbonization and KOH impregnation. The procedure was adapted from the study of Kennedy *et al (16).* The waste pineapple peel (PP) was initially washed with distilled water to remove adhered impurities from its surface. Approximately 10 grams of pineapple peel was soaked in 40 wt% KOH. The amount was enough to cover the pineapple peel completely. Slight agitation of the mixture was done to ensure proper soaking. The mixture was then heated in an oven (MEMMERT C406: 1384) to 80 °C for 1 hour and was left overnight at room temperature to help appropriate wetting and impregnation of the pineapple peel.

Activation. The activation step was adapted from the study of Foo and Hameed (*15*). In the activation process, impregnated pineapple peel obtained from previous step was dried 24 hours in an oven (MEMMERT C406.1834) at 100 ° C. The dried pineapple peel was placed into the crucible and heated in a furnace where the temperature was raised to the required end temperature at 400 ° C for 4 hours. The activated carbon was then washed thoroughly with distilled water and dried 24 hours at 100 °C. Using mortar and pestle, the dried samples called char, was pulverized. The char was then stored in a desiccator.

Characterization of Pineapple Peel (PP) and derived Pineapple Peel Activated Carbon (PPAC). Surface functional groups of PP and PPAC was characterized by Fourier transform infrared (FTIR) spectroscopy using Perkin Elmer FT-IR 100 Spectrometer at Xavier University from the scanning range of 4000–400 $cm^{-1.}$ Scanning Electron Microscopy (SEM) analysis was done at Physics Department in De La Salle University to investigate the pores of PPAC and PP using JEOL JSM 5310 SEM. For the determination of the thermal stability, Differential thermal analysis (DTA) was done at Xavier University using Netzsch Simultaneous Thermal Analyzer.

Preparation of Activated Carbon Supported by Graphene oxide (GO) catalyst. The preparation of the PPAC supported by GO catalyst was adapted from the study of Wan Z. and Hameed B. H. (*8*). Activated carbon supported by graphene oxide catalyst was prepared by impregnation method. PPAC was loaded at the GO support by adding 1.5 mg of GO to 12 mg PPAC in 3 mL of water (mass ratio is 1: 8) and was stirred for 4 hours. After impregnation, the sample was dried in an oven for 12 h at 100 °C. The mass ratio of GO-PPAC was then optimized at 1: 3, 1: 8 and 1: 12 ratios and catalytic activity was investigated by the FAME yield.

3.3 Supported Catalyst Characterization

The catalyst characterizations that were employed on PPAC supported by graphene oxide catalyst were SEM, FTIR and DTA (*17, 18).*

Transesterification: The conversion of castor oil to FAME was done in a 50 ml 2-neck round bottom flask equipped with a reflux condenser and magnetic stirrer. The transesterification reaction between castor oil and methanol was carried out in the liquid phase under atmospheric pressure at 65 °C for 2 hours with constant stirring at 1000 rpm. Three grams of castor oil was transesterified using different ratios of GO-PPAC. After the transesterification, the reaction mixture was allowed to cool to room temperature. FAME was isolated by vacuum filtration to recover the solid catalyst and followed by centrifugation to further separate the layers (FAME and glycerol). The excessive amount of methanol and water was evaporated before the chromatographic analysis. The reaction was carried out three times (*5).*

After investigating the effect of GO-PPAC ratios in transesterification reaction, the optimum mass ratio of GO-PPAC was used in another transesterification reaction using various catalyst loading of GO-PPAC catalyst which were 3, 5, 7 wt%, while the methanol/oil ratio and reaction time were being held constant**.** FAME yield was then analyzed using GC instrument at Pilipinas Kao, Inc. Jasaan, Misamis Oriental.

4. Results and Discussion

Supported Catalyst Preparation and Characterization: Producing an activated carbon from pineapple peel (PP) supported by graphene oxide includes several steps. These are carbonization, KOH impregnation, activation and impregnation of the supported catalyst.

Carbonization of the waste pineapple peel, which acts as the precursor, was a very important step. This converted the organic substances of PP into carbon-containing residue with higher content of fixed carbon. According to Orkun Y. *et al*, the activating reagents could have dissolved the cellulosic components of the precursor, thus promoting the formation of cross-links (*19).* This could be explained further by the FTIR analysis of the PP and PPAC which are shown in **Figure 1**. The major peaks in PP were 1714, 1553, 1492, 1360 and 759 cm^{-1} which can be attributed to C=O, C-N, C-H stretch, C-O stretch and N-O out of plane, respectively. In PPAC, the peak at 759 cm^{-1} disappeared which could be due to the evaporation of volatile substances such as N-O (*15).* There were additional major peaks observed in PPAC such as 3378 and 1660cm^{-1} which are assigned to O-H and C-C stretching, respectively. The activation with KOH could be the reason for the presence of C-H and C-O bands (*15 and 20).*

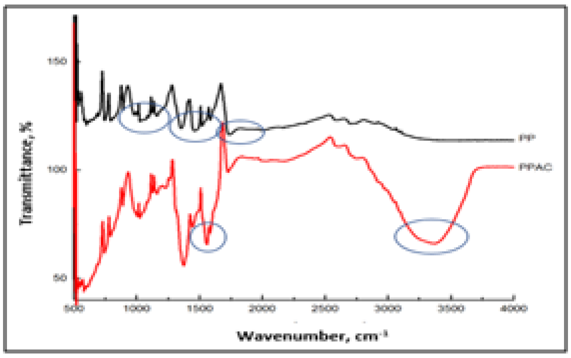


Figure 1: Overlay FT-IR peaks of PP and PPAC

The process of carbonization also created the initial porosity of the PP (*10)* and activation of the precursor PP developed further its porosity. Activation with KOH has created some ordering of the structure which resulted in a highly porous activated carbon (*11).* This can be examined in the SEM analysis. The SEM image in **Figure 2a** showed that PP has full of cavities (as pointed by the blue arrow) which could be attributed to the evaporation of volatile substances upon drying of the PP (*14).* On the other hand, PPAC in **Figure 2b** has a smoother textural image with numerous smaller pores (as pointed by the blue arrow) as also reported by Martinez M. *et al.* in their study of activated carbon derived from olive pit (*21).*

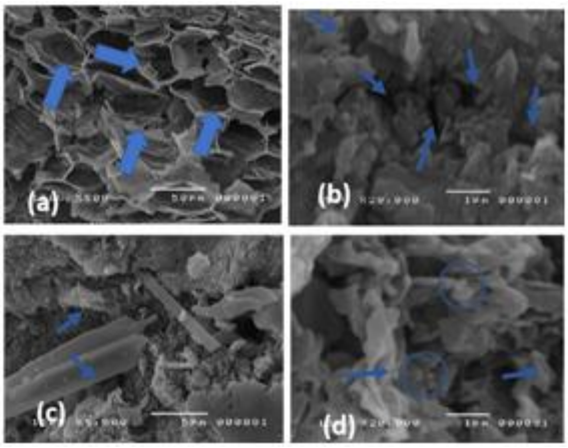


Figure 2: SEM of (a) PP, (b) PPAC, (c) GO and (d) GO-PPAC

Another crucial step in the preparation of the catalyst was the impregnation of the (PPAC) in graphene oxide (GO). This step was done for GO to act as a catalyst support to PPAC. To evaluate if there was impregnation, textural analysis through SEM was done. Comparison of the SEM images of GO before and after impregnation in **Figures 2c** and 2**d** would show that there were changes in its morphology which signify that GO was impregnated to PPAC. SEM image of GO (**Fig 2c**) has an elongated cotton-like shape as shown by the arrows while that of the GO-PPAC has a combination of a circular (as noted by a circular shape) and an elongated cotton-like shape (as pointed by the arrows) indicative of a species (molecules, ions) attached to the surface (*22).*

To further investigate and confirm that impregnation has occurred, FTIR analysis was done. **Figure 3** has important features that would corroborate with the SEM analysis. A peak worth noting is the occurrence of a band at 2974 cm^{-1} which is only found in GO-PPAC. This is assigned to the strong broad absorption of O-H. This could be due to the increase of oxygen containing functional groups after GO was bound to PPAC. The change in the band intensities can also confirm the interaction between GO and PPAC. The peaks at ~1557 cm^{-1} at ~1726 cm^{-1} and at 3400 cm^{-1} which are assigned to vibration peak of graphitic domains, C=O and OH$^-$, respectively have reduced intensities in GO-PPAC (*5*).

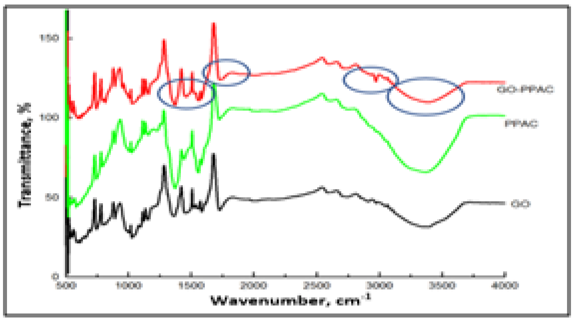


Figure 3: Overlay FT-IR spectra of PPAC, GO and GO-PPAC.

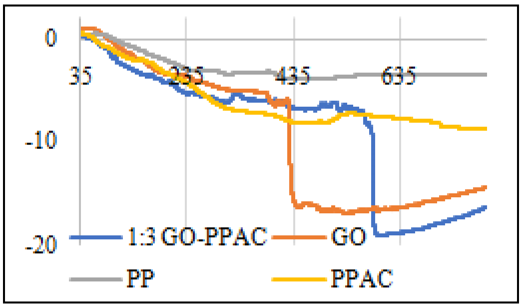


Figure 4: Overlay DTA thermogram of PP, PPAC, GO and GO-PPAC.

Figure 4 shows the overlay of Differential Thermal Analysis (DTA) diagram of PPAC, GO and GO-PPAC. The peaks of PP at around 253ºC and 314ºC correspond to the release of volatile matter from the biomass and the slight devolatilization of pineapple peel, respectively. The endothermic peak at 414ºC is the end temperature of major devolatilization of PP (*23).*

PPAC showed major endothermic peaks at 435ºC and 501ºC which are greater than the end melting temperature of PP at 414 ºC. This could imply that PPAC has the better thermal stability due to the presence of K$^+$ metal ion when KOH activating agent was added during activation. As what was reported in the study of Rodriguez E., *et al*, thermal stability and final temperature of thermal decomposition, depend on the nature of the metal ion (*24).* The thermogram of GO has a major endothermic peak at 447 ºC which corresponds to the decomposition of carbonyl functional groups. This thermal characteristic for GO was also reported by other groups (*25).* The supported catalyst, GO-PPAC exhibited an endothermic peak at 598ºC, the highest in the diagram, which could imply that it has the highest thermal stability among the four materials tested. Thus, having this characteristic would suggest that the GO-PPAC could extend its application such as super capacitors, batteries, sensors, transparent conducting film, solar cells, nanoelectronics and many others (*23).*

Transesterification: To investigate the catalytic activity of the synthesized supported catalyst, transesterification reactions were done using different ratios of GO to PPAC. The best ratio was determined first followed by the best catalyst loading. The other parameters, such as reaction time, temperature and methanol to oil ratio were held constant at 2 hours, 65ºC, and 12: 1, respectively.

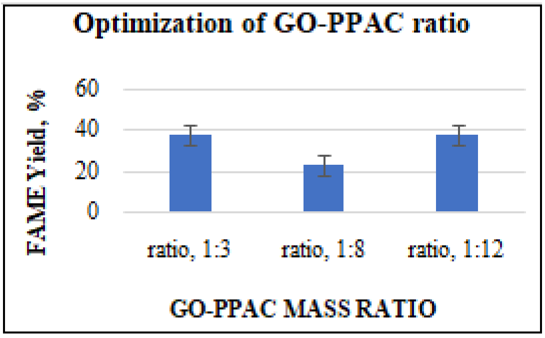


Figure 5: Optimization of GO-PPAC ratio

For optimization of GO-PPAC ratio, the following combinations were used: 1: 3, 1: 8 and 1: 12. As can be observed in **Figure 5**, the ratios, 1: 3 and 1: 12, exhibited almost similar amounts. According to t-test analysis, there is no significant difference between the amounts of the FAME yield. Thus, the ratio that was chosen as the best GO-PPAC ratio is 1: 3. This would be more cost effective than the 1: 12 mass ratio because the latter would need a larger amount of PPAC.

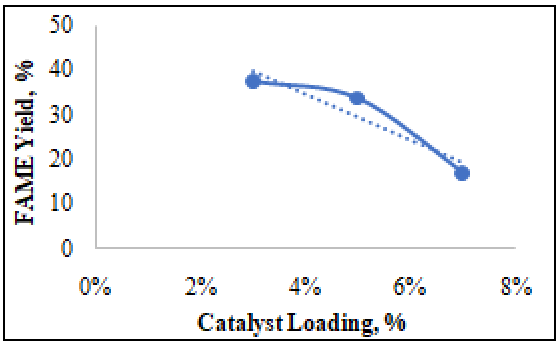


Figure 6: Optimization of catalyst loading

The 3 wt% was chosen as the best catalyst loading because it yielded the highest amount of FAME. It can also be observed in Figure 6 that the amount of catalyst loading has an inverse relation to FAME yield. This might be due to the decreasing basicity of the catalyst upon the impregnation of GO, thus catalytic activity also decreases (*15 and 26).* As can be denoted by FT-IR result which was mentioned previously that COOH and C-C might have reacted and thus might gave an H-type carbon or protonated carbon (*27).*

5. Conclusion

Activated carbon (AC) from pineapple peel (PP) was synthesized using the conventional method of using KOH as an activating agent. The AC was supported with graphene oxide (GO) via impregnation method to produce a heterogeneous supported catalyst (GO-PPAC). Scanning electron microscopy (SEM), Fourier transform-infrared spectroscopy (FTIR) and Differential thermal analysis (DTA) were employed to characterize AC, GO-PPAC, GO and pineapple peel.

Among the investigated values of mass ratios of GO-PPAC, the best ratio that yielded the most amount of FAME via transesterification reaction was 1: 3. The catalyst loading that exhibited the highest yield of 39.26% FAME was at 3 wt% GO-PPAC,

Acknowledgement

The authors would like to thank the Xavier University Kinaadman University Resource Office (KURO) for funding this project.

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