

Sulfonated Activated Sugarcane Bagasse as Heterogeneous Catalyst for Biodiesel Production From Waste Cooking Oil via Microwave Irradiation

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ABSTRACT

In the last decade, high consumption of fossil fuels has led to a serious energy crisis because of the increased energy demand for industrialization and modernization. It caused many environmental concerns because of the greenhouse gas emission along with energy security issues. These fossil fuels resources have been decreasing day by day. These issues prompted the research to find out the feasible, economical and environment friendly alternative resources of energy. Production of biodiesel is getting high concern in the world because of its unique characteristics such as biodegradable, non-toxic and sustainable source of energy. Biodiesel production using edible oils, nonedible oils and animal fats through transesterification process is rapidly increasing because of governmental incentives but still it requires cost effectiveness because biodiesel production using edible feedstock can create a huge food crisis. Conventional heating method to produce biodiesel is also time taking and high energy consumption. Therefore, the research reveals that among various waste resources, waste cooking oil is the most suitable feedstock to produce biodiesel because it is of low cost and easily available in large amount. In the present work, production of biodiesel was done using waste cooking oil and sugarcane bagasse derived heterogeneous solid acid catalyst using microwave irradiation. Catalyst was prepared by varying the sulfonation time of 8h and 10h at 150°C and reaction was run at 60°C for 10 minutes and catalyst was characterized by using different techniques i.e. Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Thermogravimetric Analysis (TGA) and product was analyzed by High pressure liquid chromatography (HPLC). The catalyst prepared at 8h gave the highest conversion 80%.

Keywords: Waste cooking oil, sugarcane bagasse, microwave

1. INTRODUCTION

In the past few years, high consumption of fossil fuels has led to a serious energy crisis due to increased demand of energy because of industrialization and modernization. It resulted in environmental concerns due to greenhouse gas emission with energy security issues [1]. These fossil fuel resources have been getting threshold and exhaust as well as depletion. These issues have prompted the research to find out the alternative energy resources which are technically feasible, environmentally acceptable and economical competitive. Biofuels as an alternative to the petro diesel are originated by inorganic ingredients instead of fossil fuels [2]. Biodiesel production is abruptly growing worldwide due to its characteristic, such biodegradable, non-toxic, and sustainable [3].

The commonly used method to produce biodiesel on commercial scale is "Transesterification". The reaction of triglycerides (1 mol) in the presence of methanol (3 mol) as a solvent and catalyst (acidic or basic) takes place to produce biodiesel and a by-product (glycerol) which is almost 10% of the total product. The process of transesterification involves three steps, in 1st step the conversion of triglycerides into diglycerides, in 2nd step the

conversion of diglycerides into mono glycerides and in the 3rd step the conversion of mono glycerides into esters take place respectively [4]. Various homogeneous and heterogeneous (acidic or basic) catalysts such as alkaline bases, metal oxides, modified polymers, hetero polyacids, zeolites, tungsten oxide zirconia (WO₃/ZrO₂), ion exchange, hydrotalcite, metal phosphite and metallic zinc have been used in the process of esterification and transesterification to increase the yield of biodiesel [5]. The selection of catalyst is highly dependent on the amount of free fatty acid (FFA) content present in the feedstock. If the FFA content is higher than pre-treatment of feedstock is needed, and heterogeneous catalyst will be suitable and for low FFA content homogeneous catalyst will be beneficial for transesterification. Simply, heterogeneous catalysts can be used for low grade feedstock and homogeneous catalysts are useful for refined oils. The major disadvantages of using homogeneous catalysts are high cost and these catalysts cannot be reused after one reaction cycle whereas, the heterogeneous catalysts are corrosive in nature. Palm empty fruit bunch (PEFB) has been used as a catalyst due to the easily available material in Asian countries, such as Malaysia is the 2nd largest palm producer country in the world. Waste PEFB burning emits a large amount of white smoke which impacts the surrounding as well as waste of

biomass. Waste PEFB has been used as a catalyst for esterification reaction. The main advantages of using PEFB as a catalyst in converting free fatty acid (FFA) into biodiesel are the relatively cheap cost, its high tensile strength and it is partially biodegradable. It also contains lignocellulosic material which makes it a suitable renewable biomass [6]. Over the years, research has been conducting on PEFB to develop a new heterogenous catalyst for biodiesel product. Hidayat et al. [7] utilized palm empty fruit bunch (PEFB) as a catalyst to obtained 87% highest conversion of free fatty acid into biodiesel in the presence of 5wt.% catalyst at 60°C. Excessive availability of agro-residue in the form of sugar cane bagasse, which is intensively generated more than 540 million metric tons per year globally. Top three countries in the world are majorly producing sugarcane bagasse, Brazil (>180 million metric tons per year), Colombia (>7 million metric tons/year), and Mexico (>15 million metric tons per year). In 2013, sugar cane bagasse production accounted for more than 1900 million metric ton per year in top leading countries. In global production ranking, Brazil was the first country which generated approximately India (40%), Thailand (19%). In Malaysia sugarcane is cultivated in the states of Perlis and Kedah. About 30000 tons per year sugarcane is produced in Malaysia per year [8]. Bagasse is residue of sugarcane which is milled for juice extraction. Bagasse is 27-28 dry weight % of the plant biomass. It is a heterogeneous material which consists of 40-45% cellulose, 20-30% lignin, and 30-35% hemicellulose with limited amount of ash and extractives. Sugarcane bagasse could be directly impregnated with concentrated sulfuric acid for one step carbonated and sulfonated due to excessive availability of hemicellulose, cellulose and lignin in sugarcane residue bagasse for catalyst preparation. Oxygen rich functional group would appear in ligno-cellulose biomass, which support the sulfonation during catalyst preparation. Esterification reaction would be taking place between free fatty acids from the waste cooking oil and methanol adsorbed on the solid acid active sites. This will enhance the acid density of prepared catalyst and increase the biodiesel production.

These properties of bagasse make this residue a promising feedstock for second generations biofuel production as well as a utilization of biomass as a valuable catalyst for biodiesel production. In this study, a microwave irradiation as heating source was followed to synthesize a bagasse assisted catalyst and it would be used as fast heating source for transesterification reaction to enhance the FAME yield. Microwave assisted biodiesel synthesized from waste cooking oil using sugarcane bagasse catalyst would be analyzed via HPLC and characterized against commercial fossil diesel. Different characterization techniques like SEM (Scanning Electron Microscope), FT-IR (Fourier transform infrared radiation) and TGA (Thermogravimetric Analysis) were used to identify the surface morphology, attachment of functional groups and thermal stability of the catalyst before and after activation. The different physicochemical characteristics of the biodiesel produced from WCO is given below in the Table 1.

Table 1 Different chemical properties of biodiesel produced from WCO [9].

Physicochemical properties	ASTM Standards	WCO Methyl ester	ASTM-6751 Biodiesel
Acid value	ASTM D664-07	2.82	<0.8
Cetane no	ASTMD613	48	47min
Calorific value	ASTM D 6751	36.22	35min
Flash point	ASTM D93	135	100-170
Fire point	ASTM D93	149	
Density g/cm ³	ASTM D1448-1972	0.864	0.86-0.90
Cloud point	ASTM D2500	5	-3—12
Viscosity cSt at 40°C	ASTM D445	3.78	1.9-6.0
Pour point	ASTM D97-05	7	-15—16
Ash content%	ASTM D482	0.03	<0.02

2. EXPERIMENTAL

2.1 Collection of Sample and Feedstock Preparation

Waste cooking oil (WCO) was collected from a café of University Teknologi Petronas. Sugarcane bagasse for the synthesis of catalyst was obtained from a juice stall in Pusing, Malaysia. Chemicals like Methanol, Sulfuric acid, iso-propanol, potassium hydroxide, phenolphthalein (as an indicator) and n-Hexane were ordered from Sigma Aldrich Malaysia. Sugarcane bagasse was washed to remove the impurities. After that, it was dried and crushed to 50µm size. Waste cooking oil was heated and filtered to remove the impurities and suspended particles.

2.2 Characterization of Waste Cooking Oil

Waste cooking oil was characterized by determining its free fatty acid content (FFA), acid value and water content.

2.3 Determination of Acid Value, FFA Content and Water Content

The milligrams of KOH required to neutralize all acid present in 1g of oil sample is known as acid value. It was determined by titrating the solution (WCO & iso-propanol) against 0.1N KOH solution until the color of the solution becomes pink. FFA content value was calculated from acid value. FFA content is equal to half of the acid content value. The water content of the WCO was determined by the 20g of oil sample in an oven at 105°C 30 and 60 minutes

respectively and from weight loss difference the water content was calculated.

2.4 Pre-Treatment of Waste Cooking Oil

The waste cooking oil was pre-treated before transesterification reaction. 50g of oil sample was firstly heated at 60°C. After heating, 27.5ml of methanol and 0.07ml of sulfuric acid were added in the oil and it was heated for 1 hour at 800 rpm. After that sample was put into a separating funnel for 2h to separate the oil layer from the bottom and methanol and water from the top. This process is called deacidification of oil.

2.5 Preparation of Catalyst

Sugarcane bagasse was partially carbonized in a tube furnace at 450°C for 1h under the continuous flow of Nitrogen. 2g of sugarcane bagasse were mixed with 50ml of Sulfuric acid (95-97%) in a round bottom flask with a condenser heated at 150°C for 8h and 10h using a hot plate and continuous stirring. After that mixture was allowed to cool down at room temperature. Then mixture was mixed with 500ml deionized water and particles were allowed to settle down and excess water was removed, and mixture was filtered and washed with hot (80°C) deionized water until the pH became neutral, and the catalyst was dried in an oven at 105°C for overnight. Oxygen rich functional group would appear in lignocellulose biomass, which support the sulfonation during catalyst preparation. Transesterification reaction would be taking place between FFA from the waste cooking oil and methanol adsorbed on the solid acid active sites. This will enhance the acid density of prepared catalyst and increase the biodiesel production.

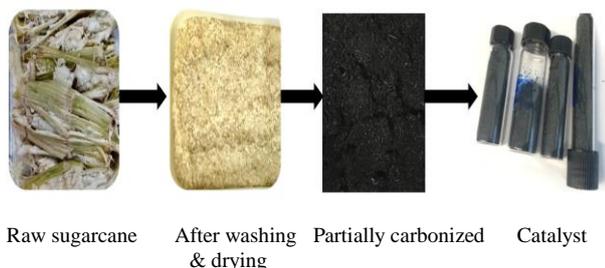


Figure 1 Different stages during the synthesis of catalyst.

2.6 Assembly of Setup for Reaction Test

Reaction was carried in a 250ml three neck round bottom flask placed in a modified microwave having a condenser to avoid the evaporation of methanol and a thermocouple to maintain the temperature of the reaction mixture. 20g of waste cooking oil was taken and heated to 60°C then methanol 1:10 molar ratio and catalyst 2wt% were added and mixture was heated at 60°C with a continuous stirring 400rpm for 20 minutes. High performance liquid chromatography (HPLC) was used for product analysis. The conversion of triglycerides to FAME can be calculated by using the following eq.1,

$$\text{Conversion (\%)} = \frac{\text{Weight of FAME}}{\text{Weight of oil}} \quad (1)$$



Microwave



Three-neck glass flask



Vacuum Filtration for separation of catalyst from the product.

Figure 2 Reaction setup.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis (TGA)

This analysis was done to determine the suitable carbonization temperature for sugarcane bagasse before sulfonation. Temperature vs weight (%) and temperature vs derivative weight (%/°C) graph shows that the degradation of biomass during different temperature ranges. TGA can be divided into three zones. 1st zone is divided into two sections; (a) 30-100°C, in this section removal of moisture takes place. (b) 100-200°C, in this section removal of bound moisture and evaporation of volatile matter occurs. In 2nd zone devolatilization and maximum mass loss takes place. This zone is further divided into two sections; (a) 200-335°C, 53% mass loss occurs due to the degradation of Hemicellulose and cellulose. (b) 335-450°C, 26% mass loss occurs due to the degradation of cellulose. This is active pyrolysis zone. 3rd zone ranges between 450-800°C and very less mass loss takes place in this zone because of the degradation of lignin. At a temperature of 500°C degradation process is almost completed [10].

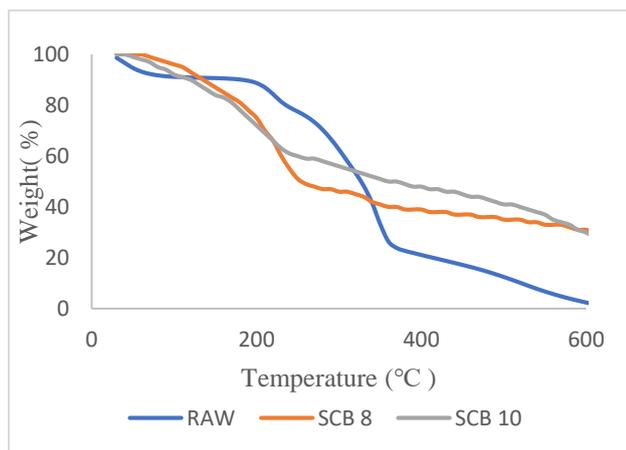


Figure 3 TGA analysis of Raw sugarcane bagasse and activated sugarcane bagasse at 150°C for 8 & 10h respectively.

3.2 Scanning Electron Microscope (SEM)

From the SEM image, the prepared catalyst appeared as flakes. This is an agreement with the low surface area and pore size for the catalyst. Particles of the catalyst are porous with micron-size. The rise in sulfonation time is not significantly affecting the morphology of the sugarcane bagasse. The particles retain some original shape after carbonization and sulfonation because of high content of lignocellulose [11].

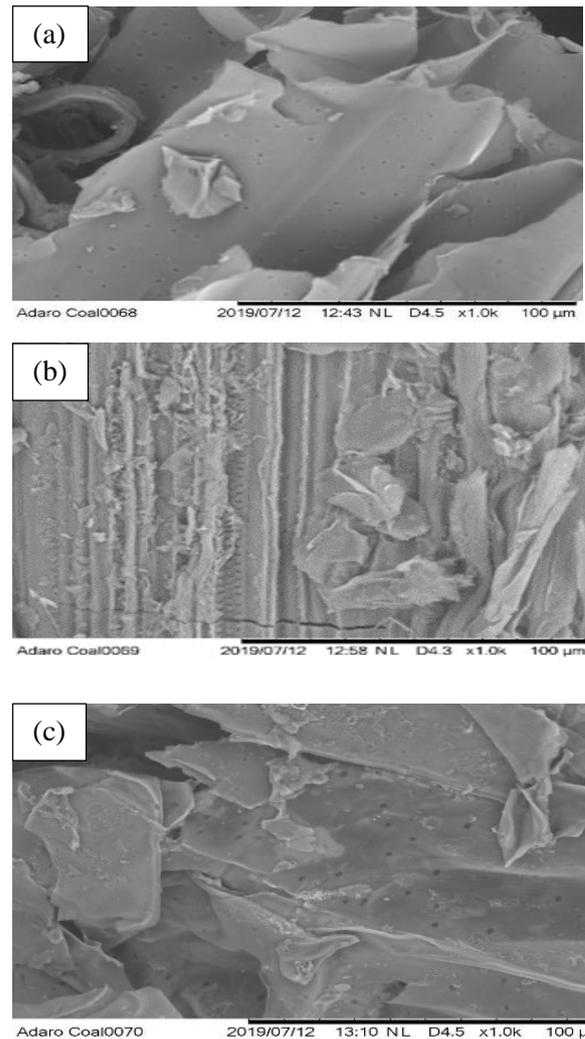


Figure 4 SEM Images of (a) Raw Bagasse (b) Activated at 150°C at 8h (c) 150°C at 10h.

3.3 FTIR Analysis of the Catalyst

Absorption band for sugarcane bagasse catalyst at 3300cm⁻¹ shows the stretching in O-H and C-H in cellulose, hemicellulose, and lignin, respectively. Broad band is due the small amount of water. While this peak is invisible in the spectrums of SCB catalysts sulfonated for 8h & 10h. The intensity of the peak decreases while the time of sulfonation increases. It proves that sulfonation took place successfully in all catalysts. 2800cm⁻¹ is the C-H stretching. Diene stretch at 1000-900cm⁻¹ region. C-Cl stretch vibration in 600-700cm⁻¹ region. S-O were recorded at 1050cm⁻¹, 1200cm⁻¹ in SCB catalysts. [12].

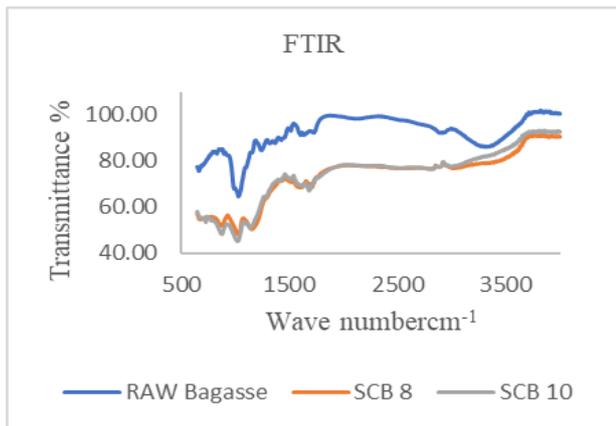


Figure 5 FT-IR spectra of raw sugarcane bagasse and activated bagasse derived catalyst for 8h and 10h at 150 °C.

3.4 Product Analysis by HPLC

The conversion of waste cooking oil (triglyceride) into fatty acid methyl acid (FAME) was calculated by HPLC. The mobile phase of HPLC was prepared by mixing 97:3 of n-Heptane and 2-propanol (300ml solution). After that the system was stabilized at 4.2MPa. Two samples were made by adding 20µL of waste cooking oil and 20µL of product into 200µL 2-propanol before injecting into the iso-propanol solution [13]. The peak in the graph (a) for WCO is showing triglycerides at a retention of 5.5-12 minutes. Whereas the peak in the graph (b) for biodiesel is showing the fatty acid methyl esters which normally lies during a retention time of 3-5 minutes. The comparison of graphs is showing the conversion of triglycerides to FAME, which was found to be 82%.

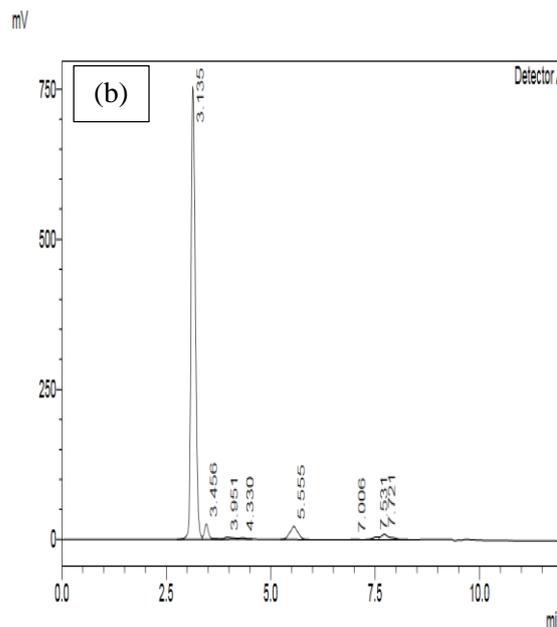
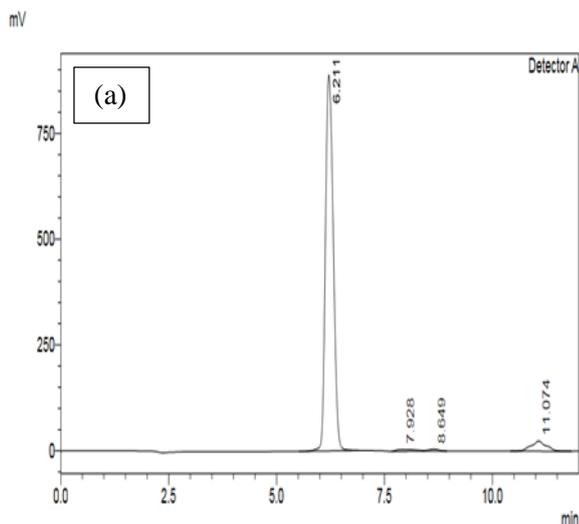


Figure 6 HPLC analysis of the FAME.

4. CONCLUSION

In this study, the effect of acid based solid heterogeneous sugarcane bagasse catalyst on the transesterification of waste cooking oil to produce biodiesel was investigated. Catalysts were prepared by varying sulfonation time to increase the sulfonic acid density and the effect of different reaction parameters e.g. reaction time, methanol to oil molar ratio, catalyst loading, reaction temperature will be studied thoroughly. The catalyst having sulfonation time 8h gave the best yield of biodiesel. The yield of biodiesel is highly dependent on the volume of methanol used as it shifts the reaction towards the right by decreasing the rate of reversible reaction. HPLC analysis showed that the triglycerides were converted to FAME in the presence of sugarcane bagasse derived heterogeneous solid acid catalyst. The purpose of these preliminary results was to check either the prepared catalyst was working. The further optimization will be made further by changing different reaction parameters and their effect on fatty acid conversion and on the yield will be studied thoroughly.

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REFERENCES

1. Ezebor, F., et al., *Esterification of oily-FFA and transesterification of high FFA waste oils using novel palm trunk and bagasse-derived catalysts*. *Energy conversion and management*, 2014. **88**: p. 1143-1150.
2. Yoon, H.-S., et al., *A comparison of energy consumption in bulk forming, subtractive, and additive processes: Review and case study*. *International Journal of Precision Engineering and Manufacturing-Green Technology*, 2014. **1**(3): p. 261-279.
3. Boey, P.-L., G.P. Maniam, and S.A. Hamid, *Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: a review*. *Chemical Engineering Journal*, 2011. **168**(1): p. 15-22.
4. Bolonio, D., et al., *Fatty acid ethyl esters (FAEEs) obtained from grapeseed oil: A fully renewable biofuel*. *Renewable Energy*, 2019. **132**: p. 278-283.
5. Yunpu, W., et al., *Review of microwave-assisted lignin conversion for renewable fuels and chemicals*. *Journal of Analytical and Applied Pyrolysis*, 2016. **119**: p. 104-113.
6. Vargas, E.M., et al., *Solid catalysts obtained from wastes for FAME production using mixtures of refined palm oil and waste cooking oils*. *Renewable energy*, 2019. **136**: p. 873-883.
7. Thushari, P. and S. Babel, *Biodiesel production from waste palm oil using palm empty fruit bunch-derived novel carbon acid catalyst*. *Journal of Energy Resources Technology*, 2018. **140**(3).
8. Bezerra, T.L. and A.J. Ragauskas, *A review of sugarcane bagasse for second-generation bioethanol and biopower production*. *Biofuels, Bioproducts and Biorefining*, 2016. **10**(5): p. 634-647.
9. Hameed, B.H., L. Lai, and L. Chin, *Production of biodiesel from palm oil (*Elaeis guineensis*) using heterogeneous catalyst: an optimized process*. *Fuel Processing Technology*, 2009. **90**(4): p. 606-610.
10. Varma AK, M.P., *Physicochemical characterization and pyrolysis kinetic study of sugarcane bagasse using thermogravimetric analysis*. *Journal of Energy Resources Technology*. . 2016 Sep: p. 1;138(5).
11. Qiu, Q., et al., *A comparative investigation on direct carbon solid oxide fuel cells operated with fuels of biochar derived from wheat straw, corncob, and bagasse*. *Biomass and bioenergy*, 2019. **121**: p. 56-63.
12. Farabi MA, I.M., Rashid U, Taufiq-Yap YH., *Esterification of palm fatty acid distillate using sulfonated carbon-based catalyst derived from palm kernel shell and bamboo*. *Energy conversion and management*. . 2019 Feb: p. 1;181:562-70.
13. RE., P., *A review of chromatographic characterization techniques for biodiesel and biodiesel blends*. *Journal of chromatographic science*. . 2011 May: p. 1;49(5):384-96.