

Study of Esterification of Waste Cooking Oil using Solid Acid Catalyst Derived from Coconut Coir

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ABSTRACT

To deal with the issues of energy security, climate changes, and environmental protection, the use of biodiesel as an alternative fuel is recognized worldwide. All these activities are leading to potential setbacks such as deforestation and escalating food prices. The use of waste cooking oil (WCO) as a feedstock and biochar based solid acid catalyst prepared from agricultural waste biomass can be the key solutions to above-mentioned setbacks. A carbon-based solid acid catalyst has been prepared by sulfonation of biochar derived from pyrolysis of coconut coir. The catalyst is characterized using FTIR, SEM, elemental analysis and total acid density analysis. The performance of prepared catalyst has been tested over esterification of FFA present in the waste cooking oil. The effects of alcohol to oil (A:O) molar ratio, reaction time and catalyst loading over the yield of esterification reaction catalyzed by the sulfonated biochar have been investigated. The results obtained conclude that Free Fatty Acid (FFA) conversion increases with the increase of A:O molar ratio, reaction time and catalyst loading. The optimal reaction conditions are A:O molar ratio 18:1, catalyst loading 5% (wt% of WCO) reaction temperature 65°C and reaction time 7 hrs for FFA conversion of 84.92%.

Keywords-- Biodiesel, catalyst, coconut coir, waste cooking oil

I. INTRODUCTION

The importance of renewable energy is well known to the world. Biodiesel is biofuel derived from renewable sources such as edible oil, non-edible oil, waste cooking oil and algae oils etc. using different catalytic and non-catalytic processes. Various processes have been developed for biodiesel productions which are classified as catalytic such as chemical or enzyme catalysis and non-catalytic such as supercritical alcohol treatment [1]. Biodiesel produced by esterification of FFA and transesterification of triglycerides with methanol has

become more attractive recently because it is renewable and environmentally friendly. Catalytic biodiesel production can be done by both esterification and transesterification process and further classified as shown in figure 1. The use of heterogeneous catalysts is reported to be the most economically viable process[2]. Therefore, developing a promising bi-functional solid acid catalyst for simultaneous transesterification of triglycerides and esterification of FFAs from WCOs feedstock is a crucial step in the commercialization of biodiesel production.

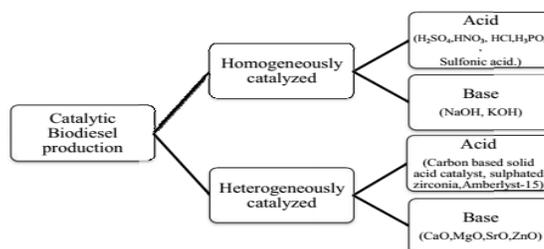


Fig.1 Catalytic biodiesel production

Also, the carbon-based solid acid catalyst derived from biomass waste with strong functionalization group such as SO₃ found useful in various studies. Since the discovery of sugar catalyst [3], also known as sulfonated carbon catalyst [4], the progress of carbon-based catalyst development has increased rapidly especially for biodiesel production. An acid sugar catalyst is prepared by incomplete carbonization of sugar, followed by sulfonation. The activity of the catalyst used in esterification of an oleic acid such as sulfuric acid is comparably provided by carbonized sugar catalyst [5] and it is found more active than sulfated zirconia and Amberlyst-15 in the transesterification of waste vegetable oil [6]. The biomass-derived carbon-based solid acid catalysts are gaining much attention as of its low cost and easy availability.

II. METHODOLOGY

Catalyst preparation

A biomass carbon-based solid acid catalysts were prepared by direct carbonization followed by sulfonation from coconut coir. The coconut coir biomass waste material was washed with distilled water to remove dust particles and then kept for drying at 100°C for overnight. The dried samples are ground in the grinder to make the fine particles and then passed through the 250µm screen, the undersize material is collected, and stored in the dry atmosphere. A defined amount of grounded coconut coir was weighed in the silica crucible and then carbonized in the muffle furnace at 60°C for 3 Hrs. The crucibles are removed after 3 hrs and the amount of obtained biochar weighed.

Biochar samples prepared from coconut coir were directly sulfonated without activation according to the method of Toda et.al [7]. 200 ml of concentrated H₂SO₄ (98%) was added to 20g of biochar in round bottom flask. The mixture was heated for 24hrs [8] After heating the mixture was cooled and filtered. The biochar catalyst is then washed with hot distilled water about 7-8 times until the wash water pH becomes neutral to ensure that catalyst is free from sulfate ions. After filtration, the biochar catalyst is oven dried at 70°C till the removal of moisture. The biochar obtained is stored for characterization.

Catalyst characterization

The prepared catalyst is further characterized using SEM, FTIR and Elemental analysis to study its mesoporous structure. The total acid density of direct sulfonated catalysts samples was determined using the standard acid-base back titration method [7]. For the esterification of WCO total acid density of catalyst was found more crucial in various studies.

Esterification of waste cooking oil.

Biodiesel was produced from WCO by esterification with methanol as alcohol reagent and biochar based sulfonated catalyst in 500 ml three-necked flat bottom flask equipped with magnetic stirrer heater and reflux condenser. The experimental setup is shown in Figure 2. For a typical run initially 100 g WCO is heated to 110°C for 30 min to remove moisture thoroughly and then cooled down to reaction temperature. The pre-dried sulfonated catalyst of defined amount of 1 % w/w basic of WCO is mixed and stirred for 15 min. The quantity of methanol was used with the specific molar ratio of 10:1 of alcohol to WCO. The pre-heated WCO is then slowly added to the mixture of methanol and catalyst. The reaction temperature of 65°C and stirring rpm is set to constant value using magnetic stirrer and heater. The reaction mixture samples were collected in regular interval of 1 hr. to check its acid value in order to find out esterification conversion and reaction is held up for 8 hrs. The reaction product slurry is then cooled to room

temperature. The reaction products and catalyst was separated using vacuum filtration method. The conversion of FFA was determined by acid value calculations.

$$\text{FFA conversion} = \left(1 - \frac{\text{final A.V.}}{\text{initial A.V.}}\right) \times 100$$



Fig 2. Esterification of WCO

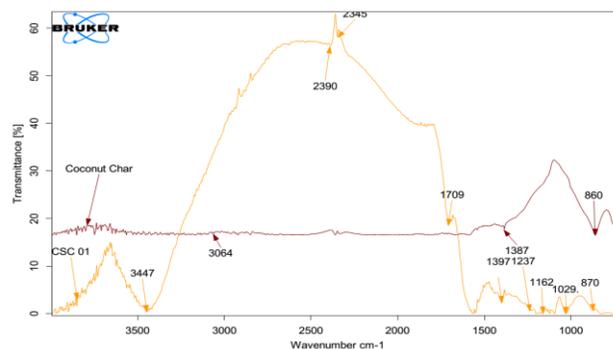


Fig 3. FTIR spectral of catalyst prepared

Catalytic Esterification Performance of the Catalysts

The yield of biodiesel is measured in terms of FFA conversion of WCO. The performance of the catalyst in esterification of WCO was studied for various parameters and the operating conditions of the experimental runs as summarized in Table 1.

Table 1. Selection of parameters for the esterification of WCO

Parameters	Studied values
Methanol to oil molar ratio	10:1, 13:1, 15:1, 18:1, 20:1
Catalyst concentration	1%, 2%, 3%, 4%, 5%
Temperature (°C)	50, 55, 60, 65

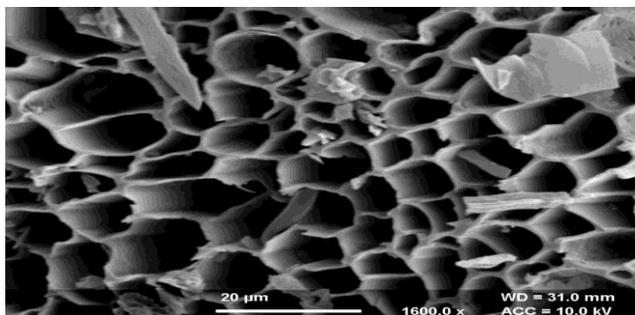


Fig 4. SEM image of sulfonated catalyst

III. RESULTS AND DISCUSSION

Catalyst characterization

According to the literature, the higher intra-particle diffusion of reactants caused due to increasing the surface area and pore structure of the catalyst is responsible for higher esterification and transesterification yield [9,10]. However, it has also been reported that the effect of total acid density and sulfonic group density is more than surface area on the activity of carbon-based (Biochar) catalysts for biodiesel production [4]. The acid density of carbonized and sulfonated biochar catalyst was found to be 3.2 mmol/g. The FTIR spectra of (-SO₃H) group bearing catalyst are shown in Figure 3. The peaks at 1029 and 870 cm⁻¹ are due to -SO₃H present in the catalyst, also the characteristic peaks at 1029 and 1162 are corresponding to the symmetrical and asymmetrical stretching mode of (-SO₂) [11,12]. These peaks are not present in the catalyst before functionalization of the catalyst using H₂SO₄ (sulfonation) which indicates the strong acidity in the catalyst. The broad peaks at >3400cm⁻¹ is attributed to phenolic (-OH) stretching vibration group particularly at 3447 cm⁻¹ [8,11] The (-COOH) aromatic acidic group can be seen at 1709cm⁻¹ [12] The overall FT-IR spectra suggested and confirmed that the solid acid derived from coconut coir biomass by direct sulfonation method consisted of aromatic carbon sheets containing sulfonic, carboxylic and phenolic acidic groups.

Elemental analysis is important in order to measure the sulfonic group density as well as the total acid density of catalyst. The percentage of carbon present in the catalyst is of importance. The sulfonic group plays an important role in esterification of WCO. The elemental analysis of sulfonated catalyst is listed in Table 2

Table 2. Elemental analysis of Catalyst Prepared

Elements	Composition (%)
Carbon	61.098
Nitrogen	0.585
Hydrogen	1.684
Sulfur	2.82

The mesoporous structure of catalyst is studied using SEM analysis and discrete pores are visible over catalyst surface as shown in Figure 4. Larger pore areas are indicative of the fact that surface area of the catalysts has increased by thermal and chemical treatments. In other words, this will make the catalyst more effective.

Effect of alcohol to oil molar ratio

The graph (Figure 5a) indicates that the FFA conversion is significantly increasing with increase in A:O molar ratio from 10: 1 to 18:1 and reaction time up to 7 hours while for molar ratio 20: 1 and reaction time of 8 hours having a minute change in FFA conversion. when an excess of methanol is used which forced the reaction to shift towards the product side. For molar ratio 20:1 the surface might be saturated with FFA and excess of methanol. Hence A:O ratio of 18:1 proves to be optimum with FFA yield of 84.82%.

Effect of amount of catalyst.

The FFA conversion is significantly increasing with increase in catalyst amount (1% to 5% of WCO) and reaction time up to 7 hours which explains that increase in catalyst amount increases a total number of available active sites which improves the reaction rate to reach equilibrium. Hence catalyst loading of 5% of WCO gives the yield of FFA as 84.82%.

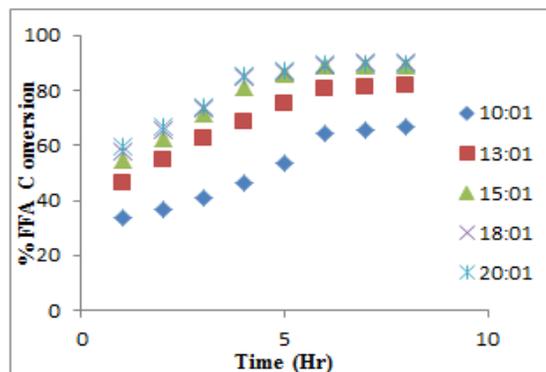


Fig 5. (a) Effect of Alcohol to oil molar ratio

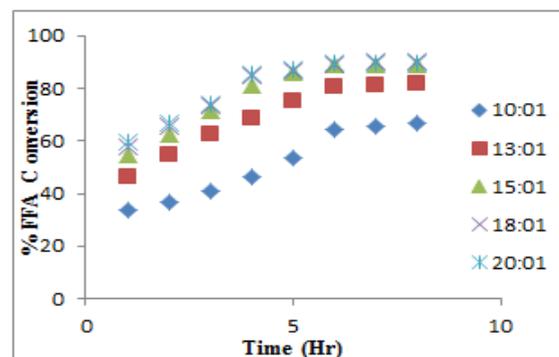


Fig 5. (b) Effect of Amount of Catalyst

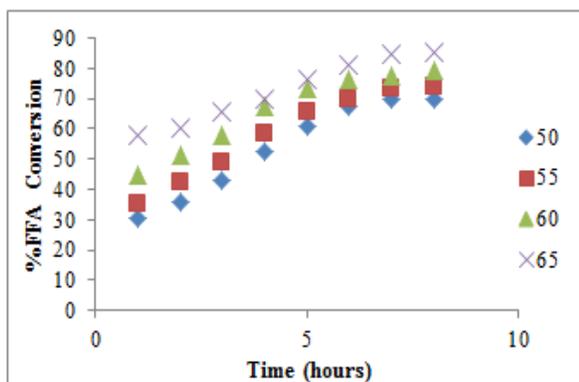


Fig 5. (c) Effect of temperature on FFA conversion

Effect of temperature

Temperature influences the rate of reaction and product yield. For biodiesel higher temperature increases reaction rates decreases the viscosity of the oil and reduces the reaction time However reaction temperature was kept up to the boiling point of methanol because the higher temperature can cause the lost of methanol due to vaporization. It is observed from Figure 5(c) that FFA yield of 84.82% is obtained at 7 hours and remains constant till 10 hours. The temperature at which it is obtained is 65°C

IV. CONCLUSION

Characterization of catalyst was done by FTIR, SEM and Elemental analysis and proved that the prepared catalyst was quite appropriate to be used for esterification of WCO. It is verified that optimal reaction conditions for high FFA conversion of 84.82% were A: O molar ratio of 18:1, catalyst loading of 5% and the reaction temperature of 65 °C for 7 hr reaction time.

V. ACKNOWLEDGEMENT

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REFERENCES

[1] Olivera S. Stamenkovic, Vlada B. Veljkovic Ivana B.Bankovic-Ilic, "Biodiesel production from non-edible plant oils," Renewable and Sustainable Energy Reviews, 16:3621–3647, 2012.
 [2] A.H.West, "Process simulation and catalyst development for biodiesel," University of British Columbia, Doctoral Dissertation 2006.

[3] M.Takagaki, A., Okamura, M., Kondo, J.N., Hayashi, S., Domen, K. and Hara, Toda, "Green Chemistry: biodiesel made with sugar catalyst.," Nature, 438:178, 2005.
 [4] X. López, D.E., Suwannakarn, K., Liu, Y., Lotero, E., Goodwin, J.G. and Lu, C. Mo, "Activation and deactivation characteristics of sulfonated carbon," Journal of Catalysis, 254(2): 332-338, 2008.
 [5] K. Hara, M. and Hayashi, S Nakajima, "Environmentally Benign Production of Chemicals and Energy Using a Carbon-Based Strong Solid Acid," Journal of the American Ceramic Society., 90(12):. 3725-3734, 2007.
 [6] M.H. Duan, Z.Q., Lou, W.Y., Smith, T.J. and Wu, H. Zong, "Preparation of a sugar catalyst and its use for highly efficient production of biodiesel.," Green Chemistry, 9 (5):434-437., 2007.
 [7] Toda, M. Takagaki, A., Okamura, M., Kondo, J.N., Hayashi, S., Dorman, K. and Hara, M.2005. Green Chemistry: biodiesel made with sugar catalyst, Nature. 438(7065):178
 [8] A. M. Dehkhoda, "Developing Biochar-Based Catalyst for Biodiesel production," University of British Columbia., Thesis 2010.
 [9] G.J. Dasari, M.A., Doskocil, E.J., Mandy, P.J. and Goff, M.J. Suppes, "Transesterification of soybean oil with zeolite and metal catalysts," Applied Catalysis A: General, 257:213-223, 2004.
 [10] G. R. Kulkarni MG, "Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification.," Green Chemistry, 8, pp. 1056-62, 2006.
 [11] B.V.S.K. Mouli, K.C., Rambabu, N., Dalai, A.K. and Prasad, R.B.N Rao, "Carbon-based solid acid catalyst from de-oiled canola meal for biodiesel production," Catalysis Communications, 14:20-26, 2011.
 [12] Lee D. "Preparation of a sulfonated carbonaceous material from lignosulfonate and its usefulness as an esterification catalyst," Molecules,18: 8168-8180., 2013.