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Sulfonated Organic Carbon Waste From Organic Waste As Solid Acid Catalyst For PFAD Esterification: A Brief Review

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Abstract— Evidently, sulfonated carbon catalyst has strong catalytic activity for oil esterification with high FFA content. The catalyst has been synthesized through two step reactions, i.e. carbonization and sulfonation processes. Plantation organic waste such as palm kernel shell and bagasse were reported as carbon source for the synthesis of solid acid catalyst based on sulfonated carbon, the waste was used as carbon source due to its cellulose and lignocellulose. FTIR characterization was applied to examine the acid sites on the catalyst surface, while XRD analysis used to investigate the crystalinity structure. Murumuru core skin was reported as sulfonated carbon catalyst in PFAD estrification with 97.2% FFA conversion, while characterization analysis showed the highest acid sites obtained at optimum operation condition with 5 wt% catalyst loading, molar ratio of 10 : 1 (metanol : PFAD) at 90 ^{o}C and 1.5h.

Keywords – Biodiesel; Solid Acid Catalyst; Sulfonated Carbon; FTIR; TGA; XRD

I. INTRODUCTION

Currently, the field of catalyst takes great interest that has being developed by many scientists in relation to its benefit in order to elevate reaction rate without undergone reaction. Heterogeneous catalyst is the interested catalyst type to be developed. Heterogeneous catalyst is a catalyst type that its catalyst phase different from reactant and product phases. This condition is different from homogeneous catalyst that all the reactant, product, and catalyst possess same phases [1].

A specific heterogeneous catalyst is an inorganic solid such as metals, oxides, sulphides, zeolite, and metal salts (CaCO3, Amberlyst-15, CaO-Al2O3, CaO, MgO), however, an organic material can also be used as catalyst such as sulfonated carbon, ion exchanger, and enzymes. The heterogeneous catalyst plays important role due to its benefits such as high product, moderate cost of material, high reaction rate, recycling, FFA conversion to yield biodiesel, and can be used for further process. The catalytic activity performance of heterogeneous catalyst can be verified from many benefits in industrial applications such as gas synthesis product through hydrogenation, dehydrogenation reaction, catalytic oxidation, and many organic compounds. The production of 90% chemicals applied solid catalysts. Due to its high benefits, the heterogeneous catalyst is fascinated to be largely studied in biomass conversion within recent years [2].

The synthesis of heterogeneous catalyst from organic waste has become more popular in the last two decades. The characterisation of waste source may influence the catalyst properties. Therefore, the catalyst for certain application is often made from similar material. Besides it can yield very active catalyst, selective, and stable, the selection of waste must be simple and safe in the process of collection, and the usage for catalyst synthesis purpose may not generate ecological problems [3]. Each cost of collecting or handling should be well calculated in the cost related to catalyst production, and not diminish the advantage of side waste product. The consumption of waste material will be very worthy if the cost for funding or environment is related to its waste disposal since this can reduce and be replaced for the cost of catalyst production.

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The sulfonated carbon catalyst is a catalyst made through sulfonation process to substitute sulfonate group (-SO3H) on the surface of organic material, which is incompletely carbonized [4]. The carbonization process is also known as pyrolysis that this process can be defined as a step where organic precursor can be converted to material carbon based. The carbonization is usually a slow process. The duration time is varied related to composition of final product, type of precursor, material thickness, and other factors [5].

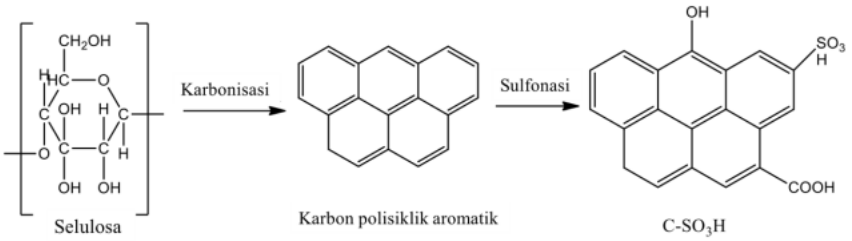

Fig. 1. Carbonization and sulfonation reactions [6].

This paper reviews reports on products of synthesis and applications of solid acid catalyst sulfonated carbon based from literatures corresponding with varied conditions of carbonization and sulfonation processes, and esterification reaction of PFAD.

II. Discussion

Biodiesel with its chemical name called Fatty Acid Methyl Ester (FAME) is defined as fuel material consisted of monoalkyl ester from long chain fatty acid coming from renewable lipid raw material such as vegetable oil or animal lard used for compression-ignition in diesel engine [7]. Biodiesel is a renewable energy, which is friendly environmental, biodegradable, and low green-house emission compared to conventional solar [8].

Esterification and transesterification are methods usually applied for conversion of oil and lipid to form biodiesel. The esterification and transesterification reaction process are usually catalysed by homogeneous or heterogeneous catalysts [9]. The transesterification reaction can be conducted when the FFA content in oil raw material lower than 4%. Alternatively, esterification reaction can be carried out by acid catalyst addition to convert FFA (>4%) to yield FAME [10].

The Palm Fatty Acid Distillate (PFAD) is a raw material used to produce biodiesel because the raw material is abundantly found and easily obtained with relatively low cost. The PFAD is consisted of high content free fatty acid (FFA) (85%) and almost 10 wt % triglycerides, and little amount squalene, sterol, and vitamin E as compared to digested palm oil containing almost 100 wt % triglycerides [11].

Biodiesel production with heterogeneous base catalysts from oils containing high free fatty acids (FFA) is associated with saponification problems [12]. On the other hand, heterogeneous acid catalysts are preferred in biodiesel synthesis because of their ease of separation, catalyst reusability, ease of handling, non-toxicity, non-corrosive properties and suitability for use in both esterification and transesterification reactions even in the case of oils having high FFA. Extensive literature is available on the use of heterogeneous acid catalysts for biodiesel production such as zeolites, zirconia sulfate, supported heteropoly acids, sulfonated carbon [13], metal oxides [14], etc. Recently, sulfonated activated carbon-based solid acid catalyst was reported as a promising catalyst for biodiesel production [3].

Five types of heterogeneous catalysts synthesized from organic waste applied for oil esterification using varied synthesis methods and esterification conditions are presented in Table 1.

TABLE I. SOLID ACID CATALYST BASED ON SULFONATED CARBON FROM ORGANIC WASTE

Carbon Source	Feedstock	Esterification Condition				% Yeild	Carbonization method	Sulfonation	Reference
		Rasio Molar Alcohol : Oil	*Catalyst Loading*	*Temperature*	*Time*				
Palm kernel shell catalyst sulfonated carbon base.	Palm Fatty Acid Distillate (PFAD)	15:1	4 wt%	65°C	1 h	95%	Pirolisis with Nitrogen Flow	Chloro Sulfonic Acid p.a	[15]
Bamboo	Oleic Acid	7:1	12 wt%	85°C	180 min	96%	Pirolisis with Nitrogen Flow	Sulfanilic Acid p.a	[16]
Waste Orange Peel	corn acid oil	-	-	65°C	-	91.68 %	hydrothermal condition	Sulfuric Acid 98%	[17]
Corn Cobs	Soybean Oil	6:1	20 wt%	75°C	20 min	88,7 %	Pirolisis with Nitrogen Flow	Sulfanilic Acid p.a	[18]
Murumuru core skin	*Palm Fatty Acid Distillate* (PFAD)	10 : 1	5%	90 C	1.5 h	97.2 %	Carbonized with Nitrogen Flow	Sulfuric Acid 98%	[19]

In order to verify the substitution of sulfonate group on carbon surface several characterizations are needed as follows:

2.1. FTIR

TABLE II. FTIR ANALYSIS OF SOLID ACID CATALYST BASED ON SULFONATED CARBON FROM ORGANIC WASTE

Carbon Source	*Puncak FTIR Wave Number (cm^{-1})*	Gugus Fungsi	Reference
Palm kernel shell catalyst	1190 cm-1 and 1030 cm-	stretching of symmetrical and asymmetrical	[15]

Carbon Source	*Puncak FTIR Wave Number (cm^{-1})*	Gugus Fungsi	Reference
sulfonated carbon base.		-SO2	
Bamboo	1089 cm^{-1} and 1116 cm^{-1}	stretching of symmetrical and asymmetrical -SO2	[16]
Waste Orange Peel	1163 cm−1	-SO2 group -SO3H	[17]
Corn Cobs	1125 and 1175 cm^{-1}	O=S=O	[18]
Murumuru core skin	1032 cm^{-1}	Stretching	[19]

The FTIR analysis was carried out to examine the functional groups in the catalyst [20]. The FTIR spectra shows the weak band is attributed to Bronsted acid sites that display important role in esterification process, which is indirectly enhancing catalytic activity of the catalyst [15]. In addition, a strong transmittance band was observed around 1300 cm^{-1} and 1000 cm^{-1} for respective sulfonated catalyst attributed to stretching of symmetrical and asymmetrical -SO2 that verified the existence of -SO3H katalis [21]. The stepwise removal of C-O-C in sulfonated catalyst is caused by carbonization process that shows molecular structure of cellulose, hemicellulose and lignin in untreated catalyst undergone dehydration yielding bond rupture [19].

2.2. XRD

TABLE III. XRD ANALYSIS OF SOLID ACID CATALYST BASED ON SULFONATED CARBON FROM ORGANIC WASTE

Carbon Source	*XRD Pattern*	Band	Reference
Palm kernel shell catalyst sulfonated carbon base.	2θ = 10°–30° 2θ = 40°–50°	Broad (Amorf)	[15]
Bamboo	2θ = 10°–30° (002) 2θ = 40°–50° (101)	Broad	[16]
Waste Orange Peel	52.38°, 53.70°, 55.80°	quartz nature	[17]
Corn Cobs	2θ = 10°–30°	Broad	[18]

Carbon Source	*XRD Pattern*	Band	Reference
	2θ = 40°–50°		
Murumuru core skin	2θ = 15°–30° (002) 2θ = 40°–50° (101) graphite	Broad	[19]

Table. 2 shows the XRD patterns of the prepared catalyst, either before or after sulfonation that present one broad band and one weak band at 2θ = 10°–30° and 2θ = 40°–50° corresponding with C (0 0 2) and C (1 0 1), respectively [15] [16] [17] [18] [19]. The broad band around 2θ = 10°–30° is attributed to characterized amorphous carbon containing aromatic carbon layer. In the meanwhile, a sharp band of untreated carbon catalyst is established for three dimensional structure of graphite. Carbonization process at high temperature combined with sulfonation process with strong acid yields bond cleavage of C-O-C at precursor carbon. This process yields more rigid and more amorphous sulfonated carbon due to increased disorder of carbon layer. The structural transformation of sulfonated carbon catalyst probably displays important thing in catalyst activation during esterification [15].

2.3. TGA

TABLE IV. TGA ANALYSIS OF SOLID ACID CATALYST BASED ON SULFONATED CARBON FROM ORGANIC WASTE

Carbon Source	*dehydration*	Devolatization	Completly the decomposed	Reference
Palm kernel shell catalyst sulfonated carbon base.	25-200 °C	400-800 °C	>800 °C	[15]
Bamboo	-	-	-	[16]
Waste Orange Peel	100 °C	190 °C to 700 °C	900 °C	[17]
Corn Cobs	25-100	350-600	>600	[18]
Murumuru core skin	100 °C	168-307 dan 330-390 °C	>400 °C	[19]

TGA was applied to determine thermal stability of the catalyst that showed significant main weight removal for respective catalysts from 400 to 800°C corresponding with stepwise decomposition of cellulose component (O-H, C-O and C-C bonding in carbon structure) in the catalyst [22]. The percentage of weight removal is different for each catalyst that the sulfonated catalyst showed higher percentage of weight removal compared to that one of without sulfonated catalyst. This finding is probably caused by formation of -COOH and -OH molecules during sulfonation process [19]

Due to the adsorbed moisture on catalyst, initial weight loss of water was occurred up to 100 °C temperature. Second weight loss is observed between the temperature range 160 °C to 800 °C which may be due to the decomposition of -SO3H, -COOH groups and the small amount of carbon support. The total weight loss occurred up to 900 °C and the rest exist as graphene-like carbon bodies [18].

III. CONCLUSION

This article has studied two kinds of organic waste to be beneficiated as carbon source for the synthesis of sulfonated solid acid catalyst carbon base. Several literatures applied the same method for catalyst synthesis, i.e. pyrolysis method with nitrogen

gas flow to yield incomplete carbon from raw material. This paper has also explored five kinds of carbon sources. Applying several different esterification reaction conditions yielded different percentage of conversion. The higher percentage of conversion was found for the catalyst from Murumuru core skin, i.e. 97.2% at optimum operation condition with 5 wt % catalyst loading, molar ratio of 10:1 (methanol : PFAD) at 90^{o}C and 1.5h.

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