

Corncob residue as heterogeneous acid catalyst for green synthesis of biodiesel: A short review

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Abstract

The utilization of an appropriate catalyst in biodiesel production depends on the free fatty acid content of vegetable oil as a feedstock. Recently, heterogeneous acid catalysts are widely chosen for biodiesel production. However, these catalysts are non-renewable, highly expensive and low stability. Due to the aforementioned drawbacks of commercial heterogeneous acid catalyst, a number of efforts have been made to develop renewable green solid acid catalysts derived from biomass. Published literature revealed that the application of the biomass derived solid acid catalysts can achieve up to 98% yield of biodiesel. This article focused on corncob as raw material in solid acid catalyst preparation for biodiesel production. The efficient preparation method and performance comparison are discussed here. The corncob derived heterogeneous acid catalysts provides an environmentally friendly and green synthesis for biodiesel production.

Keywords: Biodiesel; heterogeneous acid catalysts; green synthesis; biomass; corncob

1. Introduction

The depletion and drawbacks of fossil fuel have shifted the world attention to renewable energy sources [1–3]. It leads biofuel such as biodiesel and bioethanol have become more attractive as an alternative green fuel [4–7]. Biodiesel is a substitute for petroleum-based diesel fuel and it offers several advantages including clean emission, non-toxicity, and biodegradability [8–9]. Moreover, biodiesel possesses higher flashpoint, higher cetane number [10–11], and zero-composition of sulfur provides better lubricity compared to diesel fuel [12].

Biodiesel, generally known as fatty acid methyl ester (FAME), is derived by the transesterification or esterification of vegetable oil and fat with short chain alcohol in the presence of a catalyst (figure 1) [13–15]. Commonly, transesterification/esterification is carried out by using homogeneous catalysts such as NaOH, KOH and H₂SO₄ [16–17], each of which has advantages and disadvantages. A homogeneous base catalyst offers high catalytic activities, a faster reaction rate, and a lower temperature reaction [18–19]. However, the reaction using a homogeneous base catalyst is very sensitive to the existence of free fatty acid (FFA) and water in the reaction system [20–21]. Furthermore, that kind of reaction induces soap formation and deters the purification process [20–22–23]. Meanwhile, a homogeneous acid catalyst is capable of processing the reaction that uses feedstock

containing high FFA without soap formation. Here, the very slow reaction rate and high corrosivity of acidic condition become the major drawbacks of the homogeneous acid catalyst utilization [24–25]. The consideration of negative effect homogeneous catalyst on transesterification/esterification generates a huge interest in the heterogeneous catalyst. It provides many advantages such as simple product separation and purification, non-corrosivity and recyclability [20–26].

The number of heterogeneous basic and acid catalysts has been studied, developed and successfully utilized in both laboratory and industry. Calcium oxide, calcium methoxide and hydrotalcite are commonly used as the solid basic catalysts in transesterification [13]. They give a promising catalytic activity in transesterification reaction with the high yield of biodiesel. Unfortunately, the heterogeneous basic catalyst is only suitable for highly refined vegetable oils (FFA<1%). The stability of heterogeneous basic catalyst could be low and reduced due to water and moisture during storage and handling [4]. The heterogeneous acid catalyst is more preferred to be used in biodiesel production using low quality vegetable oil (FFA>1%). It could be esterified FFA into biodiesel efficiently [2–27–28]. Mansir et al. [21] stated that the hydrophobic surface of the solid acid catalyst prevented the by-product such as water and glycerol to deactivate the active sites of the catalyst.

Zeolite, ion exchange resin, silica-alumina, sulfonated polystyrene and hetero-polyacids are the examples of heterogeneous acid catalyst that are generally used in biodiesel production [29].

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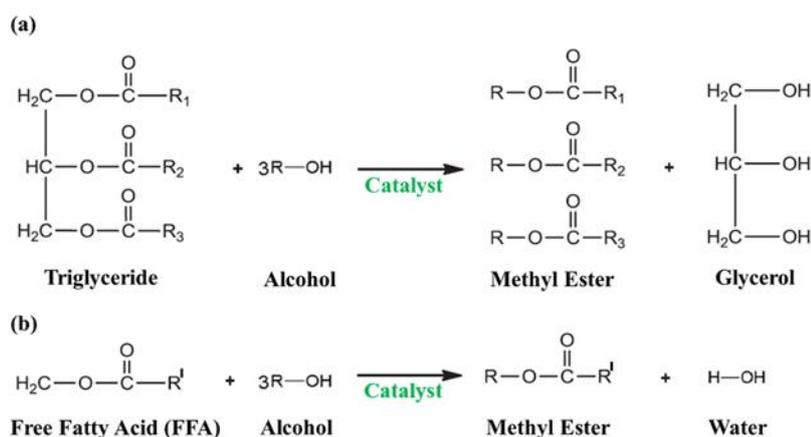


Fig. 1. (a) Transesterification reaction, and (b) esterification reaction for biodiesel production

The “green technology” principle drives the utilization of biomass as raw material for many purposes [7–30–34] including for the development of heterogeneous acid catalyst. The heterogeneous acid catalysts that are prepared from biomass offer biodegradable and environmentally friendly catalyst, and it is considered as low-cost material [35]. Comparing the conventional solid acid catalyst such as Amberlyst-15, biomass provides higher surface area than conventional solid acid catalyst such as Amberlyst-15 [36]. The agricultural crop residues one example of biomass that recently gains an attention as the low-cost raw material for heterogeneous acid catalyst preparation including sugarcane bagasse, oil palm trunk, peanut hull, sugar beet pulp, coconut shell, or corncob [35–37–39]. Based upon its chemical composition and abundant availability as agricultural residue, corncob is highly potential to be a solid acid catalyst for chemical reaction including the esterification of high-FFA vegetable oils to produce biodiesel. This study reviews the development of heterogeneous acid catalysts derived from corncob for biodiesel production. The preparation method of this catalyst here became the highlight of this study. The performance of corncob derived solid acid catalyst on biodiesel production was also compared to provide a better insight for their future development in the field of high active solid acid catalyst.

2. Current Problem of Homogeneous Catalyst for Biodiesel Production.

The most common method to produce biodiesel is by performing the transesterification reaction between vegetable oil and short chain alcohol in the presence of homogeneous base catalyst. This reaction gives a faster reaction rate and higher yield of biodiesel. Unfortunately, the alkaline-catalyzed transesterification is only suitable for high refined vegetable oil as the main raw material for biodiesel. Consequently, the low quality of raw material such as waste cooking/frying oil and non-edible vegetable oil lead to soap formation due to the high free fatty acid (FFA) and water content of those materials. The water will hydrolyze triglyceride and generate more FFA during reaction. Hence,

the saponification reaction will occur along with the transesterification to form stable emulsion or soap. It will then consume large amount energy during purification. The one method to solve the problem of low-quality raw material is by using acid-catalyzed esterification and it is typically performed before the transesterification. The utilization of homogeneous acid catalyst is able to reduce and convert FFA into alkyl ester (biodiesel) efficiently in esterification reaction. However, the homogeneous acid catalyst leads to reactor corrosion. Another challenge of homogeneous acid catalyst utilization is the huge wastewater production during the purification process [40]. Heterogeneous catalyst is a good alternative to replace the homogeneous one. The heterogeneous catalyst provides a number of superior properties such as simple separation, being non-corrosive to reaction system and being environmentally friendly.

Many types of heterogeneous catalyst have been studied. It has been found that the catalyst is able to manage and reduce the FFA content of low-quality feedstock for biodiesel production process. Amberlyst, protonated-nafion, and sulfated zirconia are the heterogeneous acid catalysts applied in biodiesel synthesis. However, those catalysts have low acid density, the small pore size, faster deactivation, and low stability.

As the implementation of green technology, it is necessary to find the biodegradable, non-toxic, environmentally friendly, and low-cost material to synthesize the heterogeneous acid catalyst. Therefore, the lignocellulosic material exhibits a high potential as raw material of heterogeneous acid catalyst. Lignocellulose is plant dry matter, which is called biomass that is reliable to be converted into porous carbon material for solid catalyst preparation. Due to the requirement of low production cost, biomass waste is getting more popular as a solid catalyst raw material. It is found abundantly as the result of human agricultural activities [41–42]. The utilization of biomass waste also provides a solution for the disposal problem of biomass waste [43–44]. The transformation of biomass waste into heterogeneous catalyst can enhance their economic value [35]. Biomass waste derived heterogeneous catalyst may differ in surface porosity and structural properties due to the different chemical composition and physical properties of biomass waste [14].

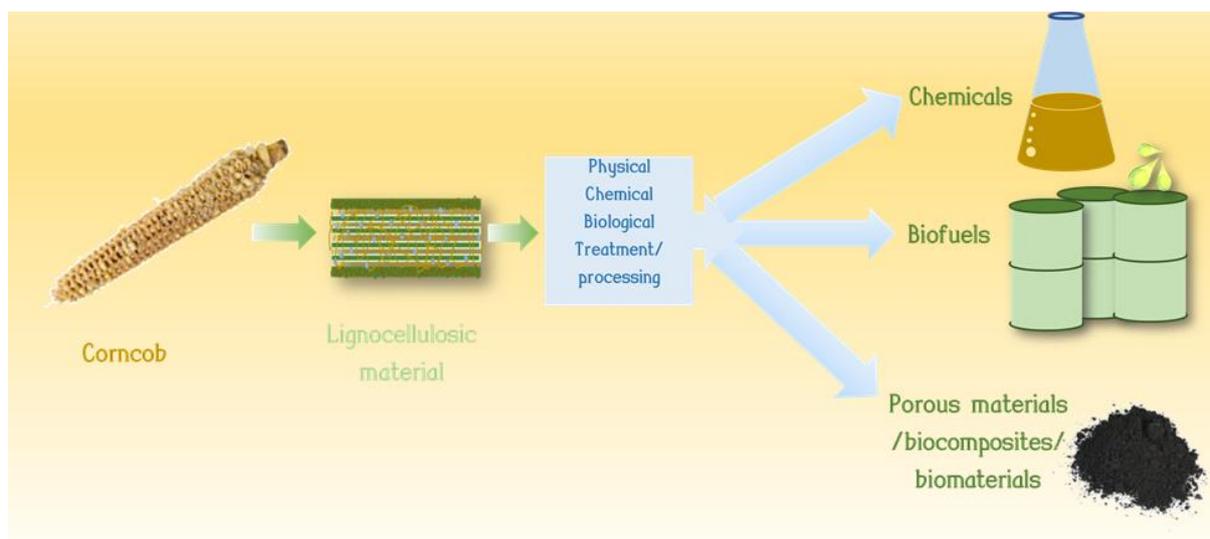


Fig. 2. Utilization of corncob residue for value-added materials

3. Corncob Residue as a Heterogeneous Acid Catalyst for Biodiesel Production.

Corn (*Zea mays L.*) is one of the largest agricultural crops in Indonesia besides rice. As reported by Ministry of Agriculture, annual corn production in Indonesia is 30 million tons per year [45]. It has been estimated that around 21% of the corn production will produce corncob as crop residue [46]. The large-scale of corncob residue as a byproduct of corn production presents new challenges and environmental issues to consider. Corncob residue is generally subjected to dump or incinerate causing air pollution. On small scale, corncob residue is used as a fuel in direct combustion for cooking, heating, and other purposes. It is necessary to find a solution to convert the corncob residue into high value-added materials by a simple green technology [47]. As an agricultural waste, corncob residue is mainly composed of lignin, cellulose, and hemicellulose. It has been found that corncob residue contains 42-45% of cellulose, 35-39% of hemicellulose and 14-15% of lignin [48]. Corncob residue is also composed of three tissue fractions: chaff, woody ring and pith [49]. Due to its chemical composition and structure, the corncob residue has an important application in biofuels, food, and chemical industries (figure 2) [50]. The requirement of low cost and green catalyst development which is derived from lignocellulosic material is a driving force to utilize corncob as a heterogeneous acid catalyst in chemical reactions [51–52]. The lignocellulosic content of corncob can be thermally treated and chemically activated into acidic carbon-based catalysts [39–51–53]. In addition, corncob has a fixed carbon content of 15.9 %w/w [54], The value is comparable to other agricultural residues (11.71-35.2 %w/w) that are used as the raw material for the synthesis of solid acid catalysts [55–58]. The previous researches mentioned exactly the same reason why the corncob has been selected as raw material for heterogeneous acid catalyst [50–53–59–60]. The corncob-derived heterogeneous acid catalyst is expected to be used efficiently to catalyze the esterification reaction of low-quality feedstock in biodiesel production and could solve the current problem of catalyst utilization in biodiesel production. The high catalytic activity, simple separation, and the reusability are the main goal in corncob-derived heterogeneous acid

catalyst synthesis process. To reach the goal, there are several techniques applied to synthesize and modify the corncob-derived heterogeneous acid catalyst. The most common pathway employed to synthesize acid-activated solid catalysts from lignocellulosic materials is through carbonization, which is followed by chemical activation [61–64]. The lignocellulosic materials are carbonized to remove any volatile matters by thermal decomposition and obtain porous carbon. Nata et al. [65] carbonized a corn cob at 400°C for 1 h to generate biocarbon before chemical activation, and they found that the concentration of carbon increased up to 79.45%. A similar method was also performed by Rocha et al. [51], who prepared a corncob-derived solid acid catalyst by carbonization at 500°C for 1 h. To produce high-quality carbon, a hydrothermal carbonization method is offered. The carbon material is formed at low temperatures under high-pressure conditions [66]. This method can generate a higher amount of porous hydrochar as a carbon product [67]. Ma et al. [39] performed hydrothermal carbonization at 180°C by using corncob as the feedstock. The same method was also used by Ibrahim et al. [53] for solid acid catalyst preparation from corncob. The hydrothermal carbonization was performed at 200°C for 10 h. Those studies successfully exhibited hydrothermal carbonization as a suitable process to produce porous carbon materials.

To obtain a corncob-derived heterogeneous acid catalyst with high porosity and activity, chemical activation such as the sulfonation method was employed [35–68–69]. The simple way of sulfonation is by using thermal treatment of biochar with concentrated H_2SO_4 [24]. Fuming sulfuric acid [70], p-toluenesulfonic acid (PTSA) [44], 4-benzenediazonium sulfonate [36], and hydroxyl ethyl sulfonic acid [65] also have been utilized as sulfonating agents. This sulfonation was performed by heating the mixture of biochar and sulfonating agent to synthesize the catalyst. There are two common ways of sulfonation on corn cob as acid catalyst preparation, reflux system, and thermal treatment using an autoclave Teflon reactor. These two methods have a different effect on BET surface area and pore properties of catalyst [53–71]. Ibrahim et al [53] found that the surface area of solid catalysts before and after sulfonation by using a reflux system

was almost identical, i.e. $8.76 \text{ m}^2.\text{g}^{-1}$ and $8.40 \text{ m}^2.\text{g}^{-1}$, respectively. The pore properties slightly deteriorated and $-\text{SO}_3\text{H}$ groups were dispersed and incorporated within the pores. Meanwhile, the sulfonation using thermal treatment provides high porosity that can enlarge the surface of the

active area. Therefore, thermal treatment is more preferred to insert $-\text{SO}_3\text{H}$ groups into the surface of carbon precursor. Figure 3 describes the employed pathway to synthesize solid acid catalyst from corncob using thermal treatment.

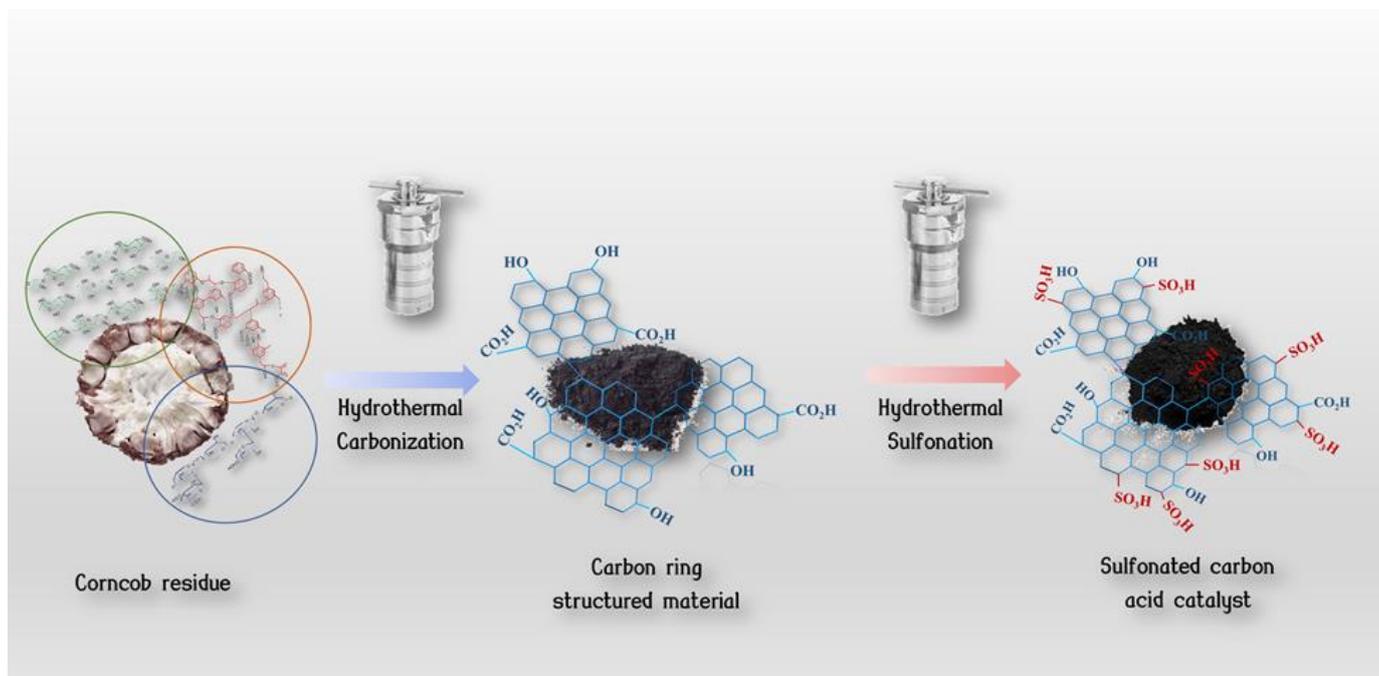


Fig. 3. Synthesis pathway of solid acid catalyst from corncob

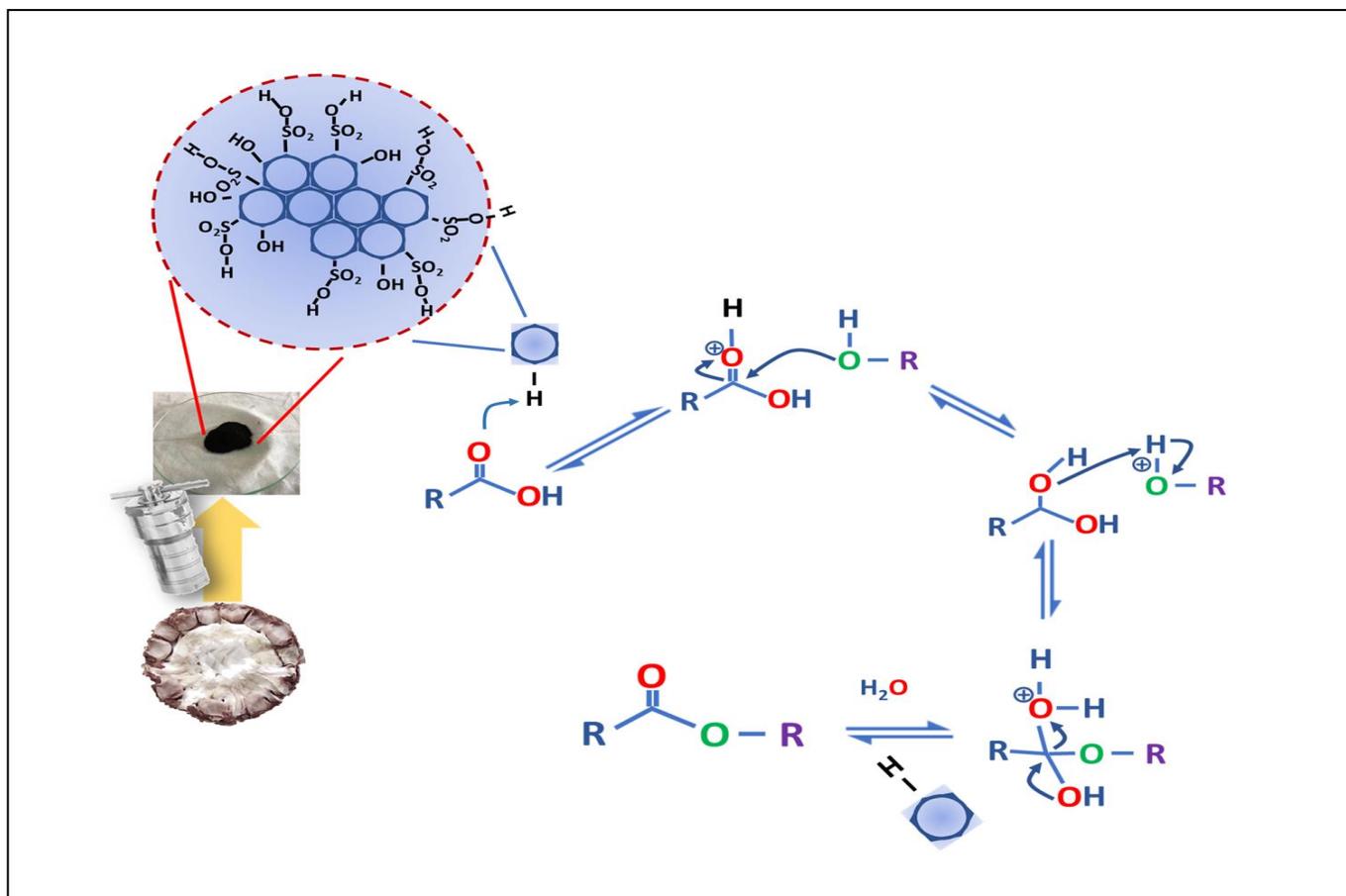


Fig. 4. Proposed mechanism pathways for esterification reaction using corncob derived sulfonated solid catalyst

Table 1. A literature report on biodiesel production over corncob-derived solid acid catalysts

Catalyst preparation method	Esterification feedstock	Catalyst loading (wt%)	Temperature (°C)	Yield/Conversion (%)	Refs.
Pyrolysis carbonization and sulfonation	Highly acidic waste oil	3		98	[50]
Hydrothermal carbonization and hydrothermal sulfonation	Oleic acid	10	80	89.2	[39]
Impregnation, pyrolysis carbonization and sulfonation	Oleic acid	10	65	90	[59]
Impregnation, pyrolysis carbonization and sulfonation	Refined soybean oil	20	75	88.7	[51]
Impregnation, pyrolysis carbonization and sulfonation	Palm fatty acid distillate	5	100	93.49	[60]
Hydrothermal carbonization and reflux sulfonation	Palm fatty acid distillate	3	70	92	[53]

After sulfonation process, the surface area of corncob-derived heterogeneous acid catalyst tended to decrease. It was due to the insertion of $-SO_3H$ groups on the surface. Hussain and Kumar [59] reported the change of surface area before and after sulfonation of corncob-derived heterogeneous catalyst in which the surface area decreased after sulfonation from $1268 \text{ m}^2\cdot\text{g}^{-1}$ to $641 \text{ m}^2\cdot\text{g}^{-1}$. They claimed that the decrease on surface area after sulfonation indicated that the $-SO_3H$ groups successfully grafted onto surface, which acted as the active sites. The synthesized catalyst was applied in the esterification of Karanja oil in the presence of methanol. The conversion of FFA reached 90%. Rocha et al. [51] also reported the same tendency of decrease on the surface area of corncob-derived catalyst after sulfonation, from $739.4 \text{ m}^2\cdot\text{g}^{-1}$ to $730.8 \text{ m}^2\cdot\text{g}^{-1}$. They used the synthesized catalyst in the transesterification of soybean oil with ethanol, resulting in biodiesel yield of 88.7%. On the other hand, the sulfonation process also generate larger pore size. Tang et al. [60] found that sulfonated-carbonized-corn-cob had larger average pore size (3.79 nm) compared to carbonized-corn-cob (2.68 nm). The catalyst was utilized in the esterification of palm fatty acid distillate with methanol and reached 93.49% of FFA conversion. Larger pore size provides the accessibility of reactants with large molecular size going to the active sites. The proper size of pore could reduce the mass transfer resistance of the flow of reactants to reach the active sites. Ngaosuwan et al. [72] mentioned that the FFA and triglyceride molecules could pass through a cylindrical pore with 2 nm diameter.

The heterogeneous acid catalyst can be classified into Brønsted-type (sulfonic acid-containing material) and Lewis-type (mixed sulfated oxides-containing material). Both types of acid catalyst can be used in the esterification of FFA in the presence of short-chain alcohol to produce biodiesel. However, the mechanism is slightly different. The Brønsted-type catalyzes the esterification of FFA by the protonation of the acid group to give an oxonium ion, which is readily

attacked by an alcohol through an exchange reaction to produce alkyl ester after losing proton. The Lewis-type catalyzes the esterification of FFA by direct coordination of the FFA to the acid metal site. Nata et al. [65] and Ibrahim et al. [53] confirmed the Brønsted acid-type on the corncob-derived heterogeneous sulfonated catalyst by titration method and TPD- NH_3 analysis. The sulfonated-carbonized corncob exhibited Brønsted acid sites at $T_{\min} 120^\circ\text{C}$ and $T_{\max} = 550^\circ\text{C}$ with total acid density of $2.64 \text{ mmol}\cdot\text{g}^{-1}$ and $13.00 \text{ mmol}\cdot\text{g}^{-1}$, respectively. Furthermore, a high total acid density of corncob solid acid catalyst results in high FFA conversion and biodiesel yield. It is due to $-SO_3H$ that induces the hydrophilicity of the carbon surface from corncob, allowing alcohol molecules to enter the carbon bulk and promote the esterification reaction of FFA to produce biodiesel [73–74]. Ibrahim et al. [53] proposed a mechanism of esterification of palm fatty acid distillate (PFAD) catalyzed by a sulfonated solid catalyst from corncob (HTC-S). The solid acid catalyst provides protons those accepted by FFA. The $-SO_3H$ proton donor groups are generated by three oxygen atoms that pull the electrons cloud from sulfur and hydrogen. Afterward, the alcohol molecule attacks the protonated carbonyl group to form an intermediate that will release a water molecule to produce a protonated ester. In the last step, the proton is transferred back to the acid-solid catalyst and yields an ester or biodiesel (figure 4).

A variety of studies have been conducted to investigate the performance of corncob-derived solid acid catalysts as a potential heterogeneous catalyst for biodiesel production. The reaction time, temperature, catalyst loading, and alcohol to reactant molar ratio were evaluated to justify the catalytic activity of corncob-derived heterogeneous acid catalyst. The response of catalytic activity was expressed in FFA conversion or biodiesel yield.

The esterification of waste vegetable oil or fatty acid such as oleic acid in the presence of alcohol using corncob derived heterogeneous acid catalyst is a liquid-liquid-solid system. It

requires the longer reaction time than homogeneous system to provide sufficient mass transfer between the liquid and the solid phase. Arancon et al. [50] reported that 98% of FAME yield was obtained after 6 h reaction using corncob derived heterogeneous acid as catalyst in the esterification of waste oil. In 2014, Ma et al. [39] also reported that for the same type of catalyst, the esterification of oleic acid reached 89.2% of product yield after 2 h. Another study from Ibrahim et al. [53] revealed that the maximum FFA conversion (92%) was obtained after 2 h. They performed the esterification of palm fatty acid distillate in the presence of methanol catalyzed by corncob derived heterogeneous acid catalyst. According to this study, FFA conversion remained steady at 92% without any significant increase when the reaction time was increased into 4 h. Farabi et al. [75] stated that since the esterification is reversible reaction, further prolonged reaction time might shift the reaction toward the reactant.

Thermodynamically, esterification reaction is an endothermic reaction. According to Tang et al [60] the activation energy of the esterification reaction between palm fatty acid and methanol, which was catalyzed by corncob-derived heterogeneous acid was found to be $+23.36 \text{ kJ}\cdot\text{mol}^{-1}$. Increasing the temperature could drive the equilibrium toward the product [76]. Moreover, an increase in reaction temperature could reduce the mass transfer limitation between vegetable oil, alcohol, and solid catalyst. High temperature could decrease the viscosity of vegetable oil, and increase the miscibility between methanol and oil; thus, the FFA conversion will increase [53]. However, further increase in reaction temperature could not give a significant enhancement on FFA conversion due to the alcohol that tends to evaporate [77]. Ibrahim et al. [53] found that increasing the reaction temperature from 65°C to 70°C increased FFA conversion from 88% to 92%. The FFA started to reduce FFA conversion when the reaction temperature increased from 70°C to 80°C . The optimum reaction temperature of esterification between palm fatty acid distillate and methanol catalyzed by corncob-derived heterogeneous acid was 70°C . Another study by Hussain and Kumar [59] exhibited the optimum reaction temperature of esterification between Karanja oil and methanol using the same type of catalyst at 65°C with 90% conversion of FFA.

The corncob-derived heterogeneous acid catalyst provides acid active sites to facilitate the esterification reaction which can increase the FFA conversion rate. A large number of acidic sites could increase the availability of H^+ during esterification reaction [78]. However, excess catalyst in reaction system can lead to a mixing problem [76], the catalyst particles tend to self-agglomeration [78], and inhibit the mass transfer between catalyst, alcohol and feedstock [71]. According to Hussain and Kumar [59] the excess catalyst amount in reaction system causes the catalyst particles only float around the reactant and it could not increase the reaction rate. Hence, the optimum catalyst loading according to Ma et al. [39] and Hussain and Kumar [59] was 10%. It is different from what Ibrahim et al.[53] found in which the optimum amount was 3%, and 5% based on study performed by Tang et al. [60].

Stoichiometrically, the esterification reaction requires one mole of alcohol for one mol of vegetable oil. It is due to the

esterification reaction that is a reversible reaction. The excess mol of alcohol is required to drive the reaction towards the product. For esterification reaction, which is catalyzed by corncob-derived heterogeneous acid, the optimum alcohol-to-oil molar ratio is different dependent upon the feedstock and the amount of catalyst. Ma et al. [39] used the molar ratio of methanol-to-oleic acid, 10:1 and reached the best conversion of FFA at 89.2%. Hussain and Kumar [59] found the highest conversion of FFA, 90% with 20:1 of methanol-to-Karanja oil molar ratio. Ibrahim et al. [53] revealed that the optimum molar ratio of methanol-to-palm fatty acid distillate was 15:1 and reached 92% of FFA conversion. Other study by Tang et al. [60] found that 30:1 was the optimum molar ratio of methanol-to-palm fatty acid distillate. However, excess alcohol could dilute the reaction system and reduce the contact between catalyst and oil, and further it could hinder the protonation of oil and reaction rate becomes slow. Ibrahim et al [53] studied the effect of methanol-to-palm fatty acid distillate molar ratio on esterification reaction catalyzed by 3% corncob-derived heterogeneous acid at 70°C for 2 h. they found that 15:1 was the optimum molar ratio of methanol-to-feedstock. Further increase in molar ratio of methanol-to-palm fatty acid to 20:1 and 25:1 decreased the FFA conversion. It is proven that large excess of alcohol in reaction system leads the low reaction rate.

Reusability is a very important property of corncob-derived heterogeneous acid catalyst. The reusability test is performed for several cycles' reaction under an optimized condition. Previous studies exhibited that the performance of corncob-derived heterogeneous acid catalyst decreased after several cycles. Arancon et al [50] revealed that after 2 cycles reuse of catalyst, the FAME conversion only reached 17%. Ma et al. [39] reported that it remained at 60% of FFA conversion after 8 cycles to reuse the catalyst in reaction. Ibrahim et al. [53] reported that after 5 cycles the FFA conversion remained 60%, and Tang et al. [60] also reported after 5 cycles the FAME yield remained 50%. The significant decrease in FFA conversion or FAME yield after several cycles to reuse corncob-derived heterogeneous acid as catalyst might be due to the leaching of the active sites [75], the blockage of the active sites by unreacted reactant and product [76], and the deactivation of active sites by water as by-product of esterification reaction. The later one is difficult to avoid since the water generates during the esterification. The -OH groups, which are also attached on surface of catalyst allow water adsorption. According to Hussain and Kumar [59] there is a competition between oil as reactant and water to adsorb on catalyst surface to lead to the deactivation of catalyst. Therefore, corncob-derived heterogeneous acid catalyst with high water resistant is desirable.

4. Perspectives, Challenges, and Future Prospect

According to the physical/chemical characterization and performance, the corncob-derived acid catalyst has high potential as a green-active catalyst for FFA esterification in biodiesel production, The utilization of corncob-derived heterogeneous acid catalysts could reach up to 90-98% of FFA conversion and 85% of biodiesel yield. Table 1 summarizes biodiesel production that utilizes corncob as solid

acid catalysts. The challenges of corncob-derived solid acid catalyst utilization in the esterification reaction of vegetable oil are similar with the solid acid catalysts derived from other biomass waste. The low reaction rate, deactivation of catalyst by water as esterification by-product, formation of side reaction and the difficulty of maintaining the stability of performance in repetitive use are some general challenges of corncob-derived solid acid catalyst utilization as listed in table 2.

Some studies are required to further modify the surface of corncob-derived solid acid catalyst which is allowable to

control the accessibility of vegetable oil molecules into the acid active site and to maintain the stability of the acid active sites. As the catalyst is easy to be deactivated by water, there could be interesting if the surface of catalyst modifies and engineers for having water resistant properties using novel method. However, the proposed ideas and methods to enhance the catalytic activity of corncob-derived solid acid catalyst should be in harmony with the final goal, providing the simple, safe, environmentally friendly and cost-effectiveness method to synthesize biodiesel.

Table 2. The drawbacks and possible causes for the utilization of corncob-derived heterogeneous acid catalyst.

Drawback	Possible causes	Ref.
Longer reaction time	Mass transfer limitation between liquid and solid phase	[50–53]
Higher reaction temperature	Miscibility between high-viscosity feedstock and methanol; catalytic acid site covered by water (by-product of esterification) absorbed onto surface.	[59–60]
Sel-agglomeration of catalyst particles	excess catalyst loading	[39–53–59–60]
The hindrance of feedstock protonation	Larger methanol amount could dilute the system	[53]
Formation side reaction	The reaction drive toward the reactant by water (hydrolysis of product)	[59]
Deactivation of active acid site	The -OH groups on surface of catalyst attract water, and water hydrolyzes the active site.	[59]

5. Conclusion

Heterogeneous acid catalysts have an enormous potential to replace conventional catalysts in biodiesel production with good efficiency. They are suitable for low quality feedstock containing high FFA and able to reduce the production cost for biodiesel production. Recently, biomass waste derived heterogeneous acid catalyst is the best candidate for the cost reduction purpose and safe for the environment. Corncob is one of biomass wastes that has been utilized as raw material for solid acid catalyst preparation. A sulfonated corncob derived heterogeneous catalyst has been successfully synthesized by hydrothermal technique both for carbonization and sulfonation. The catalyst has been applied in the esterification reaction of the low-quality vegetable oil and exhibited a high yield of biodiesel. However, further development of corncob derived heterogeneous acid catalysts is still required for a better performance in biodiesel production.

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