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Advances in biomass derived low-cost carbon catalyst for biodiesel production: preparation methods, reaction conditions, and mechanisms

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Biodiesel is a less hazardous, environmentally friendly biofuel that has been extensively investigated in modern years to ensure that we lessen our dependency on fossil fuels and mitigate climate change. While fossil fuel substitutes like biodiesel may help transition to a less polluted world, industrial-scale manufacturing still relies highly on chemical catalysis. However, heterogeneous solid catalysts result in less activity for biodiesel production due to their deactivation effects, porosity, surface area, material stability, and lower reactivity under moderate conditions. The "sulfonated carbons" are metal-free solid protonic acids distinguished by their distinctive carbon structure and Brønsted acidity ($H_0 = 8-11$). Heterogeneous sulfonated catalysts derived from waste biomass were a significant focus of the most advanced biodiesel processing techniques for simple and low-cost manufacturing processes. This study discusses the advantages and disadvantages of various catalysts, biomass sources and properties, synthesis of catalysts, and factors influencing the insertion of active sulfonic sites on biomass surfaces. Additionally, transesterification and esterification reaction mechanisms and kinetics are discussed. At last, future directions are provided for young, dynamic researchers.

1. Introduction

According to contemporary energy legislation, climate change and energy efficiency must be tackled simultaneously through technical advancements. The consumption of renewable energy among the public and scientific community has piqued attention due to the faster depletion and consumption of fossil fuels and the high emissions of toxic gases. Due to their renewability and non-toxicity, the widely accepted techniques for alternative fuels that partly replace fossil fuels are bioethanol and biodiesel. According to ASTM D6751, biodiesel is defined as the fatty acid alkyl esters of animal fats and vegetable oils that are obtained from various feedstocks.[1–3]

Biodiesel is a clean, renewable, non-toxic and biodegradable biofuel.[4] A variety of feedstock based on agriculture, wood waste, energy crops, plant-oil based, and aquatic biomass are helpful to produce biodiesel. Numerous major countries have accessibility of prospective bio-resources as feedstock materials such as *Calophyllum inophyllum* (Malaysia and Australia), *Pongamia pinnata* (India, Bangladesh, and Australia), Sunflower (Argentina, Greece, Turkey, Italy, and Canada), *Jatropha curcas* (India, Thailand, Malaysia, Tanzania, Mali, Mozambique, Cuba, Peru, and Zimbabwe, Pakistan), rapeseed (Italy, Chile, Canada, Greece, and Turkey, China), oil seed palm (Thailand, Brazil, Iran, Peru, Malaysia, and Mexico), soyabean (Unites States, Italy,

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Argentina, and Canada), fish residues (Norway) and fish oil (Iran).[5] These natural assets have ideal value for biofuels generation due to biodegradability, availability, and CO_2 neutrality.[6,7] Transesterification is the most often utilized process for producing biodiesel from vegetable oil.[8,9] When an alcohol and triglycerides are reacted in absence or presence of catalyst resulted in formation of fatty acid methyl ester (FAME) and a byproduct glycerin. In comparison to other petro-diesel, biodiesel has high flashpoint and cetane number, and low cold flow properties and calorific values.[10,11] Due to these properties, biodiesel is more secure for storage and transport. As energy source, biodiesel claimed to reduce 78% of CO_2 emissions as petro-diesel.[12] The biodiesel market in India reached 383.4 million US dollar in 2022 and expected to reach 643 million US dollar by 2028. Fig. 1 displays the data of biodiesel production (from 2011 to 2021) in India which is continuously growing.

Homogeneous catalysts are favorable catalysts for synthesis of biodiesel due to their simplicity and low energy utilization. However, homogeneous catalysts have several disadvantages like non-recoverable, non-biodegradable, corrosion of instruments and recyclability.[13] These issues are easily resolved by heterogeneous catalyst. Heterogeneous catalysts are extensively investigated due to ease of separation, recyclability, non-corrosiveness of instruments and no soap formation.[13,14] There are a variety of materials that may be used to make heterogeneous catalysts, such as biochar, biomass ash, waste shells, agriculture products and activated carbon.[15] Researchers
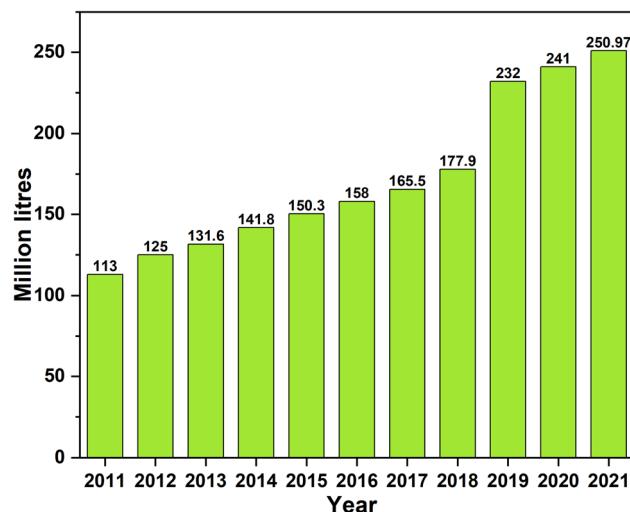
Fig. 1 Biodiesel production in India over the years (data obtained from OECD https://stats.oecd.org/Index.aspx?QueryId=107145#).

Hara and his colleagues first developed the SO_3H carbon sheets in 2004.[23] The metal free sulfonated carbon catalyst is generally prepared using concentrated H_2SO_4 with the help of carbonized organic matter.[24–26] In this review, we have added various strategies of developing low-cost catalyst for biodiesel production. Low-cost catalyst which is derived from biomass are well recognized for biodiesel formations. Although several review published on biodiesel production by utilization of carbon-based material.[15,27–30] However, there is no recent review on biodiesel production including esterification and trans-esterification process from biomass by SO_3H functionalized active site as per our knowledge. The authors try to summarizes the recent advancement in the biodiesel formation by esterification and transesterification reaction which include FFA and triglycerides. Along with this, biomass derived catalyst like sulfonated catalyst (acid catalyst) and magnetic catalyst are discussed. From this viewpoint, researchers are developed a novel and sustainable materials with the utilization of these waste and also, they have value addition for environment.

from all around the world have recently been interested in biomass-derived heterogeneous catalysts. Ecologically and economically, it makes sense to use a commercial waste product as a catalyst in the manufacturing of biodiesel.[16] Consequently, the catalyst has to have a greater surface area in order to generate a solid acid catalyst of excellent quality (external catalytic sites, hydrophobicity, etc.) having a significant pore diameter.[17] Table 1 discusses the various advantages and disadvantage of different catalyst for biodiesel production.

2. Biomass source and properties

Biomass is a readily available material that is found in nature abundantly through various agricultural activities. Recently, biomass has been considered a potential material for biodiesel production due to its low cost and easy availability. Biomass mainly contains carbon material that possesses lignin, hemi-cellulose, and cellulose. Due to these characteristics, researchers utilized biomass for high-value addition materials

Table 1 Advantage and disadvantage of catalyst for biodiesel production

Catalyst type	Example	Advantages	Disadvantages	References
Homogeneous acidic and basic catalyst	H_2SO_4, HCl, H_3PO_4, HNO_3, KOH, NaOH	High activity	Hard to separate from reaction mixture	[15] and [18]
		Shorter reaction time	Soap formation	
		Lesser purification steps	Sensitive to free fatty acid (FFA) and H_2O	
		Low cost	High temperature	
			High pressure	
			Cannot utilized in animal fats and waste cooking oil	
			Release in high quantity of wastewater	
			Corrosiveness	
Heterogeneous catalyst	CaO, MgO, Hydrotalcite, ZrO_2, TiO_2, ion-exchange resin, mixed oxide	Non-corrosion	High methanol: oil ratio	[19] and [20]
		Easy separation	Actives sites leaching	
		High reusability	High cost	
		Insensitive to FFA and H_2O	Complex synthesis procedure	
			Diffusion limitations	
			Low microporosity	
			Low acidic or basic sites	
Enzyme	Lipase	Green approach	High cost	[21] and [22]
		High specificity	Inhibition by glycerol and alcohol	
		High catalytic efficiency	Low reaction rate	
		High biodiesel purity	Enzyme denaturation	
		Fewer purification steps		
		No soap formation		

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through various processes. Biomass char has a large pore size and uneven structure. Forestry wastes include bark, leaves, branches, and other wood fragments. In general, lignocellulosic biomass has 15–25% lignin, 25–40% hemicellulose, and 35–55% cellulose, with a minuscule quantity of protein, extractives, and ash. For the pyrolysis process, the content of water in the feedstock should be less than 10%. Agricultural leftovers such as rice husks can have an ash level of up to 20%, whereas most woody biomass, devoid of "dirt" (needles and leaves), has an ash concentration of less than 2%. In terms of elemental compositions, wood residues contain somewhat more hydrogen and carbon than agricultural leftovers.

Pyrolysis, direct combustion, hydro gasification, gasification, anaerobic digestion, liquefaction, trans-esterification, esterification and alcoholic fermentation are the principal methods for getting energy from biomass. Relying on the bioresource and the type of energy required, each technique offers distinct benefits.[31] Recently, there has been an upsurge in demand for farming residues as substitutes for woody cellulosic fibers because of growing awareness of environmental concerns, global deforestation about the low-cost residues as well as burning the residues, in comparison to plant fibers. Additionally, using agricultural residues can help nations with a dearth of forestry resources address their wood resource shortfall. Rice, wheat, maize stover, barley straw, coconut husk, sorghum stalks, sugarcane bagasse, banana, and pineapple leaves are the primary lignocellulosic agricultural leftovers. So, the demand for agricultural residue is continuously increasing instead of producing energy from woody biomass. Agro-industrial waste, pruned biomass, arable crop residues, and biomass derived from the farming of energy crops are all examples of solid agricultural feedstock. Table 2 provide the summary of various biomass resources obtained from agriculture, forest and other sources.

3. Catalyst synthesis by biomass

The sulfonated catalysts are fabricated using various techniques by utilization of biomass. The biomass contains a large amount of oxygen, carbon, and less amount of calcium, potassium, magnesium, and sodium.[36] Generally, sulfonated carbon catalysts can be fabricated by two processes known as hydrothermal carbonization (HTC) and pyrolysis, followed by sulfonation.

Araujo et al.[37] created the catalyst through the utilization of acai seed. The powder of acai seed was heated at 600 °C in a tubular furnace under nitrogen for 2 h. About 35 weight percent of carbon was produced when acai stone debris was carbonized. The obtained carbonaceous material was sulfonated with H_2SO_4 and stirred for effective mixing. After that, the solution was washed with distilled water several times until no sulfate was detected by the $BaCl_2$ solution. In another similar type of study, the corn straw was heated at various temperatures, followed by sulfonation.[38] A 100 mL flask was filled with 10 mL of fuming sulfuric acid and heated in an oil bath at 80 °C for 240 min. The mixture was cooled and washed to remove impurities using a vacuum pump. Finally, the resulting material was dried at 80 °C for 4 h in a vacuum before using an esterification reaction. Microalgal biomass was also utilized for the esterification reaction. First, the microalgal biomass was de-oiled by lipid extraction via the Soxhlet extraction process.[39] The biomass was de-oiled and then dried in an oven to remove all traces of solvents before the carbon catalyst was prepared. Synthesis of the de-oiled microalgal biomass (DMB) catalyst required two steps: first, carbonization of DMB, and then, sulfonation of the resulting biochar using sulfuric acid. In another work, a solid acid catalyst was produced by sulfonating three different carbonaceous materials (algal biomass, moringa, and rice husk).[40] Previously to sulfonation, the material was ground into powder form. 20 mL of 2 M H_2SO_4

Table 2 Various biomass sources

Category	Example	Characteristics	References
Agricultural activities	Rice husk, rice straw, wheat straw, corn stover, begasse	Low cost Easy availability High photosynthesis ability High cellulose content Low harvest time Less nitrogen and sulfur than coal	32, and 33
Forest	Wood	Higher carbon content Fewer ash contents High cellulose content A high density of biomass Less nitrogen and sulfur than coal	34
Perennial grass	Indian grass, sugarcane bagasse, reed canary	Improve soil quality Carbon sequestering Easy and fast growth Low fertilizers dependance Decrease dependency on forest biomass	35
Aquatic plant	Brown algae, green algae	Bioremediation capability Low nutrition requirement Short life cycle High biomass potential yield	35

was added to a 100 mL Teflon autoclave and heated in a microwave at 200 °C for 30 min while 5 g of sample were stirred at a slow pace. The microwave temperature ramped for 5 min at 200 °C, held for 30 min at 200 °C, and then decreased to 40 °C. The sample was then dried overnight at 60 °C in the oven before being hand-milled into a fine powder. The fine powder was then mixed in the microwave reactor with 20 mL of 20% SO_3 fuming H_2SO_4. For 30 min, sulfonation was done in a microwave. The material was dried at 150 °C for 12 hours after being cooled to 40 °C.

HTC's approach of creating carbonaceous materials from naturally occurring biomass combines the use of renewable resources with attractive porosity and stability. Gaurav and Ahmaruzzaman successfully synthesized a sulfonated carbon material *via* the facile hydrothermal carbonization (HTC) method in a single step at a low temperature.[14] The as-synthesized material is fabricated using waste citrus limetta peel. The successful insertion of active sulfonic sites was observed using FTIR spectroscopy. EDS analysis also supports the data of FTIR. In another similar type of study, areca nut husk was used as a carbon precursor for the fabrication of sulfonated carbon catalyst by the HTC method.[10] The author used two temperatures, 80 °C and 100 °C. The crushed areca nut husk was prepared using a batch experiment in the ratio of 1 : 10 and 1 : 20. The author observed that increasing the temperature results in the breakage of the carbon structure. Carbonizing biomass in supercritical ethanol and then sulfonating the resulting alcohothermal chars has resulted in the first-ever synthesis of a novel solid acid with enhanced stability. Alcohothermal chars were more stable after being sulfonated because oxygenated functional groups and sulfonic groups were simpler to load on them than on hydrothermal or pyrolytic chars.[41]

4. Factors influencing the SO₃H acid density

4.1. Effect of temperature

Temperature plays a significant impact on the insertion of SO_3H actives sites on the biomass surface. High temperature causes biomass dehydration and bond breaking of numerous carbon skeletons, which results in the formation of amorphous structures includes polycyclic aromatic skeleton.[42] Gaurav *et al.* noticed that the high temperature of the areca nut husk causes the breakage of cellulose, hemicellulose, and lignin part of biomass which forms polycyclic aromatic hydrocarbon.[10] As further the temperature rises, these groups disintegrate, resulting in a decrease in functionalization efficiency. The anchoring of the SO_3H functional group may be in jeopardy due to the rise in carbonization temperature.[43] However, the degree of functionalization increases with decreasing carbonization temperature. This means that materials functionalized at lower temperatures will likely have a larger density of acid sites. The carbon structure was expected to enhance reactant diffusion, allowing for more excellent anchoring of acid groups and the generation of active SO_3H sites. Biomass components were

decomposed at higher temperatures which do not form an appropriate skeleton for insertion of SO_3H actives site. For example, Joyleene *et al.* fabricated woody biomass at a temperature of 450, 675 and 875 °C. The biomass pyrolyzed at 450 °C (2.6 mmol g⁻¹) has the highest total acid density followed by 675 °C (1.2 mmol g⁻¹) and 875 °C (0.43 mmol g⁻¹).[44]

4.2. Effect of sulfonation

The insertion of the SO_3H active site is done with the help of various sulfonating agents like conc. sulfuric acid, fuming sulfuric acid, aminobenzene sulfonic acid, chlorosulfonic acid, p-toluene sulfonic acid, hydroxyethyl sulfonic acid, sulfosalicylic acid, and other.[45] Among all these acids, concentrated sulfuric acid is used for insertion of SO_3H acidic sites due to low cost.

As aforementioned, temperature significantly affects the stability and activity of sulfonic acid. Limited sulfonation leads to the formation of unstable and readily decomposed material. As the temperatures increase, an undesired multi-sulfonated group may reduce catalytic activity. At low carbonization temperatures, biomass structure does not deteriorate. Consequently, surface groups are produced that can more effectively react with sulfuric acid, promoting increasing inclusion of sulfonic groups on the carbon catalysts surface. The reduction in sulfonation surface areas was caused by carbon network breakdown and high-temperature acid group dehydration. The adverse impact on the S content of the catalyst may be ascribed to the low thermal robustness of SO_3H groups.[46] Sulfonic groups were inserted *via* various pathways, *i.e.*, functionalization method and chemical modification. Depending upon these techniques and carbon precursors, the sulfonic density ranges from 0.05 to 7.3 mmol g⁻¹.[23,45] At the initial point, the sulfonic acid insertion in the biomass surface increase by increasing the wt% of sulfuric acid. The higher rate of carbonization-sulfonation reaction as the sulfuric acid wt% increases could explain the increase in insertion of sulfonic active sites. After reaching an optimum value, there was no effect on the reaction rate, but at high sulfuric acid wt%, the rate of carbonization-sulfonation decreases resulting in decrease in the S-content.[10]

4.3. Effect of time

Time also plays an essential role in the insertion of sulfonic acid active sites. In comparison to the wt% of sulfuric acid reaction temperature, reaction time has a significant influence on carbonization-sulfonation. The increase in the reaction time has a positive effect on the catalyst procedure, leading to a rise in its S-content, resulting in an increase in total acid density until the optimum time is reached. However, more increase in reaction time does not effect on s-content;[46] hence the acid density will be the same. Lancer and Kucera stated that sulfonation-desulfonation is a reversible reaction.[47] Prolonged time at high temperatures leads to a decrease in total acid density. As a result, the substantial decrease in strong acid density seen throughout the protracted sulfonation process can always be accounted by the desulfonation process. In another study, the increase in the time from 1 h to 4 h resulted in

increase the acid density to 4.2 mmol g^{-1}, but in the same reaction condition, the decrease in the acid density has noticed in 8 h (2.9 mmol g^{-1}).[48] This change in the acid density beyond the optimum value is due to subsequent decrease and functionalization phase of the pyrolyzed carbon material.

5. Process of biodiesel formation

5.1. Esterification reactions

The high cost of producing biodiesel is directly related to the current high price of oil. Waste cooking oil for transesterification processes is common but not used because of the oil's high impurity levels, particularly its high FFA content. The esterification of an acid catalyst would be preferable.

Memon *et al.* evaluated the potential of *Mangifera indica* peels for biodiesel production by varying the amount of concentrated sulfuric acid at various time intervals.[49] The maximum catalyst yield for biodiesel production was obtained when six hours of time was taken to sulfonate the *Mangifera indica* peel due to highly acidic groups like –OH, –COOH, and –SO$_3$H. The as-synthesized catalyst has a wide surface area (42.13 m^2 g^{-1}), high pore volume, and porosity. The reusability study of the catalyst was observed up to 4 cycles showing the excellent stability of the catalyst. In the esterification process between methanol and oleic acid (OA), researchers used an acid catalyst derived from *Sargassum horneri* carbon.[50] The lower amount of lignin and a more significant amount of total cellulose (hemicellulose and cellulose) in *Sargassum horneri* relative to terrestrial plants indicate modest pyrolysis conditions. Due to this, the carbonization synthesis temperature was varied from 250 to 550 °C. The *Sargassum horneri* gives maximum biodiesel at 300 °C having conversion of 96.4%. Due to the high carbon concentration in its elemental composition, it is well suited for producing carbon-based materials. Catalytic efficiency in the esterification process required for biodiesel manufacture may be increased by the availability of sulfonic acid groups and carbonization for forming amorphous carbon layers. After the four-cycle, the recovered catalyst was sulfonated again, which gave the maximum yield of 95.4%. MnFe$_2$O$_4$ and CoFe$_2$O$_4$ ferrite nanoparticles loaded with sulfonated lignin (SL) were used for the esterification of OA.[51] SL was deliberately produced by reacting sugarcane bagasse lignin with acetyl sulfate (SO$_3$H agent). In order to create the magnetic nanoparticles, two distinct solids were created using differing reaction proportions. In the esterification processes, MnFe$_2$O$_4$-SL and CoFe$_2$O$_4$-SL displayed the highest conversion of OA into FAME, at around 80%.

Waste *Citrus limetta* peels (SCLPB) were used for the production of biodiesel from oleic acid. The EDS and FTIR data show the insertion of sulfonic actives site, which were helpful for the reaction process. SCLPB catalyst's porous nature was beneficial for the conversion of oleic acid into methyl ester. The self-oxidation of oleic acid at higher temperature result in the formation of multiple esters, as shown by the GC-MS data.[14] Due to the catalyst's high surface area (32.210 m^2 g^{-1}), OA diffusion occurs on the catalyst's surface, enhancing catalytic activity. Mesoporous materials, which enable the reactants to diffuse

into the pores, may facilitate faster reaction rates. In another similar study, areca nut husk was synthesized using the HTC method. Due to the active sulfonic group, high S-content (3.12%) and high acid density (1.88 mmol g^{-1}) of the fabricated catalyst were noticed. Acid-base back titration was used to calculate the acid density of the fabricated catalyst. The as-synthesized catalyst was reusable for up to 4 catalytic cycles. The insertion of sulfonic actives sites into the catalyst surface shows a nucleophilic substitution reaction. The formation of covalent bonds between the sulfonic group (SO$_3$H) and the catalyst surface increases the acid density. The conversion of OA into methyl oleate was fast-forwarded by weak (–OH, –COOH) as well as strong acidic groups (SO$_3$H), thus increasing the reaction process.[10]

Tang compared the catalytic efficiency of biomass waste generated (corncob biomass, empty fruit bunch, and papaya seed) carbon-based acid catalysts used in the esterification reaction of methanol and palm fatty acid distillate (PFAD) to assess the feasibility in the manufacturing of biodiesel.[52] An effective sulfonation of the catalyst support was achieved by the arylation of 4-benzene diazonium sulfonate. The synthesized carbon catalyst had a high porosity and a surface area that varied from 639.68 to 972.66 m^2 g^{-1}. At optimum conditions, corncob shows the highest FFA conversion of 93.49% and FAME production of 72.09%. The FAME production was found to be reasonably high after just two reaction cycles when using a sulfonated AC catalyst produced from corncob waste. It was determined that the esterification process was irreversible pseudo-homogeneous. In a similar study, biomass obtained from marine algae, moringa oleifera seed, and rice husk (RH) surfaces were incorporated with the SO$_3$H group and assessed their activity for the esterification process. It was noticed from the ion exchange titration method that the rice husk was bearing the most active sulfonic group having a value of 4.24 mmol g^{-1}.[40] Algal biomass surface contains lower sites for binding the SO$_3$H group; as a consequence, the acid site density found was 0.27 mmol g^{-1}. The result shows that high SO$_3$H site insertion was due to greater surface area and high porous carbon structure. The surface of SO$_3$H-RH has a more significant potential to connect SO$_3$H groups and create active sites for FFA to biodiesel conversion. EDS analysis also confirms the presence of sulfur along with carbon and oxygen, which actively participate in the reaction. Monk fruit seeds (*Siraitia grosvenorii*) were also used to develop sulfonated carbon catalysts for biodiesel synthesis.[53] The efficiency of the fabricated catalyst was assessed using palmitic acid. The catalyst shows 98.5% efficiency under various conditions (4 wt%, 120 °C, 6 h). Phenylation with trimethoxy phenyl silane and sulfonation with chlorosulfonic acid were the two methods used for surface functionalization. Phenyl groups added by trimethoxy phenyl silane phenylation would intercalate on the monk fruit seed pore and surface. The SO$_3$H groups produced by the chlorosulfonic acid would then be replaced with the phenyl rings during the sulfonation process, creating strong covalent bonds. Table 3 showing the summary of various catalyst for production of biodiesel from esterification process.

Table 3 Various SO$_3$H functionalized catalyst for esterification reaction

Biomass source	Acid density (mmol g^{-1})	Optimization parameters	Yield (%)	Kinetics	References
Mangifera indica peels	3.46	1 : 10 (OA : CH$_3$OH), 5 wt%, 65 °C, 4 h	98.6	1st	49
Sargassum horneri	1.40	1 : 15 (OA : CH$_3$OH), 10 wt%, 70 °C, 5 h	96.4	—	50
Sugarcane bagasse	1.8	1 : 10 (OA : CH$_3$OH), 100 °C, 6 h	79.50, 78.5	—	51
Citrus limetta	—	1 : 20 (OA : CH$_3$OH), 5 wt%, 70 °C, 3 h	96	—	14
Areca nut husk	1.88	1 : 25 (OA : CH$_3$OH), 9 wt%, 80 °C, 1 h	96.4	1st	10
Corncob	2.07	1 : 30 (OA : CH$_3$OH), 5 wt%, 100 °C, 4 h	72.09	1st	52
Rice husk	4.24	—	99.9	—	40
Siraitia grosvenorii	7.61	−4 wt%, 120 °C, 6 h	98.5	—	53
Orange peel	0.93	1 : 10, 2.15 wt%, 3 h	92.8	—	54
Corncob	2.05	1 : 12, 10 wt%, 65 °C, 4 h	98.5	—	55
Cacao shell	4.56	1 : 7, 5 wt%, 45 °C, 4 h	93	—	56
Acai seed	0.74	1 : 12, 5 wt%, 100 °C, 1 h	88	—	57
Palm oil empty fruit bunch	1.96	1 : 50 (OA : CH$_3$COOCH$_3$), 10 wt%, 100 °C, 8 h	50.5	—	58
Acai stone	1.97	1 : 12, 5 wt%, 100 °C, 1 h	93	—	37
Sargassum horneri	1.62	—, 2 h	96.6	—	59
Potato peel	1.6	1 : 12, 5 wt%, 80 °C, 2.5 h	97.2	1st	60
Rice husk	2.26	1 : 24, 8 wt%, 80 °C, 1 h	99.6	1st	32
Walnut shell	2.06	1 : 16, 9 wt%, 85 °C, 1 h	99.01	1st	4
Corn straw	2.64	1 : 7, 7 wt%, 60 °C, 4 h	98	—	38
Soldier fly larvae shells	—	1 : 8, 10 wt%, 65 °C, 6 h	93.2	—	61
Ginger straw	1.05	1 : 9, 7 wt%, 64 °C, 3.5 h	93.2	—	62
Murumuru kernel shell	4.2	1 : 10, 5 wt%, 90 °C, 4 h	97.2	—	48

5.1.1. Esterification reaction mechanism and kinetics. In-depth research has been done on the esterification reaction between oleic acid with alcohol when acid catalysts with SO$_3$H groups are used.[63–65] The mechanism of esterification includes the following steps.

(1) Generation of carbocation and protonation of oleic acid carbonyl oxygen.

(2) Formation of unstable intermediate due to nucleophilic attack by hydroxyl group at positive carbon and deprotonation from unstable intermediate.

(3) Formation of water and methyl oleate.

Since methanol is a weak alkali and SO$_3$H is a strong acidic group, the esterification reaction does not begin until the second step in this well-established esterification process. As a result, protonating the methanol molecule is challenging due to the very acidic nature of SO$_3$H. In contrast, the oxygen in methanol molecules receives a small amount of "negative charge" through the addition of weak acid groups like –COOH, the deprotonated version of which may establish a hydrogen bond with the –OH group in the methanol molecule {Fig. 2}. Because of this "negative charge," the nucleophilic nature of the methanol is enhanced, which speeds up the esterification process and improves the conversion.

Generally, the esterification reaction follows pseudo-1st order kinetics due to excess of methanol.[4,10,66–68] Following factors should be considered for kinetics of esterification reaction-

1. The esterification process is the only responsible in biodiesel production.

2. The non-catalytic process is not important.

3. The reversible process was little affected by the addition of more methanol to the reaction mixture.

However, some researcher used the pseudo 2nd order kinetics[69,70] and pseudo homogeneous third order kinetics.[65,71]

5.2. Transesterifications reactions

Due to high oil prices, the transesterification process is still used for biodiesel production. The esterification process for biodiesel production requires high methanol and free fatty acid molar ratio. The biodiesel production process from waste cooking oil is gaining attention due to its value addition. Waste cooking oil contains high-free fatty acids.[32] An acid catalyst might be used to transform the feedstock's high FFA content into biodiesel.

Leesing *et al.* used an integrated process for biodiesel formation by yeast-based catalyst and catalyst derived from durian peel (DP).[72] Catalyst derived from durian peel shows enhanced activity on insertion of sulfonic sites, and FAME production efficiency reaches 81.57%. Before sulfonation, the acid density of the catalyst was just 0.01 mmol g^{-1}, whereas, after sulfonation, the acid density reached 1.22 mmol g^{-1} showing the incorporation of active sulfonic sites on the durian peel surface. The greater heat capacity of FAME generated led to an estimate of energy production between 32.44 - 34.90 MJ kg^{-1}. From 1000 kilograms of waste DP, the suggested bio-refinery idea produced 16.0 kg of yeast lipid, 101.2 kg of yeast biomass, 717 kg of DP-SO$_3$H catalyst, 70.4 kg of yeast wastes, and 79.7–82.6 kg FAME. In another study, microalgal biomass was de-oiled and then sulfonated to produce biodiesel. The catalyst was characterized by various techniques to check the
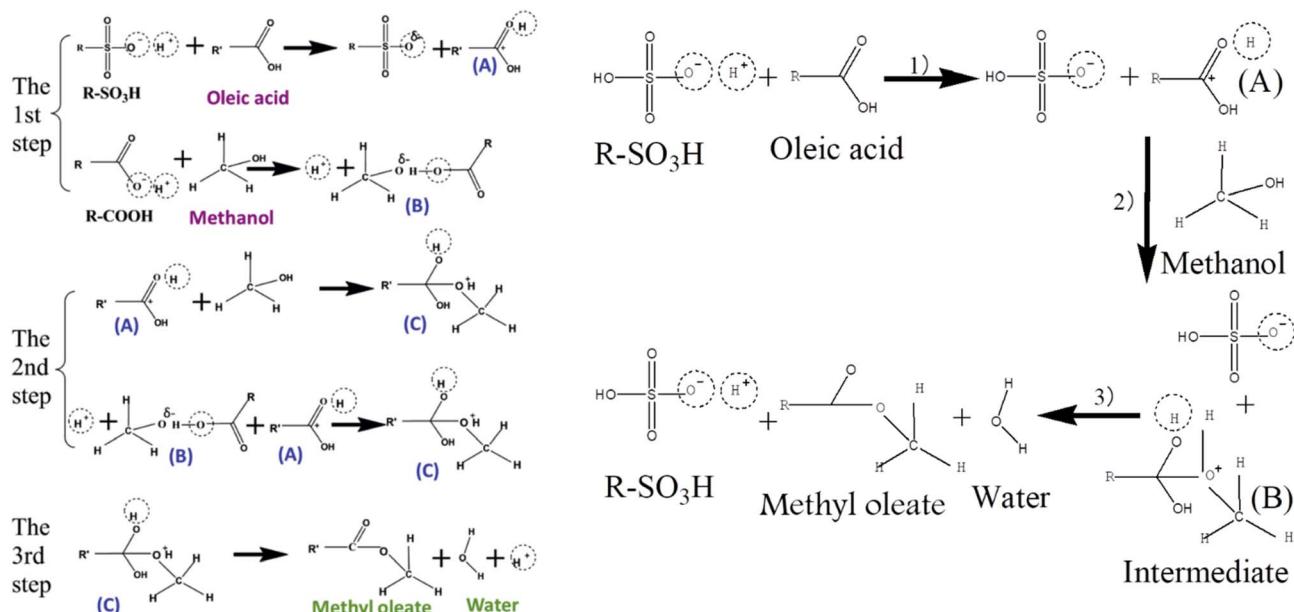
Fig. 2 Reaction mechanism of esterification process by SO_3H functionalized carbon material.[63]

morphology, incorporation of sulfonic sites, and surface area. The as-synthesized catalyst shows high efficiency using waste cooking oil (WCO) (96.25%) and microalgal oil (AO) (94.23%). The catalyst reusability study shows that the catalyst can be used for up to four cycles (≥90%) with a little loss in activity.[39] Orange peel is a primarily generated waste material obtained from food industries. Carbonization followed by sulfonation treatment was used to make the solid acid carbon catalyst from waste orange peel—the SO_3H group attached to the orange peel with a covalent bond. SEM images show that sulfonation has altered the surface of the orange peel with some cracks, partial disintegration, and partial oxidation. The fabricated catalyst has a large surface area of 44 m^2 g^{-1} and an acid density of 1.57 mmol g^{-1}. Catalyst efficiency is demonstrated using the transesterification of maize acid oil, yielding cost-effective biodiesel. Maize acid oil is a low-cost feedstock with an acid value of 127.21 mg KOH/g. Under optimal circumstances, Box–Behnken design achieves 91.68% biodiesel conversion.[73] In another study, corncob as a carbon precursor was used for transesterification reaction from soyabean oil. The optimal reaction conditions consisted of a microwave power range of 0–600 W, an oil-to-alcohol molar ratio of 1 : 6, a catalyst-to-oil mass ratio of 20%, and a reaction period of 20 min. The catalyst effectively accelerated the transesterification process in as little as 20 min, resulting in an 88.7% yield of pure biodiesel. The catalyst was utilized five times in succession without losing its catalytic activity.[74]

Bastos *et al.*[75] used the murumuru kernel shell (an agricultural waste) to develop an acid catalyst in biodiesel production from jupati oil. Based on a 2^3-central composite design, the response-surface approach was applied to determine the optimal reaction conditions. The as-fabricated catalyst was characterized by various techniques such as SEM-EDS, FTIR,

TGA, XRD, and total acid density. Methanol/oil molar ratio, catalyst concentration, and temperature were optimized in jupati biodiesel synthesis, yielding optimum reaction conditions of 30 : 1, 6, and 135 °C, respectively. The FAME production under these optimization conditions reaches 91.8%. The reusability studies of fabricated catalysts have shown less activity due to chlorophyll presence. Purified jupati oil also helps in the high catalytic activity, whereas unpurified vegetable oil results in catalytic loss of up to 60%[76]—the presence of pheophytin resulting in a decrease in activity. Strong adsorption of oil contaminants on sulfonated catalyst renders the active acid sites inactive after one cycle.[77] The problem was fixed by utilizing an adsorbent made from the murumuru nuts shell, which successfully removed 92.5% of the chlorophyll, left 0.9 ppm pheophytin level. As a result, the author proposes using the acid solid extracted from the murumuru kernel as a bifunctional catalyst for both biodiesel synthesis and chlorophyll eradication from vegetable oils. The synthesized catalyst shows excellent catalytic activity in four cycles in jupati oil. There was only a little decline in catalytic activity over time due to the leaching of acid sites.

During transesterification reaction, microalgal oil was purified with the help of various treatment method which results in high cost and energy loss. Lipid-rich wet algae obtained from *Nannochloropsis salina* can be converted into biodiesel without losing nutrient algae nutrient content by *in situ* transesterification process under microwave-assisted supercritical ethanol optimization conditions.[78] The lipids in wet algae may be extracted and trans-esterified into biodiesel in a single step using this method. In order to assess the oxidative and thermal stability of wet algae-derived ethyl esters, a thermogravimetric analysis was carried out in both oxygen and nitrogen atmospheres. The catalyst-free and green solvent *in situ*

transesterification process shows promise as a practical method for producing algae biodiesel. In another study, microalgal oil was used untreated to produce biodiesel. First, rice husk was sulfonated with the help of microwave acid treatment. The sulfonated rice husk was employed *in situ* transesterifications of *Parachlorella kessleri* (microalgal) biomass.[79] After optimizing the catalyst dosage, it was determined that a reaction duration of 30 min at room temperature (25 °C) yields the maximum FAME production with 30 mg catalyst. The author found that the surface area of rice husk fluorocarbon was high than sulfonated rice husk. However, the efficiency of the biodiesel production of sulfonated rice husk was better than rice husk fluorocarbon, which means that the surface area is not enough for the transesterification reaction. Due to the large area of rice husk fluorocarbon, actives sites become inactive due to the adsorption of triglyceride on its surface. These results demonstrated that the cell wall of the microalgae was ruptured by the sulfonated rice husk solid acid catalyst and that the triglyceride contents were released. These results demonstrated that the cell wall of the microalgae was ruptured by the sulfonated rice husk catalyst and that the triglyceride contents were released.

Quah *et al.*[80] fabricated the magnetic biochar from waste palm kernel shell (PMB) followed by sulfonation to generate active sulfonic sites—the optimization study was done with the help of response surface methodology. The biodiesel yield reaches up to 90.2% under optimum conditions. The incorporation of an iron layer, which may significantly enhance the catalyst separation performance in the biodiesel manufacturing process, allows PMB-SO$_3$H to be developed as a potential heterogeneous catalyst, which has significant practical implications. In another study, woody biomass was pyrolyzed at 450, 675, and 875 °C and sulfonated at 150 °C using fuming H$_2$SO$_4$.[81] Canola oil was used to assess the transesterification process of the synthesized catalyst. The author observed that the efficiency of biodiesel formation was dependent on total acid density and surface area, suggesting the highest efficiency of biodiesel was obtained at 675 and 875 °C. The biochar's carbon sheets become more reoriented toward a more graphite-like structure at higher carbonization temperatures, resulting in a decrease in the overall acid density despite an increase in surface area. Due to increased stiffness, sulfonic acid groups were more challenging to incorporate into activated carbon sheets at 875 °C. Carbonization at high temperatures helps form linked rigid carbon frameworks; may address this lack of activity by tuning the carbonization temperature to promote the creation of polycyclic aromatic carbons, which can then be sulfonated.[82] Table 4 demonstrate the various biomass derived catalyst for biodiesel formation.

5.2.1. Transesterification reaction mechanism and kinetics. Transesterification reaction mechanism of sulfonated carbon catalyst is shown in Fig. 3.[83] Transesterification reaction possess following process-

1. Triglyceride adsorbs on the catalyst surface, and SO$_3$H provides the sites through interaction betwixt ester linkage and acid sites/protons.

2. Further, two electrons from oxygen atoms in C–O–C are thought to have been donated to SO$_3$H groups. The oxygen atom attack most likely weakens the C–O–C bond, forming the carbonyl carbon OR1.

3. The adsorption of ethanol or alcohol follows a similar pattern. Sulfate ions increase ethanol's nucleophilicity to give protons (H$^+$). The attack on C–O–C by sulfate ions reduces the binding strength of the carbonyl carbon –OR. The carbonyl carbon is subsequently attacked by nucleophilic ethanol, yielding CH$_3$CH$_2$COOR. Finally, the ethanol protons (H$^+$) replace SO$_3$H in R–OSO$_3$H to generate glycerin, diglycerides, or monoglycerides.

Pseudo-homogeneous first-order[84] and second-order reaction models[85] for acidic catalyzed reactions are often used in heterogeneous catalyzed processes. Moreover, the Langmuir–Hinshelwood[86] and Eley–Rideal model,[65] both of which investigated the limiting factor in the chemical reaction process, have been published in the literature. The main difference between the Eley–Rideal model and the Langmuir–Hinshelwood model was that the Langmuir–Hinshelwood model assumes that two reactants (alcohol and triglyceride) were simultaneously adsorbed on the catalyst surface for reaction, while the Eley–Rideal model assumes that only one reactant (alcohol and triglyceride) was adsorbed on surface of catalyst for reaction.

6. Discussion and future perspectives

Biomass (a carbon material) is the most studied comprehensive material due to its low cost and easy availability. Among the family of solid protonic acids, the SO$_3$H-functionalized carbon compounds, also known as "sulfonated carbons," are a recent addition due to their high Brønsted acidity and low

Table 4 Various SO$_3$H functionalized catalyst for transesterification reaction

| Source	Acid density	Optimization parameters	Efficiency (%)	References
Durian peel	1.22	1 : 10, 9 wt%, 65 °C, 10 min	81.57	[72]
Micro-algal biomass	3.25	1 : 11, 3 wt%, 60 °C, 6 h (WCO)/1 : 11, 4 wt%, 70 °C, 8 h (AO)	96.25, 94.23	[39]
Orange peel	1.57	1 : 15, 5 wt%, 65 °C, 4.5 h	91.68	[73]
Corncob	0.89	1 : 6, 75 °C, 0.4 h	88.7	[74]
Murumuru shell	4.19	1 : 30, 6 wt%, 135 °C, 4 h	91.8	[75]
Rice husk	4.25	—, 30 mg, 25 °C, 0.5 h	100	[79]
Palm kernel shell	1.92	1 : 13, 3.66 wt%, 65 °C, 1.7 h	90.2	[80]
Woody biomass	1.2	1 : 15, 65 °C, 5 wt%, 3 h	44.2	[81]
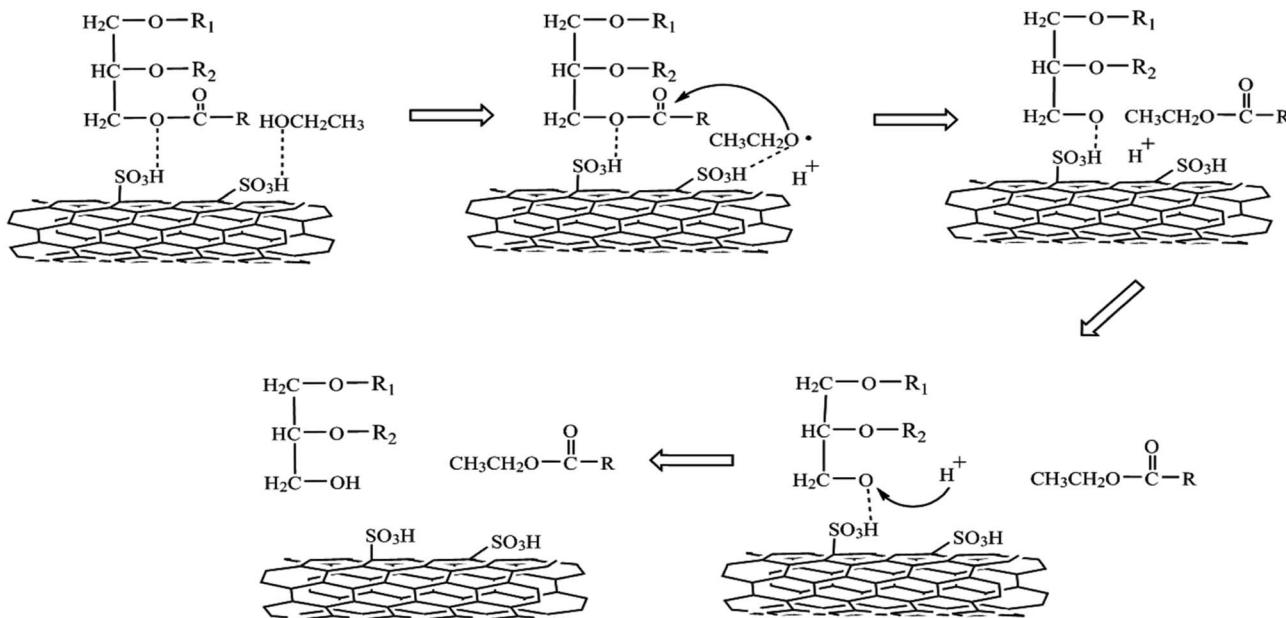
Fig. 3 Probable reaction pathways for transesterification reaction by SO_3H active sites.[83]

manufacturing cost.[24] These acidic carbons with SO_3H groups are typically generated by sulfonating amorphous carbon sources. SO_3H functionalized materials are used as a substitute of liquid sulfuric acid due to their high mechanical, thermal, and chemical stability, as well as their surface and pore structure.[25,87] Due to these properties, SO_3H catalysts are used in multiple applications, including esterification, transesterification, electrocatalysis, water treatment, CO_2 reduction, and energy storage.[45] A wide range of carbonaceous material is obtained depending on the carbon precursor, having varying textural features and functionalized SO_3H group. Due in part to dwindling resources of novel and rare earth metals typically utilized as catalysts in industrial processes, the application of heterogeneous carbon catalysts in electrochemical and organic transformation processes has significantly advanced over the last decade. The sulfonated carbons with high specific surface areas are potential catalysts for the transformation of large hydrophobic and hydrophilic compounds since they are water-tolerant and compatible with hydrothermal reaction conditions.

Fig. 4(a) shows the effect of temperature and time on the total acid density caused due to OH, COOH, and SO_3H. The total acid density is directly linked to biodiesel production. High total acid density results in an increase in the biodiesel production yield. Among the reaction methods, microwave and ultrasonic methods cause a high biodiesel yield in less time {Fig. 4(b)}. There are numerous approaches for the functionalization of carbonaceous material for SO_3H grafting. Sulfonation coupled with carbonization (HTC) is an effective and straightforward approach for the fabrication of SO_3H functionalized carbon catalyst, which possesses high SO_3H acid density. Despite the high SO_3H acid density, these carbonaceous materials possess high oxygen functional sites, less porosity, and low

thermal stability. Consequently, the carbonaceous materials fabricated using the HTC method cannot be used at high temperatures and hydrophobic mediums. Additionally, these carbons exhibit low levels of polycondensation and a soft (less rigid) structure. Moreover, HTC methods cause serious environmental issues due to the utilization of significant amount of H_2SO_4, which results in the emission of hazardous acid gases like SO_2 and SO_3 and the production of neutralizing waste generated during washing and carbonizing.

In another method, biomass is pyrolyzed in the absence of oxygen (in the presence of N_2 or Ar) to form biochar (carbonaceous material).[88] The carbonization temperature has a direct influence on the surface of biochar. The catalyst synthesized at low carbonization temperature (400–600 °C) has a significant impact on the structure. Several acids, like H_3PO_4, HCl, and $ZnCl_2$, improve the dehydration process, which results in an increase in the surface area and pore diameter of the synthesized carbonaceous material. A high temperature (greater than 600 °C) results in the breakage of carbonaceous structure. Then the synthesized biochar was functionalized with various activating agents such as sulfuric acid, toluene sulfonic acid, chlorosulfonic acid, fuming SO_3, *etc.* The biochar has aromatic carbon structure in which the aromatic hydrogens are substituted by the SO_3H groups during the sulfonation process. The incorporation of the SO_3H active site on the biochar surface results in a slight decrease in the surface area of the carbonaceous material. The simultaneous carbonization and sulfonation process preserve the meso/nanostructure of the carbonaceous material, which bonded covalently with SO_3H sites. The insertion of SO_3H sites depends on a number of factors, including sulfonation time, temperature, amount, and type of sulfonating agent {Fig. 4(a)}. After grafting, a number of SO_3H functionalized materials are obtained, which differs in
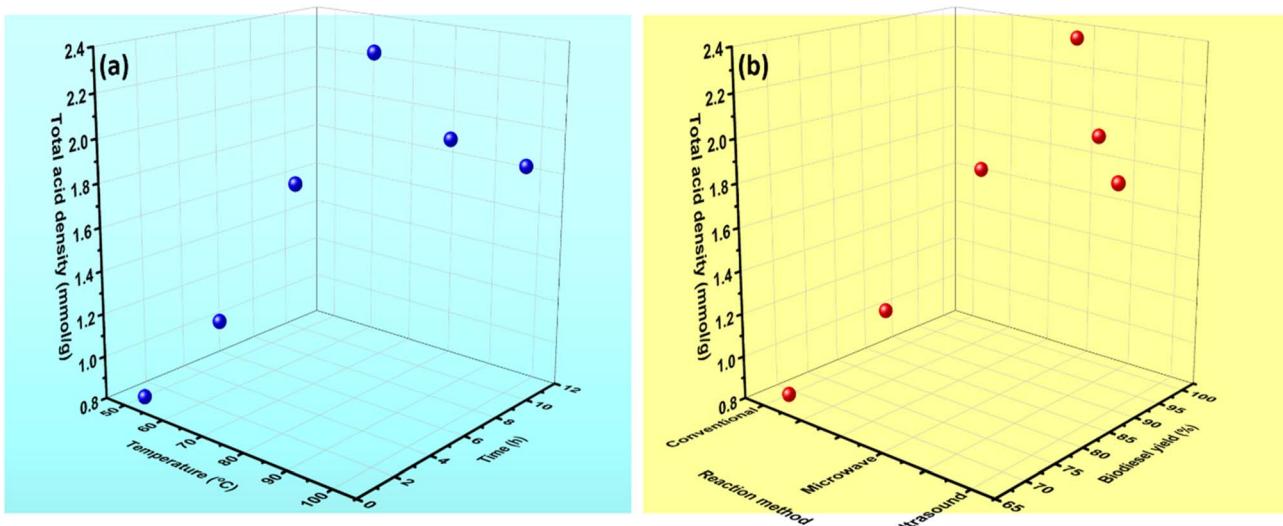
Fig. 4 (a) Effect of temperature and time on total acid density, and (b) effect of total acid density on biodiesel production.

terms of SO$_3$H density, textural properties, and surface chemistry ((hydrophilicity/hydrophobicity). The catalyst activity directly depends on the total acid density, SO$_3$H acid density, surface area, pore size, and the number of functional groups. However, the reusability study shows that the sulfonated carbon catalysts show effective reusability up to 4 to 5 cycles. The loss of total acid density due to SO$_3$H site leaching is the reason for the loss of activity. On the other hand, the catalysts often experience activity loss due to reversible deactivation by ion exchange and pore blockage brought on by impurity adsorption. Biochar, hydrochar, and partly carbonized materials, all of which exhibit a modest polycondensation degree after being functionalized by sulfonic acid treatment, are known to undergo fast irreversible deactivation under high-temperature, high-pressure conditions. The carbonaceous material is deactivated in the alcohol medium due to the creation of sulfonate ester under high pressure.

The exact mechanism of deactivation of SO$_3$H functionalized carbon catalyst is not clear till now. Additional experiment investigations like NMR, mass, and FTIR spectroscopic methods and molecular modelling may give insights details of deactivation, activation, and stability of actives sites under various conditions. The large-scale production of biodiesel from the SO$_3$H functionalized carbon catalyst requires reaction kinetics by mathematical modeling. Density functional theory and molecular modeling elucidate the adsorption–desorption of products, reactants, and impurities (H$_2$O and humins) on the catalyst surface. The selectivity, activity, activation, and deactivation of sulfonated carbon catalysts can be better understood by these modeling methods. Further research in flow fixed-bed reactors, in particular, should be conducted to assess catalyst durability beneath commercially acceptable conditions. More study should be carried out to assess the stability of SO$_3$H active sites in the presence of oxidizing and reducing environment as the carbonaceous material has shown promising for

bifunctional metal fabrication by selective deposition on oxygenate surface.

Glycerol formation during the transesterification process resulted in an increase in the cost of biodiesel synthesis. A simple approach is considered to remove glycerol from the reaction mixture. Nearly 10% of glycerol was produced from transesterification reactions. Glycerol can be valorized by numerous methods, such as acetalization, dehydration (acrolein), esterification (acetin formation), etherification, and transesterification (glycerol carbonate), which are used further for fuel additives. The heterogeneous acid catalysts are useful for the glycerol valorization and reduce the expense of biodiesel production.

Although biomass is a cheap carbon precursor for the development of biodiesel. However, highly refined vegetable oil resulted in a high biodiesel cost, which retard the growth of biodiesel synthesis. The waste cooking oil should be beneficiary, but the high free fatty acid content should not be neglected. So, it is better to use waste cooking oil after pretreatment. FFA such as oleic acid and others are also good choices for biodiesel production.

Nanoparticle incorporation into sulfonated carbon catalyst significantly enhance the activity of the catalyst thus improving the biodiesel production. In addition, the use of nano-catalysts eliminates the need for cleansing, thereby reducing the expense of biodiesel production.

7. Conclusion

In this review, the authors discuss the utilization of various biomass-derived heterogeneous catalysts for biodiesel production. The economically viable biodiesel manufacturing needs moderate reaction conditions and an acceptable molar alcohol ratio. The SO$_3$H functionalized carbon catalysts are a novel type of solid acid catalysts for biodiesel generation with a unique carbon structure, chemical inertness, Brønsted acidity,

structural diversity, surface hydrophobicity, and high thermal and mechanical durability. The catalyic activity of the SO_3H functionalized carbon material depends on the temperature, sulfonating agent, and time. The sulfonation process parameters determine the acid density and biodiesel production. The higher the total acid density of the catalyst, the higher the biodiesel production. The heterogeneous catalyst derived from biomass shows excellent reusability for up to four or five cycles. In addition, the mechanism and kinetics of biodiesel production were investigated throughout this study. In addition to being a cheap, readily manufactured, stable, and effective biodiesel production catalyst, the catalyst also benefits from being synthesized from biomass, making it a more environmentally friendly option.

Conflicts of interest

There are no conflicts to declare.

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