CHEMICAL ENGINEERING TRANSACTIONS

VOL. 89, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Jiří Jaromír Klemeš

ISBN 978-88-95608-87-7; **ISSN** 2283-9216

DOI: 10.3303/CET2189082

Starch-derived Solid Acid Catalyst for Biodiesel Production: A Mini Review

Wan Ting Tan[a], Mazura Jusoh[a], Zaki Yamani Zakaria[a,b,*]

[a] School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Malaysia
[b] Centre for Engineering Education, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Malaysia
zakiyamani@utm.my

An international agreement to combat the global climate change issue - Paris Climate Agreement which involved participation of 190 parties as of January 2021, showed the world's concern on the global climate change issue. Greenhouse gas emission, especially carbon emission due to combustion of fossil fuels for both industrial and residential uses has created a severe effect on environment. In the last few decades, significant attention has been paid on biodiesel as a potential alternative source of energy for replacement of fossil fuel. Biodiesel is commonly produced through transesterification process with the presence of catalyst. Homogeneous catalysts that had been widely used in the biodiesel production caused difficulty in separation, unable to be reused and easily to be consumed during the process, while heterogeneous solid acid catalyst hold multiple competitive advantages such as their surface hydrophobicity features, reusability and mechanical stability. Various effective heterogeneous metal-based catalysts are costly, consequently more study has been focused on heterogeneous carbon-based catalyst that synthesized by biomass which is more cost effective. Among numerous carbon-based catalysts, carbohydrate-derived catalyst especially starch emerged as an effective and potential catalyst for sustainable biodiesel production. In this study, starch-derived heterogeneous solid acid catalysts for biodiesel production are briefly reviewed. The utilization of these catalysts may be the new direction towards a cheaper, cleaner and greener synthesis of biodiesel.

1. Introduction

In the last few decades, we relied heavily on the consumption of fossil fuels for the generation of energy that could be used for both industrial and residential purposes. It is estimated that 44 × 10^{15} kg of atmospheric carbon was generated in a year due to consumption of fossil fuels, equivalent to 400 times the value of annual carbon set by primary productivity of current global biota (Dukes, 2003). Serious environmental impacts due to continued reliance and consumption of fossil fuels has created awareness and demands for sustainable and renewable energy as replacement of fossil fuels (Zailan et al., 2020). To combat climate change, international agreement such as Paris Climate Agreement that involved participation of 190 parties as of January 2021, showed the world's apprehensions and attentions on this environmental issue. The Sustainable Development Goals (SDGs) which is also known as global goals were introduced and adopted by United Nations Members States in 2015, in order to achieve a better and sustainable future. There are 2 out of 17 SDGs related to environmental issue, which are Goal 7 (Affordable and Clean Energy) and Goal 13 (Climate Action). Other countries such as China and Japan also realized the negative impact of usage of fossil fuel energy to environment and decided to ban import and sales of petrol and diesel car, while promoting electric vehicle (EV) or hybrid car as alternatives.
Biodiesel (methyl ester) has emerged as one of the alternative solutions to solve current world environmental issues and energy crisis, as replacement of fossil fuel for energy generation (Bohlouoli and Mahdavian, 2019). Chemically, biodiesel can be defined as a linear long fatty acid alkyl esters chain that produced through the transesterification process of feedstock oils and alcohol in the presence of catalyst (Guan et al., 2009). Transesterification can be catalysed homogeneously or heterogeneously to reduce the activation energy of the reaction and enhance the process output. Previously, homogenous catalysts had been widely used in the biodiesel production, as they are efficient in converting feedstock with low FFA content and water into

Paper Received: 21 June 2021; Revised: 15 September 2021; Accepted: 14 November 2021
Please cite this article as: Tan W.T., Jusoh M., Zakaria Z.Y., 2021, Starch-derived Solid Acid Catalyst for Biodiesel Production: A Mini Review, Chemical Engineering Transactions, 89, 487-492 DOI:10.3303/CET2189082

biodiesel (Rizwanul et al., 2020). When feedstock with higher FFA content which is more economical such as waste cooking oil and palm fatty acid distillate is used, problems such as soap formation that affect catalytic activity, product separation difficulties arise (Tan et al., 2019). Homogeneous catalysts are not reusable and easily to be consumed in the process (Mathew et al., 2021)

Heterogeneous acid catalyst is a potential and effective alternative catalysis method compared to conventional biodiesel production process that employs homogeneous catalyst, due to its simplistic and environmentally friendly features and its ability to the promote both esterification and transesterification process simultaneously (Nata et al., 2017). Heterogeneous solid acid catalyst was also found to hold multiple competitive advantages such as their surface hydrophobicity features, reusability and mechanical stability (Ning and Niu, 2017). Various effective heterogeneous metal-based catalysts are costly; consequently more study has been focused on heterogeneous carbon-based catalyst derived from biomass which is more cost effective.

Among numerous carbon-based catalysts, carbohydrate-derived catalyst especially starch, emerged as a promising catalyst for sustainable biodiesel production (Lou et al., 2008). The objective and focus of this review is to discuss the heterogeneous solid acid catalyst that are derived from carbohydrate especially starch, as a potential catalyse that can be used to enhance the process performance of biodiesel production, as this may be a new direction towards more economical and greener synthesis route in biodiesel production.

1.1 Source, structure and composition of starch

Starch is one of the polysaccharide and natural polymer that can be abundantly found in various parts of plants, such as roots, stems, tubers, leaves, fruit and seed. Starch is generated though photosynthesis reaction and it is stored within the plant bodies as source of food and energy for plants. Commonly, wheat, rice and barley as cereals grains are one of the major sources of starch. The seeds of legumes like peas, pulses and beans, tubers like ginger, potato and sweet potato, groundnut and immature vegetables or fruits are also the main sources of starch (Nawaz et al., 2020).

Chemically, starch have the chemical formula of $(C_6H_{10}O_5)_n$ and can be defined as a homopolymer of α-Glucopyranose units. Starch is composed of two kinds of polysaccharides chains, which are amylopectin and amylose. Amylopectin has a branched structure with both α1–4 and α1–6 glycosidic linkages linking the monomers together. Amylose has a linear structure with α1–4 glycosidic linkages connecting the glucose monomers, as shown in Figure 1 (Nawaz et al., 2020). Usually, starch consists of more amylopectin than amylose (70 – 80 % of amylopectin and 20 – 30 % of amylose). Starch’s structure in terms of its crystallinity, size, and arrangement of polymers within the granule and chemical properties will be affected by the amylose/amylopectin ratio.

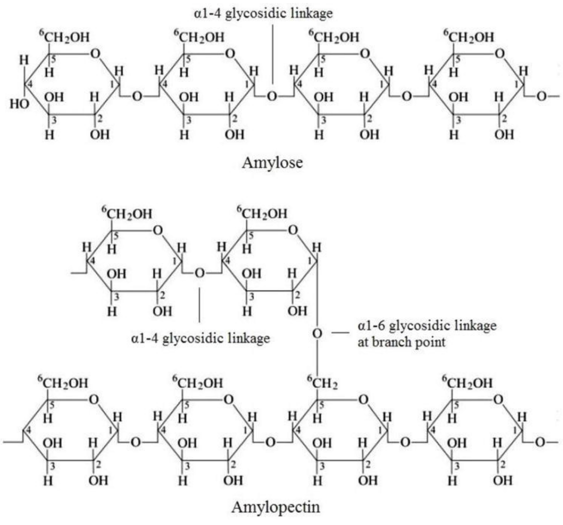

Figure 1: Structure of amylose and amylopectin in starch (Nawaz et al., 2020)

1.2 Sulfonated carbon-based solid acid catalyst

For the uses of heterogeneous catalysts in reaction, the reactive materials or mixtures are in different phases, and the reaction will take place at the surface of catalyst. Heterogeneous catalyst that can be used to enhance biodiesel production can be divided into acidic and alkaline types.

Solid phase catalyst used in the reaction process can be separated easily after the completion of esterification and transesterification reactions for repeatedly uses. It is often more cost-effective and eco-friendly.

Heterogeneous type catalyst will also reduce the biodiesel filtration process, results in a lower energy and water consumption. Heterogeneous catalysts synthesis process might be complex and expensive, which lower down the overall cost effectiveness in biodiesel production.

Sulfonated Carbon Based Solid Acid Catalyst (CBASs) is a type of potential heterogeneous solid acid catalyst that can be used to enhance the performance in biodiesel production. It can use either carbohydrate or biomass as raw materials and carbon precursors of the catalyst. CBASs had grab researches' attentions as it hold several significant advantages as: i) Can tolerate with high FFA content and water content in reactant mixtures - CABSs can tolerate with high FFA and water content in the feedstock oil (Escobar et al., 2009). This means low quality oil can be utilized as feedstock oils, without affecting the quality of product (biodiesel) synthesized; ii) Reliable reusability - CBASs as one of heterogeneous solid acid catalyst can ease the separation of mixtures after the reaction (Hara, 2010). The heterogeneous solid acid catalyst can be separated and reused in next reactions to reduce the costing for catalyst in biodiesel production; iii) Chemically inert and can carry out esterification and transesterification process simultaneously - CBASs are chemically inert, which prevent the undesired side reactions and changes along the process (Hara, 2010). It also allows the esterification and transesterification process to occur simultaneously and save costs for extra equipment, buildings, stages required to complete the process for biodiesel production; iv) High affinity for esterification and transesterification reaction - CBASs shows high affinity for both esterification and transesterification chemical reactions in synthesis of biodiesel (Clohessy and Kwapinski, 2020). CBASs also have better activity for both processes, compared to some existing and readily available solid acid catalyst like sulphated zirconia and niobic acid; v) Have strong Bronsted and Lewis acid sites, high pore volume, high average pore size, unique porosity, high acid site density, and hydrophobic surface - CBASs have been shown as a useful catalyst for the biodiesel production, as a result of having strong acidic active sites, high acid site density with hydrophobic surface that prevent leaching, large pore volume and average pore size and unique porosity that promote faster reaction rate (Lou et al., 2008).

2. Starch as carbon precursor in synthesis of sulfonated carbon-based solid acid catalyst

Carbohydrate or biomass can be used as the raw materials and carbon precursors, for the synthesis of CBASs. There are 4 types of carbon sources that can be used for synthesis of CBASs, which are refined carbohydrate, biomass residue, biochar and activated carbon (Abdullah et al., 2016).

Among the sources of carbon for catalyst synthesis, biomass residue that consists of large numbers of organic hydrocarbon compounds such as starch, have been a great option since it is environmentally friendly, economical and readily available as waste from respective industry (Abdullah et al., 2016). The usage of biomass waste in other useful manners may also help to reduce amount of waste generated and lower down industrial cost through proper and hygienic waste disposal (Chua et al., 2020). The catalysts can be synthesized by a series of steps, which are carbonization, dissociation of bonds, carbon sheets formation, followed by the formation of large polycyclic aromatics sheets (Clohessy and Kwapinski, 2020). The mechanism of sulfonated carbon-based solid acid catalyst synthesis is as shown in Figure 2.

Biomass that mainly consists of starch components will be carbonized at high temperature to remove water and reduce moisture contents of the molecules. The (-C-O-C-) bond inside the starch structure is then dissociated, forming polycyclic aromatic carbon sheets within the starch structure. The carbon sheets formed after the dissociation of (-C-O-C-) bonds are then proceeded to sulfonation process with sulfonating agents such as sulphuric acids, introducing acidic functional groups into edge of the carbon rings formed earlier. Carbonization temperature is raised again and cause the formation of the larger polycyclic aromatic sheets, along with layered polycyclic aromatic rings, that reduce the number of vacancy sites of acidic groups to attach to it. This is in agreement with Mohamed et al. (2019) study that use rice straw to synthesis catalyst.

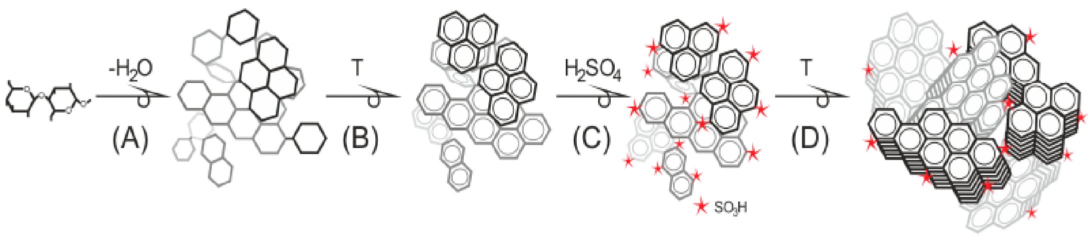

Figure 2: Mechanism of sulfonated carbon-based solid acid catalyst synthesis (Clohessy and Kwapinski, 2020)

3. Performance review of different carbon-based solid acid catalyst

3.1 Comparison of different carbon-based solid acid catalyst

Some experiments were carried out by researchers, using different type of carbon-based solid acid catalyst for synthesis of biodiesel (methyl oleate), to test and compare the performance and conversion of these catalysts. The summary of the experimental results are tabulated in the Table 1 as shown below. According to the results obtained, generally carbohydrate-derived solid acid catalysts give better performance than the rest of the acidic catalysts that used in biodiesel production. Carbohydrate-derived solid acid catalyst can be divided into few types, depending on the raw materials used as the carbon precursor of the catalyst, such as starch, cellulose, sucrose and glucose (Clohessy and Kwapinski, 2020).

Among these 4 types of carbohydrate-derived solid acid catalyst, starch-derived catalyst has the best performance against the rest. Starch-derived solid acid catalyst has the highest acid site density, highest sulphur content and highest SO_3H acid site density. Besides, it also possesses favourable properties such as large surface area, large pore volume and pore size that allowed reactants to access to SO_3H acid active sites easily, resulting in higher efficiency and performance of esterification process. Solid acid catalyst that synthesized through starch also proved to have the ability to retain around 93 % of its initial catalytic activity after 50 cycles of successive recycle and reuse, indicating that it has good operational stability in enhancing the biodiesel production process (Lou et al., 2008).

Table 1: Comparison of different carbon-based solid acid catalyst

Catalyst	S Content (wt.%)	Total Acid Site Density (mmol/g)	SO_3H Acid Site Density (mmol/g)	Surface Area (m^2/g)	Average Pore Volume (cm^3/g)	Average Pore Size (nm)	Catalytic activity (μmol min^{-1})	Yield of methyl oleate (wt%)	Reference
D-glucose	4.7	1.60	1.47	4.1	0.44	4.0	-	70	Clohessy and Kwapinski (2020)
Sucrose	5.1	1.71	1.59	5.0	0.52	5.1	-	72	
Cellulose	5.4	1.82	1.68	5.7	0.65	6.4	-	78	
Starch	5.9	1.97	1.83	7.2	0.81	8.2	-	92	
Sugar Catalyst	-	-	-	-	-	-	67	90	Zong et al. (2007)
Amberlyst 15	-	-	-	-	-	-	7	15	
Sulphated Zirconia	2.5	0.40	-	218	0.18	2.7	21	85	Lou et al. (2008)
Niobic Acid	-	0.30	-	128	-	-	1.5	6	
Biochar	-	2.60	-	1.9	0.01	2.6	-	44.2	Yu et al. (2011)
Peanut shell	-	6.90	-	12.0	-	39.3	-	90.2	

3.2 Economic assessment of carbohydrate-derived solid acid catalyst

Other than the performance and efficiency of these catalysts, raw materials that may lift up the overall production cost of biodiesel must be taken into consideration. Economic assessment of carbohydrate-derived solid acid catalyst is as shown in Table 2 below. The catalysts are synthesized using carbonisation temperature of 400 °C, sulfonation with concentrated H_2SO_4 at 150 °C for 15 h. Biodiesel production carried out using waste cooking oil (WCO) with 27.8 wt% FFA, methanol to WCO ratio of 20:1, 10 wt% catalyst loading under temperature of 80 °C for 8 h. Glucose and starch were relatively economical compared to sucrose and as raw materials of the solid acid catalyst. Referring to the catalyst performance in Table 1 and the economic assessment in Table 2, starch-derived catalyst shows relatively high potential to be a promising catalyst to enhance performance in biodiesel production. Source of starch could be in focus of future study, which may cost lower than commercial available starch powder through direct purchase.

Table 2: Economic assessment of carbohydrate-derived solid acid catalyst (Clohessy and Kwapinski, 2020)

Catalyst	Cost (USD/kg) (Sigma Aldrich)	Yield of methyl oleate (wt%)
D-glucose	39.2	70
Sucrose	93.4	72
Cellulose	196.0	78
Starch	31.9	92

3.3 Potential biomass sources of starch for synthesis of solid acid catalyst

Carbonaceous material such as activated carbon, biochar, hydrochar, carbon nanotube and ordered mesoporous carbon can be used in the synthesis of sulfonated carbon acid (Zailan et al., 2021). Esterification process will have different result and performance, depending on the type of catalyst presence in the process. Different chemical and physical properties of biomass used result different physiochemical properties of the catalyst prepared, which later affect catalytic activity of the catalyst (Rechnia-Gorcy, 2018).

Biomass residue sources that rich in carbon might be a potential raw materials for synthesis of solid acid catalyst that can be used to enhance the performance of biodiesel production (Kanokwan et al., 2016). One of the readily available biomass source is metroxylon sago pith waste (MSPW) which is easily available and abundant in quantity. In Malaysia, most of the sago palm estates are located at Sarawak. Development of state government-subsidized scheme, along with existing wild stands in the coastal area has promoted the increase of sago palm plantations (Bukhari et al., 2017).

There is approximately 400 kg of dried starch contained in the pith of a single *Metroxylon sagu* Rottb tree. Only half of starch can be extracted with current mechanical processing methods, while the other half will be retained in the residual pith waste (Mishima, 2018). Metroxylon sago pith waste (MSPW) is often generated as waste from sago refinery process and unwanted.

The main component in MSPW is starch with a minor component of lignin, cellulose, and hemicellulose as shown in Table 3 below (Bukhari et al., 2017). Starch contained in MSPW will later become carbon precursor of the catalyst prepared and this has attracted researchers' attention due to less energy intensive consumption and less preparation time, but still an effective catalyst for biodiesel production.

Preparation conditions of biomass as raw materials of starch-derived solid acid catalyst, such as operating temperature and condition, sulfonating agent, preparation time and conversion ratio to useful catalyst have to be studied, as these parameters will affect the efficiency and cost effectiveness of the catalyst. Selection of the raw materials also have to be taken into consideration, as cost of acquisition of the biomass waste or residue, quantity and availability may lift up the cost of catalysts.

Table 3: Chemical composition of metroxylon sago pith waste (MSPW) (Bukhari et al., 2017)

Component	Content (%)
Moisture Content	12.50 ± 0.01
Holocellulose	5.05 ± 1.35
Alpha cellulose	23.69 ± 0.69
Hemicellulose	11.78 ± 0.25
Ash	11.91 ± 0.43
Starch	68.92 ± 2.12

4. Conclusions

As the world moving towards a greener and cleaner energy, biodiesel as one of the alternatives energy sources has gained attention from researchers due to its potential to replace fossil fuel energy. Generation of greener and cleaner energy are often more costly than fossil fuels. Heterogeneous catalyst that hold multiple advantages and can be used to enhance the conversion and performance of biodiesel production had gained researchers attention. Synthesis of the heterogeneous catalyst which is often costly may lift up the overall production costs of biodiesel. Starch-derived solid acid catalyst had shown to be a promising catalyst that is economical and effective in biodiesel production. The cost for synthesis of starch-derived solid acid catalyst can be further lowered down, by using biomass residue that contain high starch content such as metroxylon sago pith waste (MSPW) as raw materials of the catalyst. Further studies have to be done on the conversion ratio and suitable operating conditions for catalyst synthesis and biodiesel production using starch-derived solid acid catalyst, as the utilization of these catalysts may be the new direction towards biodiesel production. Performance of cheap feedstock oils such as palm fatty acid distillate can be studied with the catalyst. With efficient and economical production route, biodiesel can be one of the cheapest, environmental and user friendly renewable energy sources, and may become one of the economic booster of Malaysia in future.

Acknowledgments

The authors would like to thank Universiti Teknologi Malaysia's Fundamental Research Grant (21H37) and Ministry of Higher Education Malaysia (MOHE) for the financial support through Fundamental Research Grant Scheme (FRGS/1/2020/TK0/UTM/02/97).

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