



UNIVERSITI PUTRA MALAYSIA

***FUNCTIONALIZATION OF CARBON CATALYST DERIVED FROM
CORNCOB RESIDUE VIA HYDROTHERMAL TECHNIQUE FOR
ESTERIFICATION OF PALM FATTY ACID DISTILLATE***

SITI FADHILAH BINTI IBRAHIM

FS 2021 52



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CORNCOB RESIDUE VIA HYDROTHERMAL TECHNIQUE FOR
ESTERIFICATION OF PALM FATTY ACID DISTILLATE**

By

SITI FADHILAH BINTI IBRAHIM

**Thesis Submitted to the School of Graduate Studies,
Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of
Master of Science**

May 2021

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ESPECIALLY DEDICATED TO

My Beloved Parents

Allahyarhamah Aminah Binti Semail & Ibrahim Bin Mamat

and

All my family members who continue supporting throughout this journey

Abstract of the thesis presented to the senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

FUNCTIONALIZATION OF CARBON CATALYST DERIVED FROM CORNCOB RESIDUE VIA HYDROTHERMAL TECHNIQUE FOR ESTERIFICATION OF PALM FATTY ACID DISTILLATE

By

SITI FADHILAH BINTI IBRAHIM

May 2021

Chair : Professor Datuk ChM. Ts. Taufiq Yap Yun Hin, PhD
Faculty : Science

Biodiesel as an energy resource was recognized as a potential low carbon alternative to overcome the declining fossil fuel reserves. However, the higher cost production of biodiesel become the main problem. In this work, low-cost biodiesel was successfully produced through esterification of palm fatty acid distillate (PFAD) over heterogeneous solid acid catalyst derived from corncob residue. This catalyst was synthesized via hydrothermal carbonization followed by chemical activation using concentrated sulfuric acid and known as hydrothermal carbon-sulfonated (HTC-S). The prepared catalysts were characterized by using X-Ray Diffraction (XRD), Brunauer - Emmett -Teller (BET) Surface Area Measurement, Fourier Transform Infrared (FT-IR) Spectroscopy, Temperature Programmed Desorption of Ammonia (NH₃-TPD) and Field-Emission Scanning Electron Microscopy (FESEM) analysis. The carbonization process leads to the cyclic carbon rearrangement by removing hydroxyl molecules and the sulfonation treatment on the carbon structure increase the acid properties with the total acid density of 13.00 mmol/g and surface area of 8.40 ± 0.15 m²/g. The esterification of PFAD over HTC-S catalyst was optimized via the one-variable-at-a-time technique, and 92% free fatty acid (FFA) conversion with a biodiesel yield of 85% were achieved at condition of 2 h reaction time, 70 °C reaction temperature, 3 wt.% catalyst loading, and 15:1 methanol-to-oil molar ratio. Various of catalyst regeneration techniques were analyzed and sulfuric acid treatment was found to be the most effective approach for restoring the active sites for spent HTC-S catalyst. The HTC-S catalyst regenerated via sulfuric acid treatment is capable to convert PFAD to biodiesel with FFA conversion until five consecutive cycles. In this work, the synthesized PFAD-derived biodiesel has complied with the international biodiesel standard ASTM D6751.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**PENGFUNGSIAN PEMANGKIN KARBON DARIPADA SISA JAGUNG
MELALUI TEKNIK HIDROTERMA UNTUK PENGESTERAN BAHAN ASID
LEMAK SAWIT SULINGAN**

Oleh

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Pengerusi : Profesor Datuk ChM. Ts. Taufiq Yap Yun Hin, PhD
Fakulti : Sains

Biodisel adalah sumber tenaga dikenali sebagai pengganti minyak alternatif yang rendah karbon dan berpotensi untuk mengatasi masalah rezab bahan bakar fosil yang semakin menurun. Walaubagaimanapun, kos yang tinggi untuk menghasilkan biodisel melalui tindak balas transesterifikasi menjadi masalah utama. Dalam kajian ini, biodisel dengan kos yang murah telah berjaya dihasilkan melalui esterifikasi asid lemak sawit tersuling (PFAD) dengan menggunakan pemangkin heterogen asid pepejal yang dihasilkan daripada sisa puntung jagung. Pemangkin telah disintesis melalui pengkarbonan hidroterma diikuti dengan proses pengaktifan kimia menggunakan asid sulfurik pekat melalui proses hidroterma karbon- sulfonasi (HTC-S). Perincian pemangkin yang dihasilkan telah dilakukan menggunakan Pembelauan Sinar-X (XRD), Brunauer - Emmett -Teller (BET), Spektroskopi Inframerah Penukaran Fourier (FT-IR), Suhu Terprogram Nyahjerapan Ammonia (NH₃-TPD) dan *Field-Emission* Mikroskopi Imbasan Electron (FESEM). Proses pengkarbonan telah menyebabkan pengstruktur semula kitaran rangkaian karbon disebabkan oleh pelepasan molekul hidroksil, dan proses sulfonasi karbon telah meningkatkan tahap keasidan pemangkin dengan jumlah keseluruhan adalah 13.00 mmol/g dan luas permukaan $8.40 \pm 0.15 \text{ m}^2/\text{g}$. Proses pengoptimuman esterifikasi PFAD menggunakan pemangkin HTC-S telah dilakukan melalui teknik *one-variable-at-a-time* (OVAT). Sebanyak 92% asid lemak bebas telah ditukarkan dan 85% biodiesel tulen telah terhasil selepas 2 jam masa tindak balas, suhu tindak balas ialah 70 °C, bahan mangkin ialah 3 wt.% dan nisbah molar metanol kepada minyak ialah 15:1. Pelbagai jenis kaedah penjanaan semula pemangkin telah dikaji dan penjanaan melalui sulfurik asid didapati teknik yang paling berkesan untuk memulihkan semula aktiviti pemangkin HTC-S yang telah digunakan. Pemangkin HTC-S dijana semula melalui rawatan asid sulfurik boleh menukarkan PFAD kepada biodisel sehingga lima kali kitaran. Biodisel yang dihasilkan daripada PFAD dalam kajian ini juga didapati telah mematuhi piawaian biodiesel antarabangsa ASTM D6751.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

| | |
|-------|---|
| ASTM | American Society for Testing and Materials |
| BET | Brunauer - Emmet –Teller |
| BJH | Barret- Joyner- Halena |
| B5 | Blending 5 Vol.% |
| B20 | Blending 20 Vol.% |
| B30 | Blending 30 Vol.% |
| B40 | Blending 40 Vol.% |
| B100 | Pure biodiesel |
| CERA | Cambridge Energy Research Associates |
| CPO | Crude Palm Oil |
| CN | Cetane Number |
| CHNOS | Carbon Hydrogen Nitrogen Oxygen Sulfur elemental analysis |
| EN | Euro Norm |
| EDX | Energy Dispersive X-Ray |
| FAME | Fatty Acid Methyl Ester |
| FFA | Free Fatty Acids |
| FID | Flame Ionization Detector |
| FP | Flashpoint |
| FTIR | Fourier -Transform Infrared |
| GC | Gas Chromatography |
| JCPDS | Joint Committee on Powder Diffraction Standards |
| MS | Mass Spectroscopy |
| OVAT | One-Variable-at-A-Time |
| PM | Particulate Matters |

| | |
|----------------------|--|
| RSM | Response Surface Methodology |
| RF | Response Factor |
| TAGs | Triacylglycerides |
| TG | Triglyceride |
| NH ₃ -TPD | Temperature Programmed Desorption of Ammonia |
| FESEM | Field-Emission Scanning Electron Microscopy |
| XRD | X-Ray Diffraction |



CHAPTER 1

INTRODUCTION

1.1 Background

Energy is very important for humanity's endeavors across every single industrial and technological sector. For century, the energy sources have been used for electricity applications likes fossil fuels, hydroelectricity, nuclear energy and so on. It has been known that the energy can be derived from sources of biomass, solid fuels, liquid fuels and others by process of transformation or conversion. Even with strong growing of renewable resources for the last few decades, fossil-based fuels persist to be the most dominant worldwide. (Takase et al., 2015; Mekhilef et al., 2011) showing in Figure 1.1.

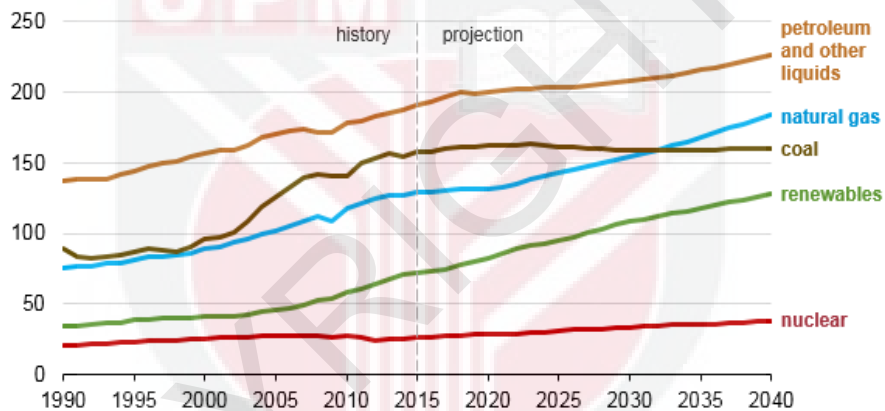


Figure 1.1: World energy consumption by energy sources (1990-2040) quadrillion British thermal units (International Energy Outlook., 2017)

Fossil fuels helps the development of country in transportation to industrial applications. Since the 19th century, this fossil fuels have been used abundantly by the humans. If this continues, it will diminish in the future. King Hubbert (1950), a geologist has estimated that the exhaust of fossil fuel will damage the development of the world (Hanania Jordan & Stenhouse Kailyn, 2015). As reported by Mansir et al., (2017) the production of oil peaking at some point and then dropping. According to American Petroleum Institute., (1999), the oil sources of the world has been predicted to drop from 2026 until 2094. However, the total world oil reserves still remain between 1.4 and 2 trillion barrels (Foreman, 2021). According to Cambridge Energy Research Associates (CERA)., (2006), they predicted that the oil remain as much as 3.74 trillion barrels in the Earth which is three times the number estimated by peak oil analysis (International Energy Agency., 2021).

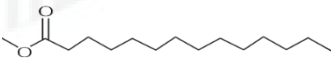
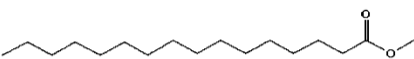
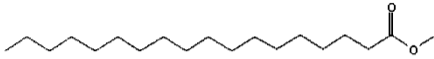

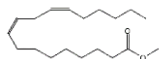
Basically, the combustion of petroleum emits hazardous gaseous such as carbon monoxide (CO), nitrogen oxides (NO_x), carbon dioxide (CO₂), etc., that will cause many problems such as acid rain and smog filled air. Besides, it can cause climate change and global warming which escalate the temperature of the Earth's atmosphere. These problems could impair the buildings, trees and give danger to the aquatic life and insects.

Therefore, the alternative way has been searched to prevent the pollution to the environment. One of the solution is, biodiesel; as an alternative renewable fuel which believed can prevent the environmental problems and safe for human health. Not only that, it is capable to be used in the combustion engines (Anwar et al., 2019). In fact, no mechanical adjustment needed for diesel engine as biodiesel have same physicochemical properties to the fossil diesel, which follow the act according to the fuel standards of US (ASTM D6751) or European (EN14214) (Hazrat et al., 2019; Chua et al., 2020).

Biodiesel emits less toxic gas and sulfur-free. In addition, the combustion of biodiesel contain higher cetane number and flashpoint compared to diesel fuel (Chua et al., 2020). Besides, reported by Hazrat et al., (2019), the combustion of pure biodiesel (B100) emits less GHG around 74% than diesel fuel.

Biodiesel production easily derived from vegetable oils and animal fats. According to ASTM, this fuel compose with alkyl esters of long chain fatty acids (Hoekman & Robbins, 2012; Parshetti et al., 2013) as shown in the Table 1.0. Theoretically, biodiesel contains higher concentration of free oxygen which is 10 – 11% by weight for a complete combustion reaction than diesel fuel. This could be reducing the harmful emissions as well as safe to the human (Zahan & Kano, 2019).

Table 1.0: Chemical structure of biodiesel

| Name | Chemical formula | Structural formula |
|------------------|------------------|--|
| Methyl Myristate | C14:0 |  |
| Methyl Palmitate | C16:0 |  |
| Methyl Stearate | C18:0 |  |
| Methyl Oleate | C18:1 |  |
| Methyl Linoleate | C18:2 |  |

(Kong, et al, 2020)

1.2 Problem statement

The fossil fuels are widely used to power the vehicles like ships, trains and airplane also generating electric power. The increasing emission of hazardous gas and particulate matter (PM) from these applications could give severe effect on the human health and the ecosystem. Moreover, the effect of hazardous gaseous in the atmosphere causing extreme increase of global temperature due to the breaking down of the ozone layers. The promising sustainable energy which is biodiesel has been found and it is a potential candidate as cleaner alternative energy for fossil fuel replacement. Biodiesel is becoming important which can reduce the toxic emission and the physical and chemical properties of biodiesel is similar to petro-diesel. Unfortunately, disadvantage of biodiesel is they are more expensive to compete with petro-diesel.

The feedstock played an important role in the biodiesel production which can reduce the cost of fuels. Palm fatty acid distillate (PFAD) is the by-product of refinery crude palm oil processing. It is much cheaper than other refined oils. PFAD is capable as biodiesel feedstock due to high miscibility of free fatty acid (FFA) in the methanol. Moreover, PFAD is not in the argument issues between food versus fuels. In spite of that, the main problem of PFAD which is containing high percentage of free fatty acid (FFA), > 90%. Therefore, strong acid catalysts are required which can convert high FFA to fatty acid methyl ester.

In general, homogeneous and heterogeneous catalyst are commonly used in transesterification reaction. Homogeneous catalyst has been used for century as they are capable to run the reaction at higher speeds. Regrettably, those catalysts cannot be reused and the process requires separation and purification steps that resulting in high cost for waste management. The heterogeneous catalysts which are reusable and easily separable could replace the homogeneous catalyst (Rechnia-gor & Malaika, 2018). The heterogeneous catalyst that is eco-friendlier which can be derived from biomass and potentially to lower the cost production. Not to mention, it is non-corrosive, environmentally friendly and can speed up the purification steps (Ayoob & Fadhil, 2020).

The sulfonated activated carbon catalyst is an excellent catalyst for esterification reaction of high FFA feedstocks compared to the traditional solid acid catalysts like protonated-Nafion, zeolites, sulfated zirconia which are bad resistance to water, easy deactivation also high preparation cost (Hussain & Kumar, 2018). According to the literature, the main reason using the carbon materials derived from biomass materials are because they give high catalytic activity during the reaction and easy to diffuse with the acidic sites of the catalyst when subjected to sulfonation with concentrated H_2SO_4 . The unique properties of mesoporous carbons are uniform pore sizes, good mechanical properties and having surface hydrophobicity that can increase the catalytic activity of the catalysts (Rechnia-Gorący et al., 2018).

Nowadays, the corncob residue become popular among the other biomass. It is lignocellulosic biomass having hemicelluloses constitute about 30 – 40%, cellulose,

lignin and other remaining is 60 – 70%. Previous studies have reported the carbonization of corncob can generate a family of microporous carbonaceous materials (Arancon et al., 2011). These components of lignocellulosic biomass possess different structural features like constituting monomer, cross-linking, crystallinity, and branching, which lead to different pyrolysis mechanisms and affect the physicochemical properties of the carbon products (Cheng & Li, 2018).

Nowadays, the hydrothermal carbonization method has been researched thoroughly in order to produce excellent carbon based catalyst which possessed a lot of surface functional group, captivating nanostructured also able to reduce the cost production and produces renewable carbonaceous materials (Heidari et al., 2019). Moreover, the carbon derived from lignocellulosic biomass via hydrothermal carbonization method appears as attractive mechanisms producing aromatic polymer structures which are stable considered as the building blocks of the hydrochar.

In addition, the hydrothermal carbonization method has several advantages over conventional pyrolysis which are; 1) hydrochar can be easily filtered from the reaction avoiding complicated drying, 2) this method able to convert wide range of biomass (dry to very wet), 3) improved hydrophobicity and lowering ash content, 4) water as an excellent solvent medium which decompose the biomass involving dehydration, retroaldol condensation, isomerization, and so on, 5) the hydrochar contains abundant functional groups, such as hydroxyl and carboxyl groups, 6) hydrothermal process is normally performed in a closed reactor at mild temperatures between 180 - 200 °C while letting the pressure to rise with the steam pressure (Cao, 2017; Titirici et al., 2012; Cheng & Li, 2018). The advantage of hydrochar which is containing high oxygenated functional group make it an effective precursor for the production of chemically activated carbon especially for the sulfonation process (Jain et al., 2016). HTC-based materials have proved not only to be sustainable, but also to possess extraordinary properties which able to surpass those of current “gold standards” (Liu et al., 2013).

1.3 Objective

The main objective of this research is to investigate the esterification reaction of PFAD in catalytic condition using hydrothermal-carbon sulfonated (HTC-S) catalyst. The specific objectives are shown below:

1. To prepare HTC-S catalyst by using the hydrothermal carbonization method followed by sulfonation process.
2. To characterize the chemical and physical properties of HTC-S catalyst using XRD, BET, FTIR, NH₃-TPD and FESEM.
3. To optimize the reaction parameters such as the methanol to PFAD molar ratio, reaction temperature, catalyst loading and reaction time for esterification of PFAD.
4. To characterize the properties of Biodiesel produced using the US (ASTM D6751) and European (EN14214) international standard method.

1.4 Scope of Research

This work covers the process of synthesis catalyst from the corncob residue via hydrothermal carbonization process followed by sulfonation with concentrated sulfuric acid. The prepared catalyst labelled as HTC-S catalyst has been characterized before catalytic activity evaluation. HTC and HTC-S catalysts were analyzed based on surface properties, acid site distribution and functional groups. Meanwhile, the catalytic evaluation was carried out by esterification reaction of palm fatty acid distillate (PFAD) to produce biodiesel.

The effects of reaction parameters on the reaction conversion and FAME yield were also evaluated. The One-Variable- at- a- Time (OVAT) technique has been used to optimize manually the variables involve to produce high production yield. These parameters included methanol to PFAD molar ratio, catalyst loading, reaction time and reaction temperature.

The esterification process was done via traditional conventional methanol-reflux method (open system). The PFAD biodiesel has been analyzed by GC/FID for determination of production yield. The PFAD biodiesel has also been tested according to US (ASTM D6751) and European (EN14214) international standard methods. This current study also investigated on the reusability test in order to produce sustainable biodiesel product.

REFERENCES

- Abbaszaadeh, A., Ghobadian, B., Omidkhah, M. R., & Najafi, G. (2012). Current biodiesel production technologies : A comparative review. *Energy Conversion and Management*, 63, 138–148.
- Abdul Kapur, N. Z., Maniam, G. P., Rahim, M. H. A., & Yusoff, M. M. (2017). Palm fatty acid distillate as a potential source for biodiesel production: A review. *Journal of Cleaner Production*, 143, 1–9.
- Abdulkareem-Alsultan, G., Asikin-Mijan, N., Lee, H. V., Rashid, U., Islam, A., & Taufiq-Yap, Y. H. (2019). Review on thermal conversion of plant oil (Edible and inedible) into green fuel using carbon-based nanocatalyst. *Catalysts*, 9(4), 1–25.
- Abdullah, S. H. Y. S., Hanapi, N. H. M., Azid, A., Umar, R., Juahir, H., Khatoun, H., & Endut, A. (2017). A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production. *Renewable and Sustainable Energy Reviews*, 70, 1040–1051.
- Adu-Mensah, D., Mei, D., Zuo, L., Zhang, Q., & Wang, J. (2019). A review on partial hydrogenation of biodiesel and its influence on fuel properties. *Fuel*, 251, 660–668.
- Agarwal, A. K., Gupta, J. G., & Dhar, A. (2017). Potential and challenges for large-scale application of biodiesel in automotive sector. *Progress in Energy and Combustion Science*, 61, 113–149.
- Ahmad, A. L., Yasin, N. H. M., Derek, C. J. C., & Lim, J. K. (2011). Microalgae as a sustainable energy source for biodiesel production: A review. *Renewable and Sustainable Energy Reviews*, 15(1), 584–593.
- Ahmad, J., Rashid, U., Patuzzi, F., Baratieri, M., & Taufiq-Yap, Y. H. (2018). Synthesis of char-based acidic catalyst for methanolysis of waste cooking oil: An insight into a possible valorization pathway for the solid by-product of gasification. *Energy Conversion and Management*, 158, 186–192.
- Akinfalabi, S.-I., Rashid, U., Yunus, R., & Taufiq-Yap, Y. H. (2017). Synthesis of biodiesel from palm fatty acid distillate using sulfonated palm seed cake catalyst. *Renewable Energy*, 111, 611–619.
- Alsultan, G. A., Asikin-Mijan, N., Lee, H. V., Albazzaz, A. S., & Taufiq-Yap, Y. H. (2017). Deoxygenation of waste cooking to renewable diesel over walnut shell-derived nanorode activated carbon supported CaO-La₂O₃ catalyst. *Energy Conversion and Management*, 151(May), 311–323.
- Alvisoa, D., Artanaa, G., & Duriez, T. (2020). Prediction of biodiesel physico-chemical properties from its fatty acid composition using genetic programming. *Fuel*, 264, 116844.

- Ambat, I., Srivastava, V., & Sillanpää, M. (2018). Recent advancement in biodiesel production methodologies using various feedstock: A review. *Renewable and Sustainable Energy Reviews*, *90*, 356–369.
- Anwar, M., Rasul, M. G., Ashwath, N., & Nabi, M. N. (2019). The potential of utilising papaya seed oil and stone fruit kernel oil as non-edible feedstock for biodiesel production in Australia: A review. *Energy Reports*, *5*, 280–297.
- Arancon, R. A., Barros, H. R., Balu, A. M., Vargas, C., & Luque, R. (2011). Valorisation of corncob residues to functionalised porous carbonaceous materials for the simultaneous esterification/transesterification of waste oils. *Green Chemistry*, *13*(11), 3162–3167.
- Aransiola, E. F., Ojumu, T. V., Oyekola, O. O., & Madzimbamuto, T. F. (2013). ScienceDirect A review of current technology for biodiesel production : State of the art. *Biomass and Bioenergy*, *61*, 276–297.
- Asakuma, Y., Ogawa, Y., Maeda, K., Fukui, K., & Kuramochi, H. (2011). Effects of microwave irradiation on triglyceride transesterification: Experimental and theoretical studies. *Biochemical Engineering Journal*, *58*, 20–24.
- Asikin-Mijan, N., Lee, H. V., Marliza, T. S., & Taufiq-Yap, Y. H. (2018). Pyrolytic-deoxygenation of triglycerides model compound and non-edible oil to hydrocarbons over SiO₂-Al₂O₃ supported NiO-CaO catalysts. *Journal of Analytical and Applied Pyrolysis*, *129*, 221–230.
- Asikin-Mijan, N., Taufiq-Yap, Y. H., & Lee, H. V. (2015). Synthesis of clamshell derived Ca(OH)₂ nano-particles via simple surfactant-hydration treatment. *Chemical Engineering Journal*, *262*, 1043–1051.
- Avhad, M. R., & Marchetti, J. M. (2015). A review on recent advancement in catalytic materials for biodiesel production. *Renewable and Sustainable Energy Reviews*, *50*, 696–718.
- Ayoob, A. K., & Fadhil, A. B. (2020). Valorization of waste tires in the synthesis of an effective carbon based catalyst for biodiesel production from a mixture of non-edible oils. *Fuel*, *264*, 116754.
- Bandosz, T. J & Karifala, K. (2015). Spent Coffee-Based Activated Carbons: Production, Properties, and Environmental Applications. *Coffee in Health and Disease Prevention*. 311-317.
- Barakos, N., Pasiadis, S., & Papayannakos, N. (2008). Transesterification of triglycerides in high and low quality oil feeds over an HT₂ hydrotalcite catalyst. *Bioresource Technology*, *99*(11), 5037–5042.
- Berhe Gebreegziabher, T., Wang, S., & Nam, H. (2019). Adsorption of H₂S, NH₃ and TMA from indoor air using porous corncob activated carbon: Isotherm and kinetics study. *Journal of Environmental Chemical Engineering*, *7*(4), 103234.

- Boey, P.-L., Maniam, G. P., Hamid, S. A., & Ali, D. M. H. (2011). Utilization of waste cockle shell (*Anadara granosa*) in biodiesel production from palm olein: Optimization using response surface methodology. *Fuel*, *90*(7), 2353–2358.
- Boonsombuti, A., Luengnaruemitchai, A., & Wongkasemjit, S. (2015). Effect of phosphoric acid pretreatment of corncobs on the fermentability of clostridium *beijerinckii* TISTR 1461 for biobutanol production. *Preparative Biochemistry and Biotechnology*, *45*(2), 173–191.
- Bora, A. P., Gupta, D. P., & Durbha, K. S. (2020). Sewage sludge to bio-fuel: A review on the sustainable approach of transforming sewage waste to alternative fuel. *Fuel*, *259*.
- Borges, M. E., & Díaz, L. (2012). Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *Renewable and Sustainable Energy Reviews*, *16*(5), 2839–2849.
- Cao, X. (2017). *RSC Advances Application of biochar-based catalysts in biomass upgrading : a review*. 48793–48805.
- Chellappan, S., Aparna, K., Chingakham, C., Sajith, V., & Nair, V. (2019). Microwave assisted biodiesel production using a novel Brønsted acid catalyst based on nanomagnetic biocomposite. *Fuel*, *246*, 268–276.
- Chellappan, S., Nair, V., Vaishakh-Nair., Sajith, V., Aparna, K. (2018). Synthesis, optimization and characterization of biochar based catalyst from sawdust for simultaneous esterification and transesterification. *Chinese Journal of Chemical Engineering*, *26*(12), 2654–2663.
- Cheng, F., & Li, X. (2018). *Preparation and Application of Biochar-Based Catalysts for Biofuel Production. 1*, 1–35.
- Chin, L. H., Abdullah, A. Z., & Hameed, B. H. (2012). Sugar cane bagasse as solid catalyst for synthesis of methyl esters from palm fatty acid distillate. *Chemical Engineering Journal*, *183*, 104–107.
- Cho, H. J., Kim, S. H., Hong, S. W., & Yeo, Y.-K. (2012). A single step non-catalytic esterification of palm fatty acid distillate (PFAD) for biodiesel production. *Fuel*, *93*, 373–380.
- Chua, S. Y., Periasamy, L. A., Goh, C. M. H., Tan, Y. H., Mubarak, N. M., Kandedo, J., Khalid, M., Walvekar, R., & Abdullah, E. C. (2020). Biodiesel synthesis using natural solid catalyst derived from biomass waste: A review. *Journal of Industrial and Engineering Chemistry*, *81*, 41–60.
- Davies, G., Sheikh, A. El, Collett, C., Yakub, I., & McGregor, J. (2021). Catalytic carbon materials from biomass. In *Emerging Carbon Materials for Catalysis*. Elsevier Inc.
- Dawodu, F. A., Ayodele, O. O., Xin, J., & Zhang, S. (2014). Application of solid acid catalyst derived from low value biomass for a cheaper biodiesel production. *Journal of Chemical Technology & Biotechnology*, *89*(12), 1898–1909.

- Dechakhumwat, S., Hongmanorom, P., Thunyaratchanon, C., Smith, S. M., Boonyuen, S., & Luengnaruemitchai, A. (2019). Catalytic activity of heterogeneous acid catalysts derived from corncob in the esterification of oleic acid with methanol. *Renewable Energy*, 1-10.
- Demirbas, A. (2008). Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Conversion and Management*, 49(1), 125–130.
- Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, 50(1), 14–34.
- Dharma, S., Masjuki, H. H., Ong, H. C., Sebayang, A. H., Silitonga, A. S., Kusumo, F., & Mahlia, T. M. I. (2016). Optimization of biodiesel production process for mixed *Jatropha curcas*–*Ceiba pentandra* biodiesel using response surface methodology. *Energy Conversion and Management*, 115, 178–190.
- Dora, S., Bhaskar, T., Singh, R., Naik, D. V., & Adhikari, D. K. (2012). Effective catalytic conversion of cellulose into high yields of methyl glucosides over sulfonated carbon based catalyst. In *Bioresource Technology*, 120, 318-321.
- Ezebor, F., Khairuddean, M., Abdullah, A. Z., & Boey, P. L. (2014). Esterification of oily-FFA and transesterification of high FFA waste oils using novel palm trunk and bagasse-derived catalysts. *Energy Conversion and Management*, 88, 1143–1150.
- Fadhil, A. B., Aziz, A. M., & Al-Tamer, M. H. (2016). Biodiesel production from *Silybum marianum* L. seed oil with high FFA content using sulfonated carbon catalyst for esterification and base catalyst for transesterification. *Energy Conversion and Management*, 108, 255–265.
- Fadhil, A. B., Nayyef, A. W., & Sedeeq, S. H. (2019). Valorization of mixed radish seed oil and *Prunus armeniaca* L. oil as a promising feedstock for biodiesel production: Evaluation and analysis of biodiesels. *Asia-Pacific Journal of Chemical Engineering*, 1–15.
- Farabi, M. S. A., Ibrahim, M. L., Rashid, U., & Hin, Y. (2019). Esterification of palm fatty acid distillate using sulfonated carbon-based catalyst derived from palm kernel shell and bamboo. *Energy Conversion and Management*, 181, 562–570.
- Farooq, M., Ramli, A., & Naeem, A. (2015). Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. *Renewable Energy*, 76, 362–368.
- Foreman, D. (2021). Is The World About To See An Oil Shortage? *American Petroleum Institute*, 1–7.
- Fraile, J. M., García-Bordejé, E., Pires, E., & Roldán, L. (2015). Catalytic performance and deactivation of sulfonated hydrothermal carbon in the esterification of fatty acids: Comparison with sulfonic solids of different nature. *Journal of Catalysis*, 324, 107–118.

- Gardy, J., Rehan, M., Hassanpour, A., Lai, X., & Nizami, A. (2019). Advances in nano-catalysts based biodiesel production from non-food feedstocks. *Journal of Environmental Management*, 249, 109316.
- Geng, L., Wang, Y., Yu, G., & Zhu, Y. (2011). Efficient carbon-based solid acid catalysts for the esterification of oleic acid. In *Catalysis Communications*, 13, (1), 26-30.
- Goh, B. H. H., Ong, H. C., Cheah, M. Y., Chen, W.-H., Yu, K. L., & Mahlia, T. M. I. (2019). Sustainability of direct biodiesel synthesis from microalgae biomass: A critical review. *Renewable and Sustainable Energy Reviews*, 107, 59–74.
- Guo, F., Fang, Z., Xu, C. C., & Smith, R. L. (2012). Solid acid mediated hydrolysis of biomass for producing biofuels. *Progress in Energy and Combustion Science*, 38(5), 672–690.
- Gupta, J., Agarwal, M., & Dalai, A. K. (2019). Intensified transesterification of mixture of edible and nonedible oils in reverse flow helical coil reactor for biodiesel production. *Renewable Energy*, 134, 509–525.
- Hanania Jordan, Stenhouse Kailyn, D. J. (2015). Hubbert's peak. *Energy Education*, 2–3.
- Hassan, N. S., & Badri, K. H. (2016). Thermal Behaviours Of Oil Palm Empty Fruit Bunch Fibre Upon Exposure To Acid-Base Aqueous Solutions. *Malaysian Journal of Analytical Sciences*, 20(5), 1095–1103.
- Hazrat, M. A., Rasul, M. G., Khan, M. M. K., Ashwath, N., & Rufford, T. E. (2019). Emission Characteristics of Polymer Additive Mixed Diesel-Sunflower Biodiesel Fuel. *Energy Procedia*, 156, 59–64.
- Heidari, M., Dutta, A., Acharya, B., & Mahmud, S. (2019). A review of the current knowledge and challenges of hydrothermal carbonization for biomass conversion. *Journal of the Energy Institute*, 92(6), 1779–1799.
- Hidayat, A., Rochmadi, Wijaya, K., & Budiman, A. (2015). Esterification of Free Fatty Acid on Palm Fatty Acid Distillate using Activated Carbon Catalysts Generated from Coconut Shell. *Procedia Chemistry*, 16, 365–371.
- Hoekman, S. K., & Robbins, C. (2012). Review of the effects of biodiesel on NOx emissions. *Fuel Processing Technology*, 96, 237–249.
- Hosseinalizadeh, R., Arshadi Khamseh, A., & Akhlaghi, M. M. (2019). A multi-objective and multi-period model to design a strategic development program for biodiesel fuels. *Sustainable Energy Technologies and Assessments*, 36, 100545.
- Hosseini, S., Janaun, J., & Choong, T. S. Y. (2015). Feasibility of honeycomb monolith supported sugar catalyst to produce biodiesel from palm fatty acid distillate (PFAD). *Process Safety and Environmental Protection*, 98, 285–295.

- Huang, M., Luo, J., Fang, Z., & Li, H. (2016). Biodiesel production catalyzed by highly acidic carbonaceous catalysts synthesized via carbonizing lignin in sub- and super-critical ethanol. *Applied Catalysis B: Environmental*, *190*, 103–114.
- Hussain, Z., & Kumar, R. (2018). Esterification of free fatty acids in karanja oil using novel corncob derived solid acid catalyst. *Materials Today: Proceedings*, *5*(9), 18045–18051.
- Hwa, S., Rashid, U., & Taufiq-yap, Y. H. (2014). Biodiesel production from crude Jatropha Curcas oil using calcium based mixed oxide catalysts. *Fuel*, *136*, 244–252.
- Ibrahim, M. L., Nik Abdul Khalil, N. N. A., Islam, A., Rashid, U., Ibrahim, S. F., Sinar Mashuri, S. I., & Taufiq-Yap, Y. H. (2020). Preparation of Na₂O supported CNTs nanocatalyst for efficient biodiesel production from waste-oil. *Energy Conversion and Management*, *205*, 112445.
- Ibrahim, N. A., Rashid, U., Taufiq-Yap, Y. H., Yaw, T. C. S., & Ismail, I. (2019). Synthesis of carbonaceous solid acid magnetic catalyst from empty fruit bunch for esterification of palm fatty acid distillate (PFAD). *Energy Conversion and Management*, *195*, 480–491.
- International Energy Agency (IEA). (2021). Ample oil storage keeps market adequately supplied. *Oil & Gas Journal*.
- Jain, A., Balasubramanian, R., & Srinivasan, M. P. (2016). Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review. *Chemical Engineering Journal*, *283*, 789–805.
- Jumaah, M. A., Yusoff, M. F. M., Salimon., J & Bahadi, M. (2019). Physical Characteristics of Palm Fatty Acid Distillate. *Journal of Chemical And Pharmaceutical Sciences*, *13*(1),1-5.
- Kastner, J. R., Miller, J., Geller, D. P., Locklin, J., Keith, L. H., & Johnson, T. (2012). Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon. *Catalysis Today*, *190*(1), 122–132.
- Kefas, H. M., Yunus, R., Rashid, U., & Taufiq-Yap, Y. H. (2018). Modified sulfonation method for converting carbonized glucose into solid acid catalyst for the esterification of palm fatty acid distillate. *Fuel*, *229*, 68–78.
- Kim, H.-J., Kang, B.-S., Kim, M.-J., Park, Y. M., Kim, D.-K., Lee, J.-S., & Lee, K.-Y. (2004). Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis Today*, *93*, 315–320.
- Kong, J., Liu, H., & Zheng, Z. (2020). Chemical Kinetics Study on Combustion of Ethanol/biodiesel/n-heptane. *Renewable Energy*, *148*, 150–167.
- Konwar, L. J., Das, R., Thakur, A. J., Salminen, E., Mäki-Arvela, P., Kumar, N., Mikkola, J.-P., & Deka, D. (2014). Biodiesel production from acid oils using sulfonated carbon catalyst derived from oil-cake waste. *Journal of Molecular Catalysis A: Chemical*, *388–389*, 167–176.

- Konwar, L. J., Wärnä, J., Mäki-Arvela, P., Kumar, N., & Mikkola, J.-P. (2016). Reaction kinetics with catalyst deactivation in simultaneous esterification and transesterification of acid oils to biodiesel (FAME) over a mesoporous sulphonated carbon catalyst. *Fuel*, *166*, 1–11.
- Kouzu, M., & Hidaka, J. (2012). Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review. *Fuel*, *93*, 1–12.
- Li, M., Zhang, H., Xiao, T., Wang, S., Zhang, B., Chen, D., Su, M., & Tang, J. (2018). Low-cost biochar derived from corncob as oxygen reduction catalyst in air cathode microbial fuel cells. *Electrochimica Acta*, *283*, 780–788.
- Liang, X., Xiao, H., Shen, Y., & Qi, C. (2010). One-step synthesis of novel sulfuric acid groups' functionalized carbon via hydrothermal carbonization. *Carbon*, *48*, 1844–1848.
- Lin, F., Liu, C., Wang, X., Hu, C., Wu, S., & Xiao, R. (2019). Catalytic oxidation of biorefinery corncob lignin via zirconium (IV) chloride and sodium hydroxide in acetonitrile/water: A functionality study. *Science of the Total Environment*, *675*, 203–212.
- Liu, R., Wang, X., Zhao, X., & Feng, P. (2008). Sulfonated ordered mesoporous carbon for catalytic preparation of biodiesel. *Carbon*, *46*(13), 1664–1669.
- Liu, T., Li, Z., Li, W., Shi, C., & Wang, Y. (2013). Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol. *Bioresource Technology*, *133*, 618–621.
- Lokman, I. M., Goto, M., Rashid, U., & Taufiq-Yap, Y. H. (2016). Sub- and supercritical esterification of palm fatty acid distillate with carbohydrate-derived solid acid catalyst. *Chemical Engineering Journal*, *284*, 872–878.
- Lokman, I. M., Rashid, U., Taufiq-Yap, Y. H., & Yunus, R. (2015). Methyl ester production from palm fatty acid distillate using sulfonated glucose-derived acid catalyst. *Renewable Energy*, *81*, 347–354.
- Lou, W.-Y., Zong, M.-H., & Duan, Z.-Q. (2008). Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts. *Bioresource Technology*, *99*(18), 8752–8758.
- Malani, R. S., Sardar, H., Malviya, Y., Goyal, A., & Moholkar, V. S. (2018). Ultrasound-intensified biodiesel production from mixed nonedible oil feedstock using heterogeneous acid catalyst supported on rubber de-oiled cake. *Industrial and Engineering Chemistry Research*, *57*(44), 14926–14938.
- Malins, K., Brinks, J., Kampars, V., & Malina, I. (2016). Esterification of rapeseed oil fatty acids using a carbon-based heterogeneous acid catalyst derived from cellulose. *Applied Catalysis A: General*, *519*, 99–106.
- Mansir, N., Taufiq-Yap, Y. H., Rashid, U., & Lokman, I. M. (2017). Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for

biodiesel production: A review. *Energy Conversion and Management*, 141, 171–182.

Mardhiah, H. H., Chyuan, H., Masjuki, H. H., Lim, S., & Lee, H. V. (2017). A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. *Renewable and Sustainable Energy Reviews*, 67, 1225–1236.

Mavakumba, H., Yunus, R., Rashid, U., & Taufiq-yap, Y. H. (2019). Enhanced biodiesel synthesis from palm fatty acid distillate and modified sulfonated glucose catalyst via an oscillation flow reactor system. *Journal of Environmental Chemical Engineering*, 7(2), 102993.

Mohamed, N. H., Soliman, F. S., El Maghraby, H., & Moustfa, Y. M. (2017). Thermal conductivity enhancement of treated petroleum waxes, as phase change material, by α nano alumina: Energy storage. *Renewable and Sustainable Energy Reviews*, 70, 1052–1058.

Mohlala, L. M., Bodunrin, M. O., Awosusi, A. A., Daramola, M. O., Cele, N. P., & Olubambi, P. A. (2016). Beneficiation of corncob and sugarcane bagasse for energy generation and materials development in Nigeria and South Africa: A short overview. *Alexandria Engineering Journal*, 55(3), 3025–3036.

Molaei Dehkordi, A., & Ghasemi, M. (2012). Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts. *Fuel Processing Technology*, 97, 45–51.

Nabi, M. N., Hoque, S. M. N., & Akhter, M. S. (2009). Karanja (*Pongamia Pinnata*) biodiesel production in Bangladesh, characterization of karanja biodiesel and its effect on diesel emissions. *Fuel Processing Technology*, 90(9), 1080–1086.

Nakajima, K., & Hara, M. (2012). Amorphous carbon with SO_3H groups as a solid Brønsted acid catalyst. *ACS Catalysis*, 2(7), 1296–1304.

Ngaosuwan, K., Goodwin, J. G., & Prasertdham, P. (2016). A green sulfonated carbon-based catalyst derived from coffee residue for esterification. *Renewable Energy*, 86, 262–269.

Niu, S., Ning, Y., Lu, C., Han, K., Yu, H., & Zhou, Y. (2018). Esterification of oleic acid to produce biodiesel catalyzed by sulfonated activated carbon from bamboo. *Energy Conversion and Management*, 163, 59–65.

Ofori-Boateng, C., & Lee, K. T. (2013). The potential of using cocoa pod husks as green solid base catalysts for the transesterification of soybean oil into biodiesel: Effects of biodiesel on engine performance. *Chemical Engineering Journal*, 220, 395–401.

Ogunkunle, O., & Ahmed, N. A. (2019). A review of global current scenario of biodiesel adoption and combustion in vehicular diesel engines. *Energy Reports*, 5, 1560–1579.

- Okoye, P. U., Longoria, A., Sebastian, P. J., Wang, S., Li, S., & Hameed, B. H. (2019). A review on recent trends in reactor systems and azeotrope separation strategies for catalytic conversion of biodiesel-derived glycerol. *Science of The Total Environment*, 134595.
- Ong, H. C., Silitonga, A. S., Masjuki, H. H., Mahlia, T. M. I., Chong, W. T., & Boosroh, M. H. (2013). Production and comparative fuel properties of biodiesel from non-edible oils: *Jatropha curcas*, *Sterculia foetida* and *Ceiba pentandra*. *Energy Conversion and Management*, 73, 245–255.
- Parshetti, G. K., Kent Hoekman, S., & Balasubramanian, R. (2013). Chemical, structural and combustion characteristics of carbonaceous products obtained by hydrothermal carbonization of palm empty fruit bunches. *Bioresource Technology*, 135, 683–689.
- Paryanto, I., Prakoso, T., Suyono, E. A., & Gozan, M. (2019). Determination of the upper limit of monoglyceride content in biodiesel for B30 implementation based on the measurement of the precipitate in a Biodiesel–Petrodiesel fuel blend (BXX). *Fuel*, 258, 116104.
- Pesaresi, L., Brown, D. R., Lee, A. F., Montero, J. M., Williams, H., & Wilson, K. (2009). Cs-doped $H_4SiW_{12}O_{40}$ catalysts for biodiesel applications. *Applied Catalysis A: General*, 360(1), 50–58.
- Puchana-Rosero, M. J., Adebayo, M. A., Lima, E. C., Machado, F. M., Thue, P. S., Vaghetti, J. C. P., Umpierrez, C. S., & Gutterres, M. (2016). Microwave-assisted activated carbon obtained from the sludge of tannery-treatment effluent plant for removal of leather dyes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 504, 105–115.
- Quah, R. V., Tan, Y. H., Mubarak, N. M., Khalid, M., Abdullah, E. C., & Nolasco-Hipolito, C. (2019). An overview of biodiesel production using recyclable biomass and non-biomass derived magnetic catalysts. *Journal of Environmental Chemical Engineering*, 7(4), 103219.
- Rechnia-Gorący, P., Malaika, A., & Kozłowski, M. (2018). Acidic activated carbons as catalysts of biodiesel formation. *Diamond and Related Materials*, 87, 124–133.
- Sangar, S. K., Lan, C. S., Razali, S. M., Farabi, M. S. A., & Taufiq-Yap, Y. H. (2019). Methyl ester production from palm fatty acid distillate (PFAD) using sulfonated cow dung-derived carbon-based solid acid catalyst. *Energy Conversion and Management*, 196, 1306–1315.
- Sani, Y. M., Daud, W. M. A. W., & Abdul Aziz, A. R. (2014). Activity of solid acid catalysts for biodiesel production: A critical review. *Applied Catalysis A: General*, 470, 140–161.
- Shajaratun Nur, Z. A., Taufiq-Yap, Y. H., Rabiah Nizah, M. F., Teo, S. H., Syazwani, O. N., & Islam, A. (2014). Production of biodiesel from palm oil using modified Malaysian natural dolomites. *Energy Conversion and Management*, 78, 738–744.

- Shu, Q., Gao, J., Liao, Y., & Wang, J. (2011). Reaction Kinetics of Biodiesel Synthesis from Waste Oil Using a Carbon-based Solid Acid Catalyst. *Chinese Journal of Chemical Engineering*, 19(1), 163-168.
- Shu, Q., Gao, J., Nawaz, Z., Liao, Y., Wang, D., & Wang, J. (2010). Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst. *Applied Energy*, 87(8), 2589–2596.
- Singh, D., Sharma, D., Soni, S. L., Sharma, S., & Sharma, P. K. (2020). A review on feedstocks , production processes , and yield for different generations of biodiesel. *Fuel*, 262, 116553.
- Singh, S. P., & Singh, D. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews*, 14(1), 200–216.
- Soares Dias, A. P., Puna, J., Neiva Correia, M. J., Nogueira, I., Gomes, J., & Bordado, J. (2013). Effect of the oil acidity on the methanolysis performances of lime catalyst biodiesel from waste frying oils (WFO). *Fuel Processing Technology*, 116, 94–100.
- Syazwani, O. N., Rashid, U., Mastuli, M. S., & Taufiq-Yap, Y. H. (2019). Esterification of palm fatty acid distillate (PFAD) to biodiesel using Bi-functional catalyst synthesized from waste angel wing shell (*Cyrtopleura costata*). *Renewable Energy*, 131, 187–196.]
- Sych, N. V., Trofymenko, S. I., Poddubnaya, O. I., Tsyba, M. M., Sapsay, V. I., Klymchuk, D. O., & Puziy, A. M. (2012). Porous structure and surface chemistry of phosphoric acid activated carbon from corncob. *Applied Surface Science*, 261, 75–82.
- Takagaki, A., Toda, M., Okamura, M., Kondo, J. N., Hayashi, S., Domen, K., & Hara, M. (2006). Esterification of higher fatty acids by a novel strong solid acid. *Catalysis Today*, 116(2), 157–161.
- Takase, M., Zhao, T., Zhang, M., Chen, Y., Liu, H., Yang, L., & Wu, X. (2015). An expatiate review of neem, jatropha, rubber and karanja as multipurpose non-edible biodiesel resources and comparison of their fuel, engine and emission properties. *Renewable and Sustainable Energy Reviews*, 43, 495–520.
- Tamborini, L. H., Casco, M. E., Militello, M. P., Silvestre-Albero, J., Barbero, C. A., & Acevedo, D. F. (2016). Sulfonated porous carbon catalysts for biodiesel production: Clear effect of the carbon particle size on the catalyst synthesis and properties. *Fuel Processing Technology*, 149, 209–217.
- Tang, X., & Niu, S. (2019). Preparation of carbon-based solid acid with large surface area to catalyze esterification for biodiesel production. *Journal of Industrial and Engineering Chemistry*, 69, 187–195.
- Tang, X., Niu, S., Zhao, S., Zhang, X., Li, X., Yu, H., Lu, C., & Han, K. (2019). Synthesis of sulfonated catalyst from bituminous coal to catalyze esterification for biodiesel

- production with promoted mechanism analysis. *Journal of Industrial and Engineering Chemistry*, 77, 432–440.
- Tao, M.-L., Guan, H.-Y., Wang, X.-H., Liu, Y.-C., & Louh, R.-F. (2015). Fabrication of sulfonated carbon catalyst from biomass waste and its use for glycerol esterification. *Fuel Processing Technology*, 138, 355–360.
- Theam, K. L., Islam, A., Lee, H. V., & Taufiq-Yap, Y. H. (2015). Sucrose-derived catalytic biodiesel synthesis from low cost palm fatty acid distillate. *Process Safety and Environmental Protection*, 95, 126–135.
- Thodhal, S., & Sathyamoorthy, G. (2020). Emerging extraction techniques: Hydrothermal processing. In *Sustainable Seaweed Technologies*. Elsevier Inc.
- Thushari, I., & Babel, S. (2018). Sustainable utilization of waste palm oil and sulfonated carbon catalyst derived from coconut meal residue for biodiesel production. In *Bioresource Technology*, 248, 199-203.
- Titirici, M.-M., White, R. J., Falco, C., & Sevilla, M. (2012). Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage. *Energy & Environmental Science*, 5, 6796–6822.
- Vicente, G., Martínez, M., & Aracil, J. (2004). Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresource Technology*, 92(3), 297–305.
- Wang, S., Wang, J., Okoye, P. U., Chen, S., Li, X., Duan, L., Zhou, H., Li, S., Tang, T., Zhang, L., & Zhang, A. (2020). Application of corncob residue-derived catalyst in the transesterification of glycerol with dimethyl carbonate to synthesize glycerol carbonate. *BioResources*, 15(1), 142–158.
- Xiao, L.-P., Shi, Z.-J., Xu, F., & Sun, R.-C. (2012). Hydrothermal carbonization of lignocellulosic biomass. *Bioresource Technology*, 118, 619–623.
- Xincheng, T., Shengli, N., Shuang, Z., Xiangyu, Z., Ximing, L., Hwei, Y., Chunmei, L., & Kuihua, H. (2019). Synthesis of sulfonated catalyst from bituminous coal to catalyze esterification for biodiesel production with promoted mechanism analysis. *Journal of Industrial and Engineering Chemistry*, 77, 432–440.
- Yaakob, Z., Mohammad, M., Alherbawi, M., Alam, Z., & Sopian, K. (2013). Overview of the production of biodiesel from Waste cooking oil. *Renewable and Sustainable Energy Reviews*, 18, 184–193.
- Yan, S., Salley, S. O., & Simon Ng, K. Y. (2009). Simultaneous transesterification and esterification of unrefined or waste oils over ZnO-La₂O₃ catalysts. *Applied Catalysis A: General*, 353(2), 203–212.
- Yan, W., Wu, Y., Chen, Y., Liu, Q., Wang, K., Cao, N., Dai, F., Li, X., & Jiang, J. (2020). Facile preparation of N-doped corncob-derived carbon nanofiber efficiently encapsulating Fe₂O₃ nanocrystals towards high ORR electrocatalytic activity. *Journal of Energy Chemistry*, 44, 121-130.

- Yesilyurt, M. K., Cesur, C., Aslan, V., & Yilbasi, Z. (2019). The production of biodiesel from safflower (*Carthamus tinctorius* L.) oil as a potential feedstock and its usage in compression ignition engine: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 1-30
- Yu, F., Han, T., Wang, Z., Xie, Y., Wu, Y., Jin, Y., Yang, N., Xiao, J., & Kawi, S. (2021). Recent progress in direct carbon solid oxide fuel cell: Advanced anode catalysts, diversified carbon fuels, and heat management. *International Journal of Hydrogen Energy*, 46(5), 4283–4300.
- Yu, H., Niu, S., Lu, C., Li, J., & Yang, Y. (2016). Preparation and esterification performance of sulfonated coal-based heterogeneous acid catalyst for methyl oleate production. *Energy Conversion and Management*, 126, 488–496.
- Yujaroen, D., Goto, M., Sasaki, M., & Shotipruk, A. (2009). Esterification of palm fatty acid distillate (PFAD) in supercritical methanol: Effect of hydrolysis on reaction reactivity. *Fuel*, 88(10), 2011–2016.
- Zahan, K. A., & Kano, M. (2019). Technological Progress in Biodiesel Production: An Overview on Different Types of Reactors. *Energy Procedia*, 156, 452–457.
- Zaheera, N., Kapur, A., Pragas, G., Hasbi, M., Rahim, A., & Yusoff, M. M. (2017). Palm fatty acid distillate as a potential source for biodiesel production: A review. *Journal of Cleaner Production*, 143, 1–9.
- Zero & Rainforest Foundation Norway. (2016). Palm Fatty Acid Distillate (PFAD) in biofuels. *Regnskogfondet*.
- Zhang, K., Han, X., Hu, Z., Zhang, X., Tao, Z., & Chen, J. (2014). Nanostructured Mn-based oxides for electrochemical energy storage and conversion. *Chemical Society Reviews*, 1–30.
- Zhou, Y., Niu, S., & Li, J. (2016). Activity of the carbon-based heterogeneous acid catalyst derived from bamboo in esterification of oleic acid with ethanol. *Energy Conversion and Management*, 114, 188–196.