DEVELOPMENT OF BIOMASS-DERIVED CELLULOSE FOR BIODIESEL PRODUCTION

TOK JIA KEE

UNIVERSITI TUNKU ABDUL RAHMAN

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Honours) Chemical Engineering**

**Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman**

May 2022

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

Signature : TJK

Name : Tok Jia Kee

ID No. : 17UEB03257

Date : 25 April 2022

APPROVAL FOR SUBMISSION

I certify that this project report entitled **“DEVELOPMENT OF BIOMASS-DERIVED CELLULOSE FOR BIODIESEL PRODUCTION”** was prepared by **TOK JIA KEE** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : yeanling

Supervisor : Dr. Pang Yean Ling

Date : 23 April 2022

Signature :

Co-Supervisor :

Date :

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ABSTRACT

Biodiesel has emerged as a promising renewable substitute to conventional fossil fuel for diesel engines. In this regard, biomass-derived cellulose can be utilised as the raw material to fabricate an eco-friendly catalyst while reducing the overall production cost for biodiesel production. Therefore, the main focus of this study is to determine the potential applicability of biomass-derived cellulose catalysts in biodiesel production. From the study, it shows that the cellulose exhibits a porous structure with high surface area which can increase the reaction rate. The cellulose also has good mechanical properties as the XRD results indicate that the peaks at around 22 ° to 23 ° are attributed to the crystalline structure of cellulose with high crystallinity. Moreover, biomass-derived cellulose catalyst is thermally stable up to 380 ℃. FTIR analysis has also confirmed the purity of the cellulose and the discruption of the cellulose linkages is found which can increase the porosity. On the other hand, biomass-derived cellulose catalyst is able to produce biodiesel yield above 85 % under optimum conditions. Investigation on the kinetic characteristics reveals that the reaction obeys pseudo first-order law and the reaction rate constants increase with the temperature. It is discovered that the activation energy of the reaction catalysed by biomass-derived cellulose is lower than that of other non-cellulose catalysts, thus improving the catalysis in biodiesel production. In addition, the thermodynamic parameters are determined where the values of enthalpy change and Gibbs free energy change are positive, indicating the reaction is endothermic and endergonic. The negative values of entropy change shows that the disorder and randomness decreases during the reaction. Overall, the results conclude that biomass-derived cellulose catalyst exhibits excellent catalytic activity which is a potential sustainable catalyst to produce biodiesel.

TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS / ABBREVIATIONS

A	Arrhenius constant, min^{-1}
C_{TG}	concentration of triglyceride, mol/L
CrI	crystallinity index, %
E_A	activation energy, J/mol
h	Planck constant, 6.626×10^{-34} J·s
I_{002}	peak intensity corresponding to crystalline region
I_{am}	peak intensity corresponding to amorphous region
k	reaction rate constant, min^{-1}
k_b	Boltzmann constant, 1.38×10^{-23} J/K
r_A	reaction rate, mol/L·min
R	ideal gas constant, 8.314 J/mol·K
R^2	correlation coefficients
t	time, min
T	temperature, K
X_{ME}	conversion of methyl ester
ΔG°	change in Gibbs free energy, J/mol
ΔH°	change in enthalpy, J/mol
ΔS°	change in entropy, J/mol·K

BP	British Petroleum
CPO	crude palm oil
DTG	derivative thermogravimetric
FAAE	fatty acid alkyl ester
FAME	fatty acid methyl ester
FFA	free fatty acids
FTIR	fourier transform infrared spectroscopy
ME	methyl ester
NaOH	sodium hydroxide
OA	oleic acid
OPEFB	oil palm empty fruit bunch
OPF	oil palm frond

OPMF	oil palm mesocarp fiber
RH	rice husk
SCB	sugarcane bagasse
SEM	scanning electron microscopy
SW	soft wood
TG	triglyceride
TGA	thermogravimetric analysis
UNEP	United Nations Environment Programme
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Renewable Energy

Nowadays, every aspect of human society runs on energy. The exponential growth of world population and the rapid development of national economies has generated a considerable demand for energy. Figure 1.1 shows that there is a dramatically increase in the energy consumption worldwide from 2000 and it is expected that the total energy consumption will achieve nearly 725 exajoules in 2050. According to British Petroleum (BP, 2020), the renewable energy consumption which includes biomass, biofuel, solar and wind energy is also predicted to increase to about 161 exajoule. By comparing to the 3 exajoules of the renewable energy consumption in 2000, there is a significant growth of renewable energy demand which drives the transition of conventional fuels to renewable fuels in the near future.

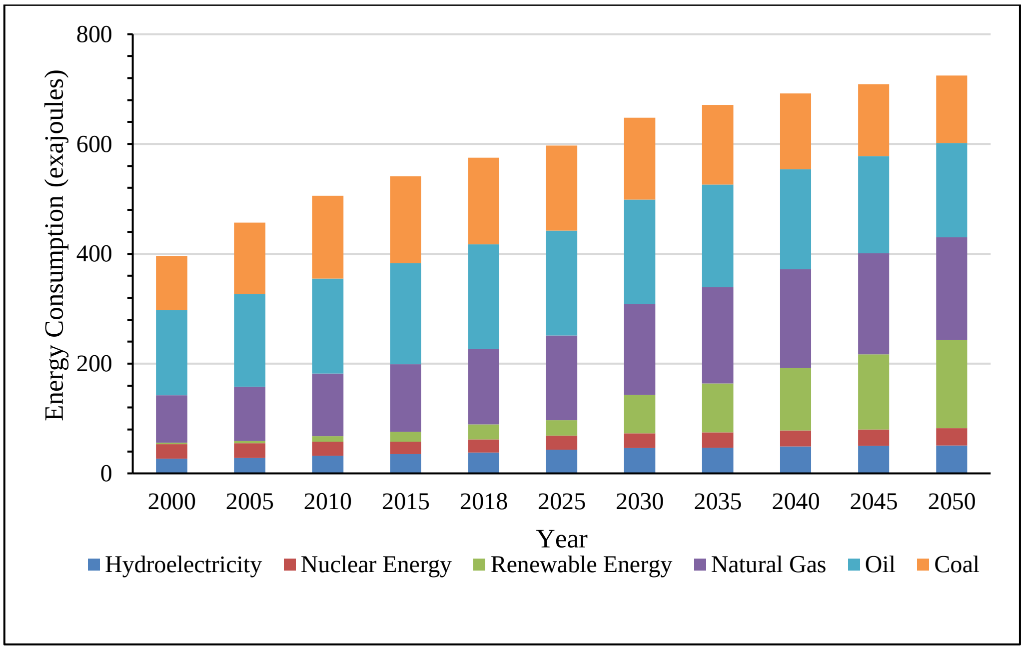


Figure 1.1: Global Energy Consumption from 2000 to 2018, with a Forecast until 2050 (BP, 2020).

Additionally, the combustion of fossil fuels has appeared as a major contributor to several environmental problems as a result of increasing energy demand. High fossil fuel energy consumption has led to excessive emission of greenhouse gases and harmful pollutants, climate change, global warming, acid rain and depletion of ozone layer. Based on the United Nations Environment Programme (UNEP) Emission Gap Report (2020), the total greenhouse gases emission has reached a record high of 59.1 gigatonnes of carbon dioxide equivalent in 2019. This value is expected to rise in future due to continuous intensive use of fossil fuels. The global emissions of greenhouse gases from all sources is increasing significantly from year to year as shown in Figure 1.2. It was observed that the highest emission is accounted by fossil carbon dioxide. Such huge volume of emissions is worrying all quarters as it could bring many adverse impacts to the environment as well as the human health and other living organisms. Therefore, development of sustainable, renewable and eco-friendly alternative energy resources is vital to overcome these problems.

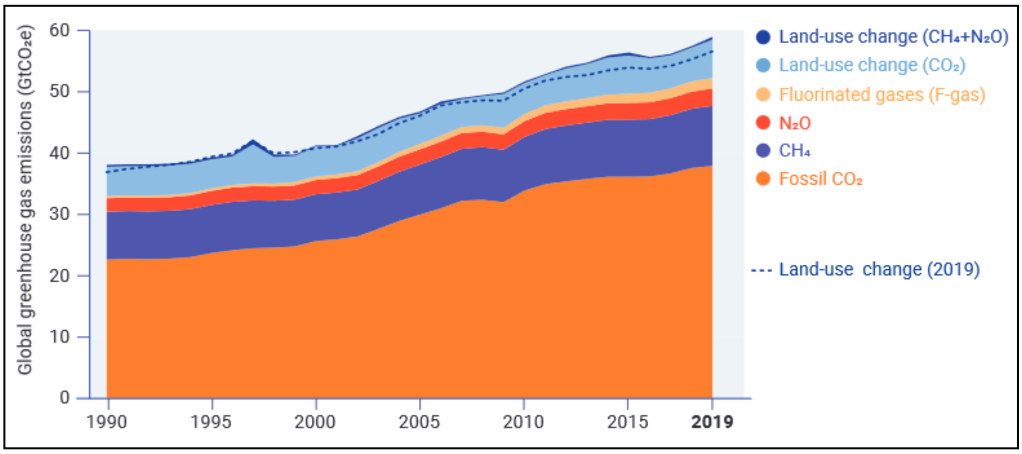


Figure 1.2: Global Greenhouse Gases Emissions from All Sources (UNEP, 2020).

1.2 Biodiesel Production

Among the renewable energy resources, biofuel is one of the superior alternative source of energy to replace fossil fuels especially in industry and transportation sector. The increase in the industrialisation and the number of vehicles fuelled with petroleum fuel has raised the needs for fuels substantially, resulting in a continuous depletion of fossil fuels. Figure 1.3 shows that approximately 37 % of total energy consumption was related to the industry sector in 2015 and 2016. Moreover, transportation sector had also contributed to about 29 % of total energy consumption which was the second highest percentage of total energy consumption besides industry sector.

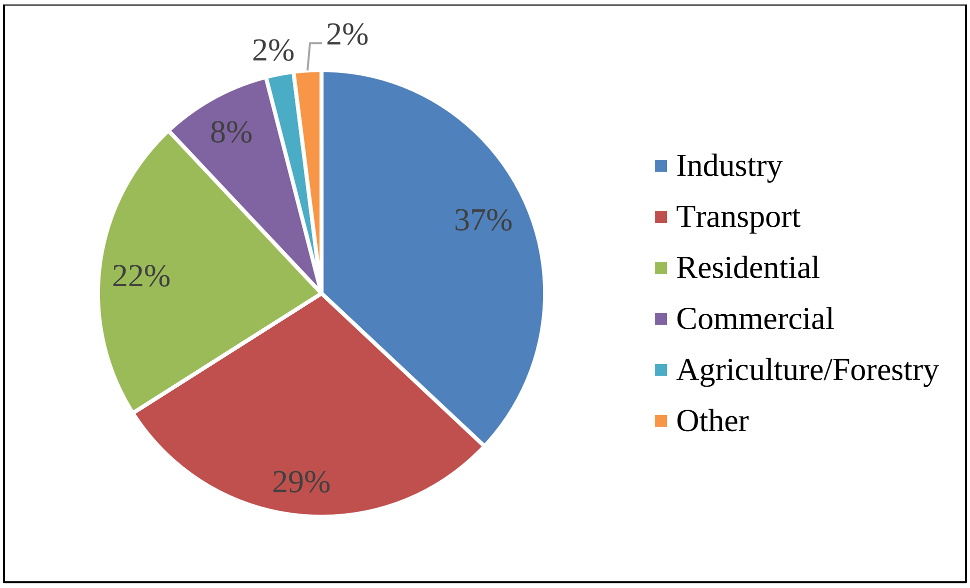


Figure 1.3: Percentage of Total Energy Consumption by Sector in 2015 and 2016 (Vooradi, et al., 2019).

There are several types of biofuel in which biodiesel is one of them that is focused in this study. Biodiesel is a liquid biofuel consisting of fatty acid methyl esters (FAME) mixture which is manufactured by transesterification reaction of triglycerides (TG) from renewable feedstocks with methanol in the existence of a catalyst (Thangaraj, et al., 2019). As a fuel for the future, it has exhibited very similar characteristics and even better properties compared to conventional fossil fuels. It is environmentally beneficial due to its renewable, biodegradable and low toxic nature compared to conventional diesel. Moreover, biodiesel has the capability to mix with petroleum-based diesel in any percentage, typically up to 10 % as most of the engines requires modification if running on pure biodiesel.

According to Ambaye, et al. (2021), biomass will contribute to about 10 to 50 % of the energy consumption worldwide until 2050, indicating the importance of biomass as one of the greatest energy resources in the world. As one of the leading palm oil producers and exporters worldwide, Malaysia produces 40 % of total global palm oil every year (Nomanbhay, Hussein and Ong, 2018). Hence, it can be said that Malaysia plays a vital role in global biodiesel production and palm oil is the primary feedstock for biodiesel production in Malaysia. Generally, there is about 94 % of biomass feedstock in Malaysia is from oil palm waste while the agricultural and forestry residues contribute to the remaining. Palm oil is considered as an excellent raw material for biodiesel production as it contains the highest oil yield among the edible oils with the lowest production cost. It is forecasted that approximately 25.6 million tonnes of crude palm oil (CPO) will be generated by the year 2050 (Zulqarnain, 2020). In fact, Malaysia is the second largest producer of palm oil worldwide after Indonesia. Figure 1.4 shows the total plantation area for palm oil production in Malaysia and Indonesia in millions of hectares. From 2004 to 2018, the production of palm oil in both countries had increased gradually to fulfil the demand.

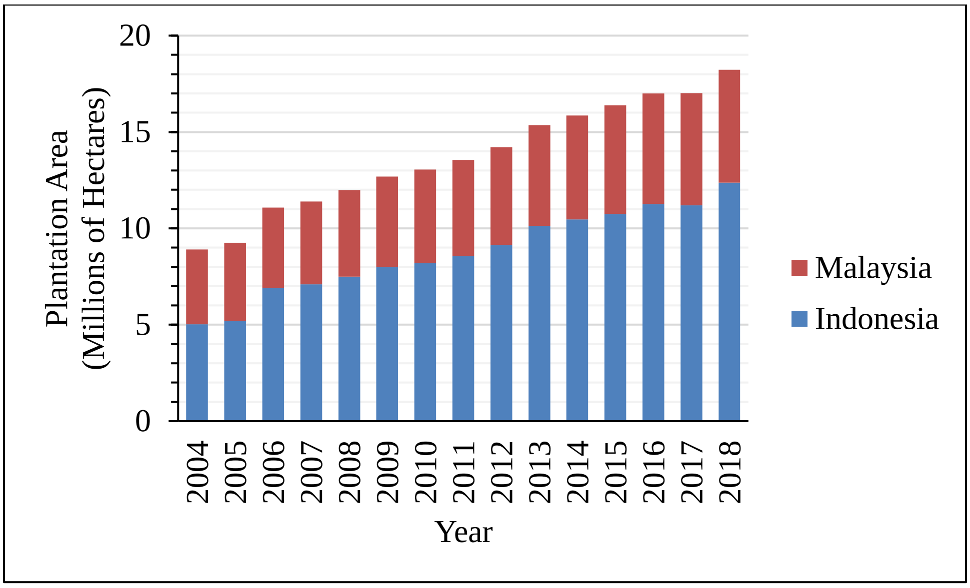


Figure 1.4: Plantation Area for Palm Oil Production in Malaysia and Indonesia (Zulqarnain, 2020).

Table 1.1 presents the potential production volume of biodiesel and the respective average production cost per litre for 10 countries. It shows that Malaysia is the leading producer for biodiesel among these countries which is potentially producing 14.54 billion litres annually. To date, Malaysia has implemented the B10 programme (blend of 10 % palm biodiesel with 90 % petroleum diesel) for the transportation sector and the B7 programme for the industrial sector. The implementation of the B20 programme for the transportation sector was also done in phases after launching in 2020 (Jaafar, 2021). However, a number of challenges are still awaiting for the implementation of higher blended biodiesel program in Malaysia although several initiatives have been put in place by the government to promote green technology and utilisation of potential biomass.

Table 1.1: Absolute Biodiesel Production by Top 10 Countries (Johnson and Holloway, 2007).

Rank	**Country**	**Potential Volume ($\times 10^6$ L)**	**Cost of Production ($/L)**
1	Malaysia	14 540	0.53
2	Indonesia	7 595	0.49
3	Argentina	5 255	0.62
4	USA	3 212	0.70
5	Brazil	2 567	0.62
6	Netherlands	2 496	0.75
7	Germany	2 024	0.79
8	Philippines	1 234	0.53
9	Belgium	1 213	0.78
10	Spain	1 073	1.71

The general biodiesel production process from biomass is shown in Figure 1.5 which includes logistics, pretreatment and conversion processes. The process starts by logistics process such as collection, handling, transportation and storage of biomass feedstocks. After that, the biomass undergoes pretreatment process which includes drying, grinding and sieving to dissociate the complex structure of biomass which is the plant cell wall in order to facilitate the conversion process of biomass. Finally, biodiesel is produced by conversion process which contains feeding, conversion, intermediate product separation and product collection.

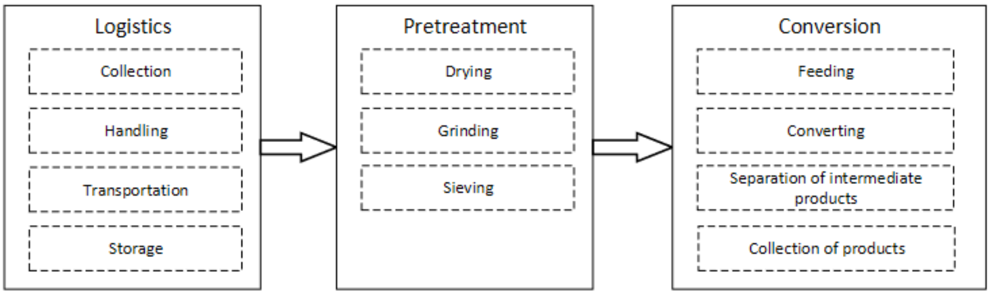


Figure 1.5: General Biodiesel Production Process from Biomass (Cai, et al., 2017).

Catalysts and raw materials are the crucial elements for biodiesel production to convert triglycerides into biodiesel during transesterification reaction. Normally, the catalysts used for biodiesel production is synthesised from costly chemical reactants, resulting in high overall production cost. In this context, apart from utilising biomass for biodiesel production, biomass also can be considered as the supporting materials to fabricate an effective and efficient catalyst in terms of cost and performance. Nevertheless, not all the biomass-derived catalyst is able to catalyse the reactions for biodiesel production. Thus, study of biomass-derived catalysts and their applications should be carried out to reduce the production costs while rendering higher yield of biodiesel.

1.3 Importance of the Study

In the past several decades, the world population is heavily relying on fossil fuels such as petroleum, coal and natural gas as a result of rapid growth of industrial and transportation development. According to BP (2018), the world's total primary energy consumption amounted to 13 511.2 million tonnes of equivalent at the end of 2017. By referring to Figure 1.6, fossil fuels were the dominant global energy resources with the primary energy consumption high to 84.70 % in the world, followed by hydroelectric, nuclear and renewable resources.

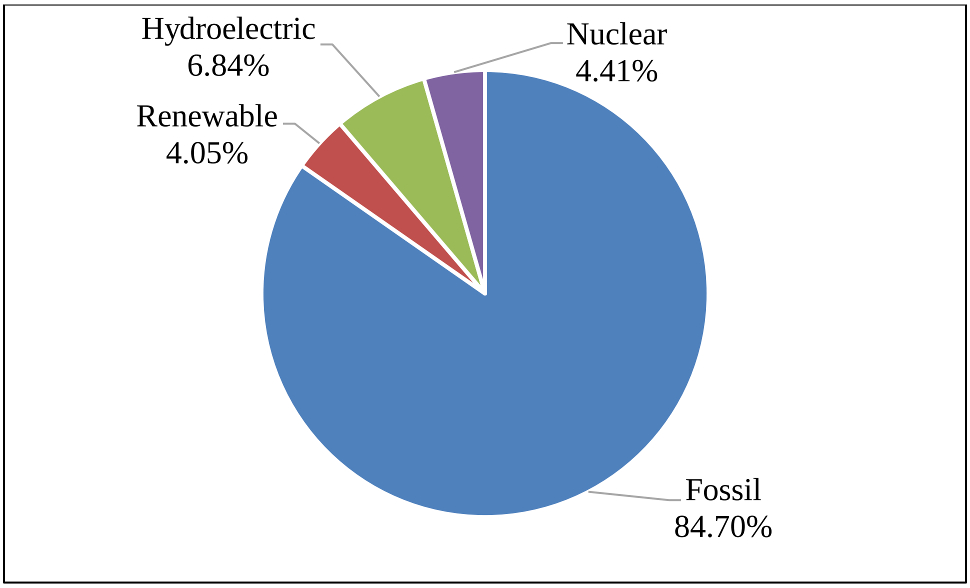


Figure 1.6: World Primary Energy Consumption in 2018 (Karakurt, 2020).

However, these conventional energy resources are finite and non-renewable resources that will be exhausted in the near future. Thus, it is essential to develop a new energy resource that is feasible as a potential substitute for fossil fuels. In this context, the biodiesel production from biomass is gathering more attention to be an alternative to replace fossil fuels for future energy supply. Cellulose catalyst synthesised from biomass can be applied to catalyse the transesterification reaction in biodiesel production. Therefore, the parameters that are expected to influence the performance of biomass-derived cellulose catalyst in the production of biodiesel are studied to achieve better biodiesel yield.

1.4 Problem Statement

It is undeniable that huge amount of biomass waste is derived from agricultural and forestry activities. Annually, 140 gigatonnes of biomass waste is generated around the world (Tripathi, et al., 2019). With the presence of dense tropical rainforest, Malaysia has actively participated in agricultural development, giving rise to abundance of biomass resources which can be transformed into energy. The annual generation of biomass waste in Malaysia is nearly 168 million tonnes including oil palm waste, rice husks, sugarcane bagasse and wood residues (Aziz and Leon, 2012).

The issue is raised when the disposal of biomass waste is not managed efficiently which may result in negative impacts to the environment. Most of the agricultural wastes are underutilised and left in the field for open burning as this is the simplest way for the farmers to discard the waste. However, such practice will cause air pollution and increase the emission of greenhouse gases. Thus, utilisation of biomass waste is one of the promising solutions in order to reduce environmental issues of waste disposal by converting it into useful bioenergy.

In addition, it is known that production of biodiesel from biomass is significant to meet the increasing energy demand worldwide. However, the production cost is still the main problem in commercialisation of biodiesel. The biodiesel cost is approximately 1.5 to 3 times that of conventional diesel fuel (Canakci and Sanli, 2008). In fact, the catalyst for production of biodiesel contributes to a large portion of overall production cost. Therefore, it is necessary to develop a cost-effective catalyst originated from biomass such as cellulose-derived catalyst.

Hence, a profound understanding of the characteristics of biomass-derived cellulose catalyst is crucial for the conversion process of biomass into biodiesel in order to reduce production cost while utilising the potential energy feedstocks.

1.5 Aim and Objectives

This research study is aimed to investigate the development of biomass-derived cellulose catalyst for biodiesel production with the following objectives to be achieved:

i. To investigate the biodiesel production using various types of biomass-derived catalysts in terms of yield.
ii. To investigate the physical and chemical characteristics of biomass-derived cellulose catalyst.
iii. To investigate the kinetics and thermodynamics of biomass-derived cellulose catalyst in biodiesel production.

1.6 Scope and Limitation of the Study

In order to attain the objectives, the following scopes are established to specify the range of the study. This research project focuses on the biomass-derived cellulose and its application in biodiesel production. The extraction methods of cellulose from biomass and the biodiesel production pathway will be determined through the literature review. Furthermore, the effects of transesterification parameters on biodiesel yield will be investigated which include methanol-to-oil molar ratio, catalyst loading, reaction temperature and reaction duration in order to improve the reaction process.

In addition, this research will study the characterisation of biomass-derived cellulose catalyst in biodiesel production such as its morphology, crystallinity, thermal stability and functional groups. The kinetics and thermodynamics studies of biomass-derived cellulose will also be conducted through journal review to further optimise the process of biodiesel production.

However, there are several limitations needed to be considered in this study. This study is based on literature reviews from previous research studies and data collection from other journals without conducting the experiments. Therefore, there may be some unavailable or inaccurate information obtained. Besides, this study also includes some own analysis and interpretations.

1.7 Contribution of the Study

Most of the related journals had discussed about the biomass-derived heterogeneous catalysts for biodiesel production. However, this study will focus on the utilisation of biomass-derived cellulose as the catalyst to produce biodiesel. The findings on the improvement of biodiesel production with the use of biomass-derived cellulose catalyst is significant as biodiesel is the potential renewable energy resource to replace fossil fuels. In addition, biomass-derived cellulose catalyst plays a key role to increase the rate of transesterification reaction while minimising the wastes generated during the process.

1.8 Outline of the Report

This report is divided into five major chapters, where it is started by giving a brief background on renewable energy. Chapter 1 highlights the significance of employing biodiesel as an alternative energy resource. Problem statement, aims and objectives, scope, limitation and contribution of the study are also discussed. Chapter 2 gives a comprehensive literature review on the potential feedstocks and the catalysts that are usually used for biodiesel production. Moreover, the various methods used to extract the nanocellulose from the biomass and the pathways to produce biodiesel are also explained extensively, followed by the parameters that affect the transesterification reaction in biodiesel production. Chapter 3 describes the research methodology used to manage the information for this study. Next, Chapter 4 presents the information and data obtained from various works conducted by different researchers which includes the characterisation of biomass-derived cellulose catalyst and the analysis and interpretation on the performance of catalyst in production of biodiesel. Besides, the challenges and future prospects of implementing biomass-derived cellulose catalyst in biodiesel production are also reviewed in this section. In the last chapter of the report, it concludes the study and provides recommendations in order to improve the research in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Feedstocks for Biodiesel Production

In the context of biodiesel, a feedstock refers to any biological material that is renewable and destined for direct usage of fuel or conversion to another form of energy. Biomass feedstocks for biodiesel production can be obtained from dedicated energy crops, agricultural residues, animal wastes and urban wastes. There are several types of biodiesel produced in various purities and compositions. In fact, selection of feedstock is one of the significant steps for biodiesel production as the purity, composition, yield and cost of biodiesel are highly dependent on the feedstocks. Besides, the local availability of feedstocks and economic aspects of biomass utilisation in a country also influences the selection of feedstock. For instance, palm oil and coconut oil are commonly used in Indonesia and Malaysia while Brazil and USA use soybean oil as their biodiesel feedstocks.

There are various types of potential feedstocks that can be used for biodiesel production which are classified based on types of feedstock sources, their limitations as renewable energy sources and their technological development. The classification of the biodiesel feedstocks are first generation feedstocks, second generation feedstocks, third generation feedstocks and fourth generation feedstocks.

2.1.1 First Generation Feedstocks

First generation feedstocks are used to produce first generation biofuels which are also known as conventional biofuels. They are generally related to the biomass that is often edible such as vegetable oils, sugar, starch and animal fats (Singh, et al., 2015). Sugar and starch crops are fermented into bioethanol while other vegetable oils and animal fats undergo chemical process to produce biodiesel.

The typical examples of edible vegetable oils for biodiesel production are coconut oil, palm oil, soybean oil, sunflower oil and rapeseed oil. Among various edible vegetable oils, palm oil ranks the highest oil yield per hectare and the biodiesel produced from palm oil has the similar properties to the conventional biodiesel. Moreover, coconut oil also can be utilised to produce biodiesel with the improved oxygenation properties for the operation of automobiles (Singh, et al., 2019). For soybean, it is known as global food crop as it is grown in many regions of North America, South America, and Asia. Approximately 66 gallons of biodiesel per acre can be produced from soybean although it has the worst crop yield (Hay, 2021). On the other hand, sunflower is a high oil content feedstock and has the higher yield compared to soybean and rapeseed with the average value of 600 pounds of oil per acre being produced (National Sunflower Association (NSA), n.d.). Only low amount of fertilizer and water is required to grow sunflower, making sunflower is widely used to produce biodiesel. Besides, rapeseed is the main biodiesel feedstock in Europe which is able to generate biodiesel with proficient stability and cold flow performance (European Biomass Industry Association (EUBIA), 2021).

It is quite popular to use first generation feedstocks to produce biodiesel at the early growth of biodiesel development due to the abundance sources. However, the specific challenges associated with the use of first generation feedstocks is the competition for food. As a result of high food demand, it will be too costly to produce biodiesel from edible oils. Moreover, first generation feedstocks require large region of agricultural lands to grow in order to produce biofuels in large scale.

2.1.2 Second Generation Feedstocks

Second generation biofuels are produced from the non-edible feedstocks which are also known as second generation feedstocks. There are also certain food crops that can be used as second generation feedstocks when they are no longer useful or consumed. The feedstocks consist mainly of lignocellulosic biomass including wheat straws, barley straws, corn husks and sugarcane bagasse and non-edible oilseeds such as Jatropha oil, Karanja oil, Mahua oil, cottonseed oil and linseed oil (Singh, et al., 2019).

The lignocellulosic feedstocks for secondary generation biofuel production are usually categorised into homogeneous biomass such as wood chips, quasi-homogeneous biomass which includes agricultural and forest residues and non-homogeneous biomass consisting of municipal solid wastes

(Lee and Lavoie, 2013). There are large amounts of by-products such as unused sawdust, branches and leaves left after the wood processing which can be converted into bioenergy. Moreover, European Technology and Innovation Platform (ETIP, 2021) reported that 139 million tonnes of agricultural crop residues which include stalks, leaves, cobs, husks and bagasse are sustainably available for biofuel production currently. Municipal wastes such as paper, rubber, plastic and food wastes also possess energy potential while reducing the landfill volumes significantly.

For oilseed crops, it was founded that Jatropha oil and Karanja oil are the most suitable seed oils for biodiesel production due to their high oil contents in their seed or kernel. There is approximately 20 – 60 % oil in Jatropha seed which can be obtained in 1 year after plantation and achieves its highest productivity after 5 years of plantation. On the other hand, Karanja seed matures after 4 – 7 years of plantation contains about 25 – 40 % oil (Singh, et al., 2019).

This feedstock possess advantages over the first generation feedstocks as it does not compete with food crops for land. The cost for this feedstock is also generally lower than the cost for first generation feedstock. In addition, lignocellulosic biomass exists in abundance on earth with the availability of 7 – 18 billion tons per year which can be utilised to produce second generation biofuels (Wang and Lü, 2021). However, the production technologies are more complex to convert such feedstocks into biofuels.

2.1.3 Third Generation Feedstocks

Algae have been considered as third generation feedstocks to produce biofuels. They refer to a diverse group of aquatic autotrophic organisms that possess photosynthesis pigments such as chlorophyll. Solar energy, carbon dioxide and nutrients are utilised to form algal biomass which contains lipid, carbohydrate, protein and nucleic acid through photosynthesis process (Sudhakar, et al., 2018). The triacylglycerides presented in the lipid are suitable to produce biodiesel.

The algal biomass can be categorised as microalgae, macroalgae and cyanobacteria. For instance, *Chlorella* and *Nitzschia* which are invisible to the naked eye belong to the primary microalgae sources for biofuel production, while macroalgae which are also referred to seaweed belong to multicellular marine algae that can be seen with the naked eye. Furthermore, *Spirulina* is a cyanobacteria biomass, which is also called blue-green algae (Wang, 2013).

Algal biomass is gaining interest as an emerging biofuel feedstock due to their high lipid content, rapid growth and excellent biomass yield. The production of third generation biofuels from algae depends on the lipid content of the algae. Wang (2013) also reported that at least 30 % of lipids contained in the microalgae cell which could be converted to biofuel.

According to Office of Energy Efficiency and Renewable Energy (EERE, n.d.), algae can be cultivated by using sea water, groundwater or surface water which includes fresh, saline and brackish water depending on the algal species. In addition, they also can grow in second-use water such as municipal wastewater, industrial wastewater and agricultural wastewater, thus reducing the problems of freshwater shortage area and barren land area for algae cultivation in order to produce biofuels.

2.1.4 Fourth Generation Feedstocks

Production of biofuels based on a combination of different technologies has distinguished fourth generation biofuels from other generation biofuels by implying carbon sequestration at the level of both feedstocks and processing technologies (International Service for the Acquisition of Agri-biotech Applications (ISAAA), 2007). Development of the fourth generation feedstocks is an emerging field as fourth generation biofuel can become a super-clean carbon neutral or even carbon negative biofuel by reducing the emissions of greenhouse gases. The main technologies for production of fourth generation biofuels include biomass genetic modification, direct solar biofuel production and artificial photosynthesis.

Raw materials with high energy content, inexhaustible, cheap and widely availability are the main considerations in the development of fourth generation feedstocks (Ahorsu, Medina and Constantí, 2018). Second and third generation feedstocks are enhanced through genetic modification to produce biomass with low cellulose and lignin contents. Besides, the production of algae with high oil contents and improved ability of carbon entrapment is also used as the main feedstocks for the fourth generation biofuels production (Ziolkowska, 2020). These genetically engineered feedstocks act as carbon capture machine to lock more carbon dioxide during the crop cultivation process.

According to Aro (2016), solar energy can be a major source to synthesis biofuel from both direct solar biofuel production and artificial photosynthesis by carrying out photosynthetic water splitting which is also known as water oxidation into its constituents. In this context, direct conversion of solar energy into chemical energy produces solar biofuel by reducing the protons to hydrogen or carbon dioxide to organic compounds.

2.2 Catalysts for Biodiesel Production

In the production of biodiesel, transesterification process should be conducted in the presence of a suitable catalyst. Catalysts are responsible in converting triglycerides to biodiesel during the reaction of transesterification. Therefore, there are various types of catalysts being explored to optimise the reaction performance. In general, catalysts used for biodiesel production can be classified into three categories, that are homogeneous catalysts, heterogeneous catalysts and biocatalysts as shown in Figure 2.1.

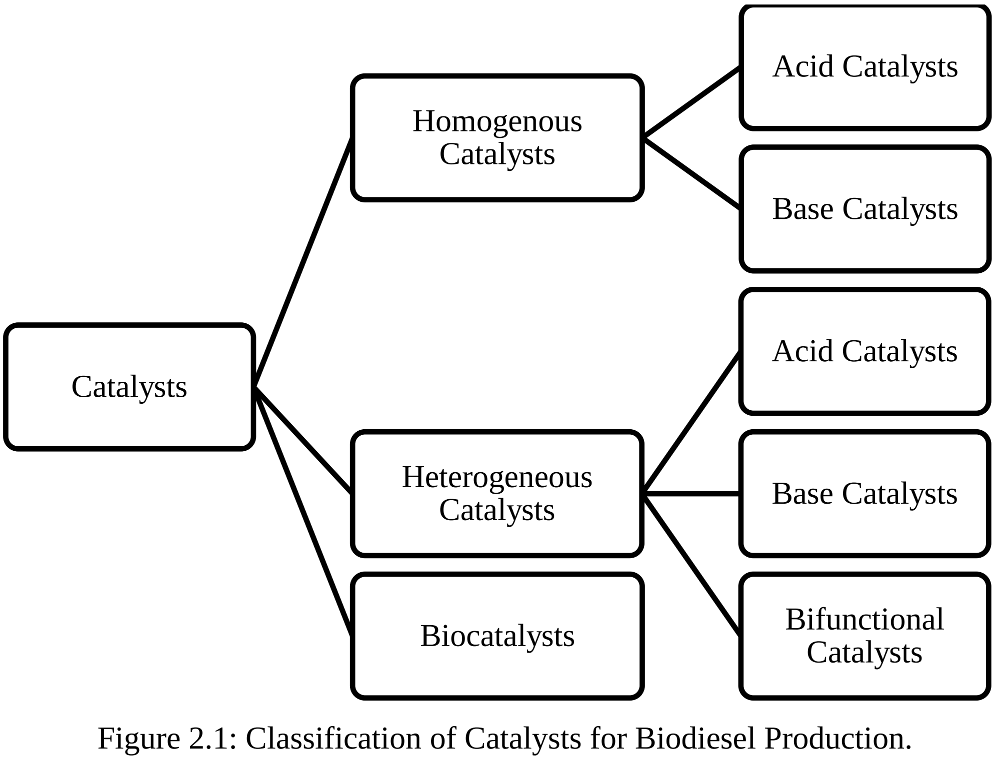


Figure 2.1: Classification of Catalysts for Biodiesel Production.

2.2.1 Homogeneous Catalysts

Homogeneous catalysts refer to catalysts that remain in the same phase as the reactants by dissolving the catalysts in a solvent. Since homogeneous catalyst is simple to use and able to complete the reaction in a short time, homogeneous catalyst is preferred to be utilised as catalyst to produce biodiesel. There are acid and base catalysts under homogeneous catalysts.

Typically, homogeneous base catalysts such as sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide are preferred over homogeneous acid catalysts to produce biodiesel due to their reactivities (Thangaraj, et al., 2019). Among these catalysts, sodium hydroxide and potassium hydroxide are mostly employed as catalysts in the biodiesel production as they are less expensive and widely available. However, the use of sodium hydroxide and potassium hydroxide will form water as a by-product in the process and reduce the biodiesel yield. In this matter, sodium methoxide and potassium methoxide can show excellent catalytic performance as they are able give better biodiesel yield which is above 98 % in short reaction time of 30 minutes without the formation of water (Atadashi, et al, 2012). Besides, studies had shown that homogeneous base catalysts were suitable to produce biodiesel from oil with low free fatty acids (FFA) content less than 2 wt %. For high FFA content up to 5 %, it was required to add extra amount of catalysts to make up the catalyst lost to soap so that the catalytic reaction could be proceeded (Fattah, et al., 2020). This is because soap could be formed as a consequence of saponification reaction of base catalysts with FFA present in the feedstock. The chemical equation is shown in Equation (2.1):

$$R - COOH + NaOH \rightarrow R - COOHNa + H_2O \tag{2.1}$$

On the other hand, homogeneous acid catalysts which are neutral to FFA can be used to catalyse the biodiesel production from oil with high FFA content more than 2 wt %. For instance, hydrochloric acid, phosphoric acid, sulphuric acid and sulphonic acids are usually utilised (Thangaraj, et al., 2019). However, acid catalysts are not commonly utilised for biodiesel production due to the disadvantage of slower reaction rate compared to base catalysts, leading to energy intensive processes. It was reported that acid-catalysed reactions are

4000 times slower than base-catalysed reactions (Vijayalakshmi, Anand and Ranjitha, 2020). Moreover, high alcohol-to-oil molar ratio is required by acid-catalysed reactions.

2.2.2 Heterogeneous Catalysts

Heterogeneous catalysts means that they exist in a phase different from the reactants. This type of catalyst mostly appears as solid that act on substrate in the liquid or gaseous reaction mixture. Active sites on the catalyst surface are able to catalyse the heterogeneous reactions. Since they are usually in solid form, it is easier to separate heterogeneous catalysts from final products. Heterogenous catalysts can be classified into acid catalysts, base catalysts and bifunctional catalysts with both acid-base character.

In comparison to homogeneous acid catalysts, heterogeneous acid catalysts are less corrosive and toxic. There are numerous acidic sites presented in heterogenous acid catalysts with different Brønsted or Lewis acidity strengths. The process of transesterification can be promoted by activating these acidic sites. Thus, the greater the amount of Brønsted or Lewis acidic sites, the higher the transesterification rate. Although heterogeneous acid catalysts are able to give better performance under moderate reaction conditions, they require high catalyst loading and the reaction rate is slower than that of heterogenous base catalysts (Fattah, et al., 2020). Cation-exchange resins and sulphated oxide-based catalysts are the examples of heterogenous acid catalysts for biodiesel production. Resin-based catalyst has become popular in the recent years as it is active at low temperature and able to retain and discharge ions simultaneously. On the other hand, sulphated metal oxides are chemically stable and super acid catalysts which can give very high conversion in the transesterification reaction (Changmai, et al., 2020).

According to Thangaraj, et al. (2019), the catalytic activity of heterogeneous base catalysts is higher than that of heterogeneous acid catalysts as they have more active sites. Metal-based oxides are usually used as heterogenous base catalysts for transesterification of oils, namely alkali metal oxides, alkaline earth metal oxides, mixed metal oxides and transition metal oxides. The examples of heterogeneous base catalysts include calcium oxide, magnesium oxide, strontium oxide, aluminium oxide-supported potassium carbonate and aluminium oxide-supported potassium nitrate. Studies showed that the stronger the basic sites of the oxides, the more effective the reaction. Calcium oxide was reported as the most widely utilised catalysts for biodiesel production among the metal-based catalyst due to its high basic strength and insolubility in alcohol (Changmai, et al., 2020). The surface structure of a metal oxide is shown in Figure 2.2 where M represents the metal. Lewis acid characteristics is represented by positive metal ions while Brønsted base characteristics is represented by negative oxygen ions.

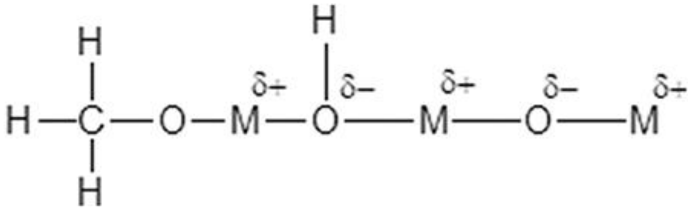


Figure 2.2: Surface Structure of a Metal Oxide (Fattah, et al., 2020).

There are also some catalysts that can be employed as acid catalyst, base catalyst or bifunctional catalyst, where it depends on the reactant type and reaction conditions. For instance, zirconium dioxide, also known as zirconia which is primary acidic in nature, and its derivatives such as zirconia-supported metal (Ca/ZrO_2, Mg/ZrO_2, Sr/ZrO_2, and Ba/ZrO_2), zirconia-supported metal oxides and sulphated zirconia (Fattah, et al., 2020). Additionally, zeolite-based catalyst also can work bifunctionally for various acid-base reactions as it can exist in various structural morphologies in different reaction conditions (Changmai, et al., 2020). The presence of acid-base character in bifunctional heterogenous catalysts makes esterification of free fatty acids and transesterification of triglycerides can be conducted simultaneously without affected by the formation of by-products during biodiesel production. Thus, the production costs can be reduced effectively by eliminating the downstream processes.

2.2.3 Biocatalysts

The conventional biodiesel production process through chemical catalysis is very energy consuming. Additionally, it will form undesirable by-products such as soaps, leading to high complexity of the separation and purification of biodiesel. However, such obstacles can be overcomed by using biocatalysts. Biocatalysts, also known as enzymes, are catalysts of natural origin that have the ability to perform chemical transformations on organic compounds. The most common biocatalysts used for biodiesel production are lipases which can be obtained from all living organisms intracellularly and extracellularly. More than 90 % of biodiesel yield can be achieved by most of the lipases (Vargas, et al., 2018).

Extracellular lipases refer to the lipases that have been recovered and purified from the microorganism cultivation broth. They can be either free and immobilized lipases. Preferably, bacteria, yeasts and fungi are used to produce extraellular lipases due to their ability to catalyse the same reaction from different lipases. Soluble lipases are free to move during the catalytic reactions. Although the preparation procedure for free lipases is easy and less expensive, they are easily inactivated and only can be used once (Chioke, et al., 2018). Thus, immobilization of lipases has drawn great attention as it is able to improve the reusability of biocatalysts. It is a modification method that attaches the enzyme onto an insoluble solid support material which can optimise the operation and temperature and lead to higher conversion and shorter reaction time (Yücel, Terzioğlu and Özçimen, 2012). *Mucor miehei*, *Pseudomonas cepacian*, *Candida antarctica* and *Rhizopus oryzae* are the primary microorganism producers for extracellular lipases while the most commonly utilised immobilized lipases include Novozyme 435, Lipozyme RM IM and Lipozyme TL IM (Gog, et al., 2012). However, the utilisation of extracellular lipases as catalysts encountered disadvantages of high cost, complex separation and purification procedures.

On the other hand, intracellular lipases, are the enzymes that attached to the producer's cell wall or remain inside the cell. Since intracellular lipases are used as whole-cell biocatalysts, purification steps are not required for its production. Thus, the major issue of costly enzymes in biological catalysis can be solved by eliminating the operation of downstream processes and recycling the lipases. Nevertheless, it is still limited to use intracellular lipases to manufacture biodiesel in large scale due to the limited mass transfer efficiency of substrate and product (Yücel, Terzioğlu and Özçimen, 2012). Additionally, whole-cell biocatalysts cannot be reused when the reaction ends. The most widely used whole-cell biocatalysts are Filamentous fungi such as *Rhizopus* and *Aspergillus* (Gog, et al., 2012).

2.3 Biomass-Derived Catalyst

In the manufacturing industry, most of the processes including biodiesel production involve the use of catalysts, no matter homogeneous catalysts or heterogenous catalysts. However, these commercial catalysts are generally limited by their expensive prices although they can provide excellent catalytic performance. As such, biomass waste has become a potential source as a catalyst in the manufacturing of biodiesel as it is abundant, cheap, renewable and sustainable while able to reduce the waste generated.

2.3.1 Lignocellulosic Biomass

Since the biomass wastes generated are troublesome if they are underutilised, various biomass wastes can be utilised as catalyst in biodiesel production. In this matter, the wastes generated from agriculture sector have gained the most popularity to be a potential candidate in the synthesis of biomass-derived catalysts. Figure 2.3 indicates the distribution of biomass waste in Malaysia in which oil palm waste accounts for the highest contribution, followed by municipal solid waste, wood residues, rick husks and sugarcane bagasse.

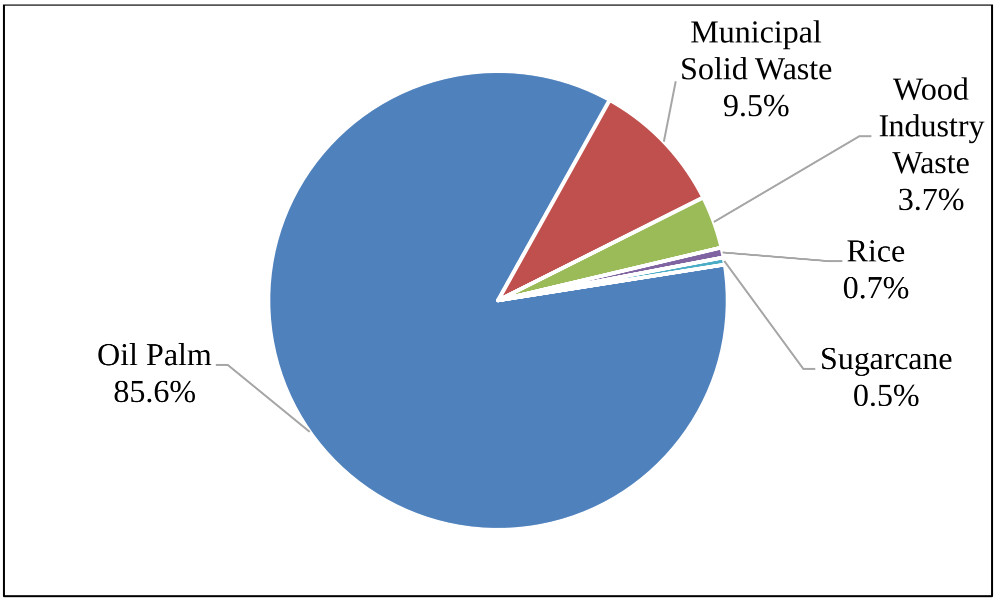


Figure 2.3: Distribution of Biomass Wastes in Malaysia (Shahbaz, et al., 2016).

Lignocellulosic biomass is the most abundant feedstock for the production of biodiesel. It is mainly composed of 40 – 50 % cellulose, 25 – 30 % hemicellulose and 15 – 20 % lignin (Fatehi, 2012). Figure 2.4 shows the plant cell wall structure of lignocellulosic biomass in which the cellulose molecules are bundled in a matrix of hemicellulose and lignin. As the primary constituent among these components, cellulose has a lot of prominent properties which make it suited for catalyst in biodiesel production such as its reactive hydroxyl groups, biocompatibility, hydrophilicity and stereoregularity (Baruah, et al., 2018).

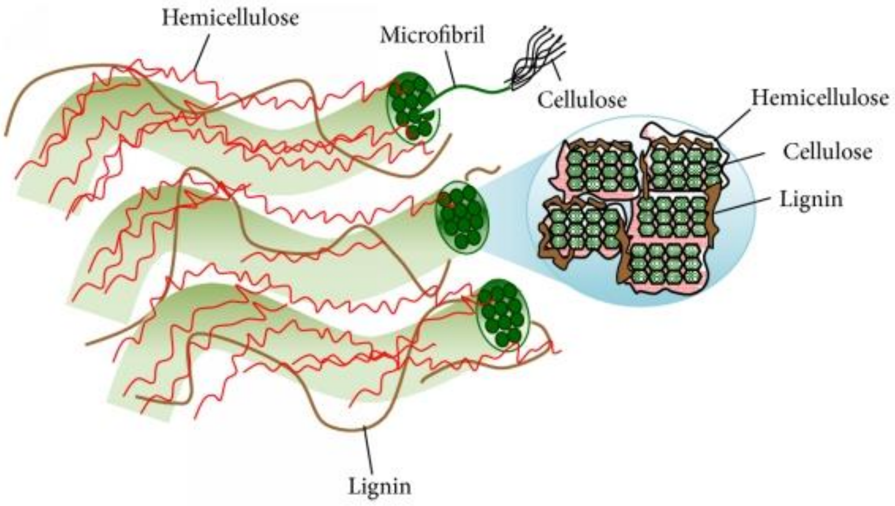


Figure 2.4: Structure of Lignocellulosic Biomass (Lee, Hamid and Zain, 2014).

2.3.2 Activated Carbon-Derived Catalyst

Activated carbon is a highly porous material which is mainly derived from compounds with high carbon content such as wood, coal and biomass sources. The most abundant renewable carbon source is cellulose, followed by lignin. According to Bhandari, et al. (2014), it can be activated physically, chemically or a combination of physical and chemical activation. Activated carbon provides a high surface area due to the presence of large number of active sites where the metal particles are anchored for the reaction to occur. The surface and inner structure of activated carbon is showed in Figure 2.5.

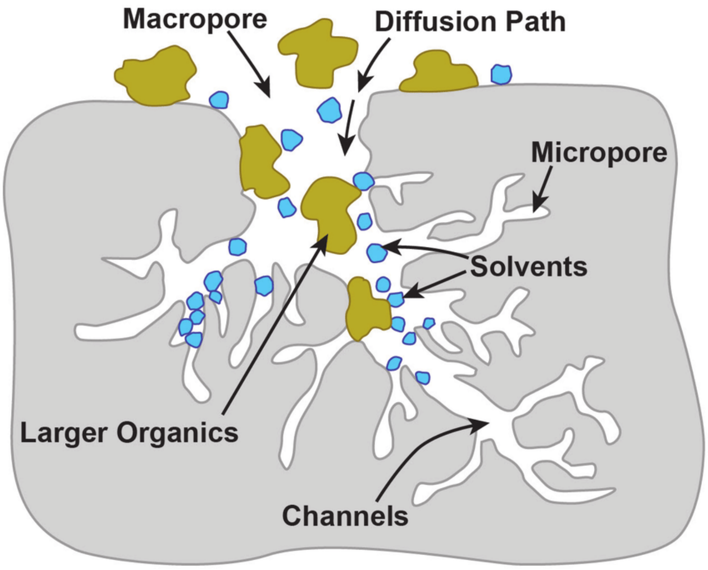


Figure 2.5: Schematic Pore Structure of Activated Carbon (Kemp, 2017).

Activated carbon-derived catalysts can be further classified into acid functionalised catalysts and base functionalised catalysts. Activated carbon derived from biomass is functionalised with an acid or base to attach acidic or basic functional groups and form active sites on the activated carbon's surface. The most common acid functionalised catalyst is sulphonated activated carbon which is able to perform the same catalytic activity as sulphuric acid. Thus, it can be utilised as an alternative for sulphuric acid in esterification and transesterification to produce biodiesel in large scale (Konwar, et al., 2014). There are three functional groups containing in sulphonated activated carbon catalysts, namely sulphonic acid, $-SO_3H$, carboxylic acid, -COOH and phenolic acid, -OH. Although the primary active site to catalyse the reaction is $-SO_3H$, the hydrophilic properties of catalyst surface can be enhanced by -COOH and -OH, making the reactants to be more accessible to the catalysts (Abdullah, et al., 2017). On the other hand, base functionalised catalysts can be prepared by amine functionalisation. For instance, ethylene diamine and propylene diamine are used as the functionalisation agents (El-Shafey, et al., 2016). The accessible active sites on the activated carbon surface are increased due to the presence of the basic amine functional groups, $-NH_2$. This makes the catalysts to be more reactive to catalyse the transesterification reaction although some of the amine groups are not accessible to the reactants as a result of the attachment of these amine groups to the polymer structure (Aghabarari, 2016).

Basically, activated carbon is mostly used as a catalyst support for calcium oxide, potassium hydroxide and lipase in the transesterification reaction. With the use of catalyst support in the heterogenous reaction, the rate of reaction can be increased by reducing the mass transfer limitation. Since the cost of the commercial catalyst supports such as silica and alumina is relatively high, low-cost activated carbon used as catalyst support can help to minimise the total production cost for biodiesel production (Abdullah, et al., 2017). Apart from the advantage of making carbon to be reusable in the production process, activated carbon-derived catalyst is able to reduce the soap formation and increase the glycerol purity (Changmai, et al., 2020). Moreover, activated carbon-derived catalyst is stable in both acidic and alkaline environments and can work readily in transesterification processes as it is resistant to heat and radiation (Narowska, Kulazynski, Lukaszewicz, 2020). Table 2.1 illustrates several examples of activated carbon catalysts derived from biomass for biodiesel production in numerous literature. Under optimum reaction conditions, these catalysts can achieve high biodiesel yield up to 96 %.

Table 2.1: Biomass-Derived Activated Carbon Catalysts for Biodiesel Production.

Type of Catalyst	**Type of Feedstock**	**Reaction Parameters**				**Biodiesel Yield (%)**	**References**
		Temperature (℃)	**Methanol-to-oil Ratio**	**Catalyst Amount (wt %)**	**Time (minutes)**		
Beech tree	Waste corn oil	62.5	3:1	0.75	60	92	Narowska, et al. (2019)
Coconut coir	Waste cooking oil	65	18:1	5	420	90.12	Jha and Sontakke (2018)
Corn cobs	Soybean oil	75	6:1	20	20	88.7	Rocha, Oliveira and Franca (2019)
Mesua ferrea linn seed shells	*Mesua ferrea linn* oil	55	6:1	10	120	95.57	Bora, et al. (2018)
T striatula waste shells	Waste cooking oil	120	40:1	11	420	96	Konwar, Boro and Deka (2018)

2.3.3 Biochar-Derived Catalyst

Biochar is a type of carbonaceous materials obtained naturally as by-product from the thermochemical degradation of biomass in an oxygen-limited environment such as biomass carbonisation, biomass gasification and pyrolysis. It has a large surface area and tailored surface functional groups (Cao, Sun and Sun, 2017). Figure 2.6 shows the abundant surface functional groups containing in biochar-derived catalysts. Since biochar has a unique chemical structure, it becomes a potential candidate to be used as a catalyst or catalyst support in different catalytic reactions after activation or functionalisation.

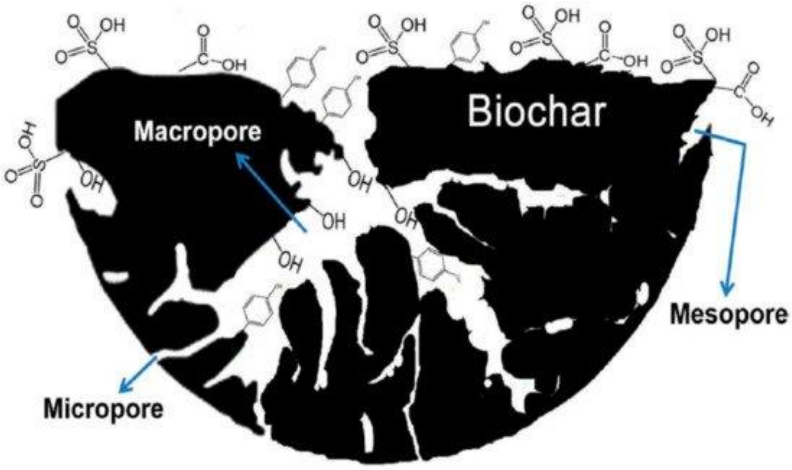


Figure 2.6: Schematic Structure of Biochar with Various Functional Groups (Cheng and Li, 2018).

Since the amounts of cellulose, hemicellulose and lignin vary with the biomass feedstock, the biochar produced will have different physicochemical characteristics. This is because the differences in structural properties of these components such as cross-linking, branching and crystallinity can lead to different thermal degradation ability. For instance, the decomposition temperature for cellulose is 315 °C to 400 °C while for hemicellulose and lignin are 220 °C to 315 °C and 160 °C to 900 °C respectively (Xiong, et al., 2017). Hence, the degradation temperature can be determined based on the contents of raw biomass in order to produce biochar with the porous structure desired.

Biochar can be functionalised with active compounds as it consists of highly cross-linking and multi-ringed aromatic structure (Abdullah, et al., 2017). There are two types of biochar-derived catalysts that can be utilised for biodiesel production, namely acid-functionalised biochar catalysts and base-functionalised biochar catalysts. Generally, high biodiesel yield can be produced from edible oils by both types of biochar catalysts. Biochar-derived catalysts are mainly sulphonated by sulphuric acid or its derivatives in acid treatment. According to Lee, Kim and Kwon (2017), it was reported that sulphonated biochars can achieve the highest yield of biodiesel products from edible oil at 88 %. The ester yields from triglycerides and free fatty acids by biochar catalysts are similar or even higher compared to non-biochar catalysts. However, biochar-derived catalysts have the tendency to deactivate after recycle for several times. Thus, it is significant to improve the stability of biochar-derived catalysts in order to increase their lifetime.

There are various inorganic elements present in the biomass which are significant for biochar formation. Commonly, the elements can be found on biochar include potassium, sodium, magnesium, calcium, iron, phosphorus, sulphur and silicon. Biomass pyrolysis can be catalysed by these elements which undergo transformation into oxides and increase the yield of biochar (Cheng and Li, 2018). The basic sites of biochar are represented by metal oxides while surface groups of phosphorus, sulphur and silicon are liable for the acid sites of biochar. In this context, higher degradation temperature can increase the ash content, thereby producing greater basic surfaces on biochar catalysts (Vakros, 2018). There are some examples of biomass-derived biochar catalysts for biodiesel production that are obtained from various literature as shown in Table 2.2. These reviews showed that more than 90 % of biodiesel yield can be produced by using biochar-derived catalysts.

Table 2.2: Biomass-Derived Biochar Catalysts for Biodiesel Production.

Type of Catalyst	**Type of Feedstock**	**Reaction Parameters**				**Biodiesel Yield (%)**	**References**
		Temperature (℃)	**Methanol-to-oil Ratio**	**Catalyst Amount (wt %)**	**Time (minutes)**		
Avocado seeds	Sunflower oil	99.5	15.6:1	7.3	300	96	Bitonto, et al. (2020)
Cultivated banana peel	Palm oil	65	15:1	4	120	98.91	Jitjamnong, et al. (2020)
Palm kernel shell	Waste cooking oil	65	13:1	3.66	102	90.2	Quah, et al. (2020)
Pomelo peel	Palm oil	65	8:1	6	150	98	Zhao, et al. (2018)
Rice husk	Palm oil	65	9:1	8	180	93.4	Zhao, et al. (2018)
Sugarcane bagasse	Waste cooking oil	60	18:1	15	15	89.19	Nazir, et al. (2021)

2.3.4 Cellulose-Derived Catalyst

Cellulose, a form of carbohydrate, is the primary structural component of cell walls in plant. Since cellulose is the most abundant carbohydrate found in Earth, it has attracted intense interest to work in catalysis reaction apart from becoming a feedstock in biodiesel production. As such, it can be utilised as a solid acid catalyst for production of biodiesel (Mohamed, et al., 2020). Figure 2.7 shows the hierarchical structure of cellulose fiber in nature. It consists of long polymer chains connected by Van der Waals forces and hydrogen bonding for the formation of microfibrils which have diameters of 3 to 50 nm. Bundles of microfibrils are then assembled to form macrofibers with diameters of 5 to 20 μm (Dumanli, 2016).

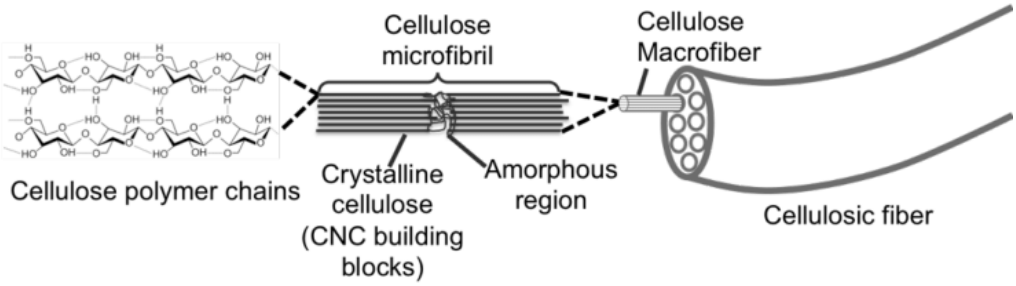


Figure 2.7: Hierarchical Structure of Cellulose (Dumanli, 2016).

Since there are large amount of hydroxyl groups in cellulose molecule, the number of intramolecular and intermolecular hydrogen bonds is increased which makes the cellulose unfavourable as a catalyst-supporting material. Therefore, this problem can be overcomed through functionalisation on the cellulose surface (Helmiyati and Anggraini, 2019). Typically, the surface functionalisation can be performed by partial carbonisation of cellulose, followed by sulphonation with sulphuric acid (Jack and Kwapinski, 2020).

The functionalised nanocellulose can be then used as nanocomposite support material. In this matter, cellulose-magnetite nanocomposites have been explored extensively due to its great chemical properties, dispersibility and superparamagnetism (Han, et al., 2016). Nanocellulose can be composited with inorganic nanoparticles such as Fe_3O_4 precursors via the interactions of Fe^{2+} and Fe^{3+} ions with hydroxyl groups on the nanocellulose chain. The particle size can be controlled by the hydroxyl groups which functions as capping agent to prevent the nanoparticles from agglomerating (Helmiyati and Anggraini, 2019).

As known, the catalytic activity is contributed significantly by the presence of active sites. In this context, cellulose-derived catalyst produced has larger pore volume and pore size, enabling the reactants to access easily. Compared to the conventional solid acid catalyst which has only one functional group, cellulose-derived catalyst consists of greater acid sites as it possesses three functional groups, that are sulphonate, carboxyl and hydroxyl groups (Wu, et al, 2019). From the research work conducted by Zik, Sulaiman and Jamal (2020), cellulose-derived catalyst demonstrated an excellent catalytic performance in biodiesel production. It can be reused up to fourth runs with the yield of biodiesel above 90 %. Repeated usage of catalyst resulted in leaching effect of active sites in the reaction system which caused the decrease in yield after the fifth run. In Table 2.3, several examples of biomass-derived cellulose catalyst to produce biodiesel which were obtained from various literature sources are presented. These studies showed that cellulose-derived catalysts can produce biodiesel with yield more than 85 % under optimum reaction conditions.

Table 2.3: Biomass-Derived Cellulose Catalysts for Biodiesel Production.

Type of Catalyst	**Type of Feedstock**	**Reaction Parameters**				**Biodiesel Yield (%)**	**References**
		Temperature (℃)	**Methanol-to-oil Ratio**	**Catalyst Amount (wt %)**	**Time (minutes)**		
Date seeds	Coconut oil	65	15:1	4	90	94.27	Jamil, et al. (2021)
Coconut residue	Waste cooking oil	65	6:1	0.5	240	98.35	Zik, Sulaiman and Jamal (2020)
Rice straw	Coconut oil	60	12:1	3.6	300	89.2	Helmiyati and Masriah (2019)
Date pits	Date pit oil	70	12:1	4.5	120	98.2	Al-Muhtaseb, et al. (2018)
Waste orange peels	Corn acid oil	65	19.95:1	5	274	91.68	Lathiya, Bhatt and Maheria (2018)

Table 2.3 (Continued)

Type of Catalyst	**Type of Feedstock**	**Reaction Parameters**				**Biodiesel Yield (%)**	**References**
		Temperature (℃)	**Methanol-to-oil Ratio**	**Catalyst Amount (wt %)**	**Time (minutes)**		
Jatropha curcas seeds	*Jatropha curcas* oil	60	12:1	7.5	60	99.13	Mardhiah, et al. (2017)
Cellulose beads	Yellow horn seed oil	60	10:1	4	40	96.22	Zhang, et al. (2016)
Microcrystalline cellulose	*Calophyllum inophyllum* oil	180	15:1	5	240	99	Ayodele and Dawodu (2014)
Cellulose powder	Palm fatty acid distillate	60	6:1	3	180	86	Gaikwad and Gogate (2015)
Cellulose powder	Coconut oil	-	-	0.6	120	90.6	Azahra and Helmiyati (2020)

2.4 Extraction of Nanocellulose from Biomass

Nanocellulose is less than 100 nanometers in size, that can be obtained from lignocellulosic biomass in a two-step process. In the first step, a pretreatment stage is necessary to expose the cellulose fibers and remove the non-cellulosic components, such as lignin, hemicellulose and other compounds. Next, nanocellulose is extracted from the pretreated cellulose fibers. There are several types of nanocellulose extraction methods, namely mechanical extraction, enzymatic hydrolysis and acid hydrolysis.

2.4.1 Mechanical Extraction

Mechanical extraction is normally characterised with a physical processing equipment to apply high shear force in order to cleavage the cellulose fibers into nanocellulose. There are several mechanical approaches which include high-pressure homogenisation, high-intensity ultrasonication and mechanical grinding.

For high-pressure homogenisation, the equipment used are homogenisers and microfluidisers which are performed by passing the cellulose pulp into a vessel under high pressure and high velocity conditions (Xie, et al., 2018). This generates impact force and shear force to disintegrate the cellulose fibers into nanocellulose. This approach usually will lead to clogging of the system if long fibers are used as biomass sources.

On the other hand, high-intensity ultrasonication is a mechanical approach that applies ultrasonic energy to extract nanocellulose. In this method, ultrasonic waves produce mechanical oscillating power in the reaction medium. When the applied ultrasonic energy is absorbed by water molecules, the cavitation effect generated will initiate the formation, expansion and implosion of microscopic gas bubbles (Mazela, et al., 2020). As a result, it causes the disintegration of intramolecular and intermolecular hydrogen bonding in cellulose fiber. Under optimised conditions, the mass transfer efficiency for nanocellulose extraction can be enhanced by using ultrasonication with the use of suitable solvent (Chowdhury, et al., 2019).

Mechanical grinding is another common technique for nanocellulose extraction. In this process, supermasscolloider grinder is widely used. The cellulose fiber is sent to the grinding area and shear stress is applied on the fiber by rotating the grindstones at approximately 1500 rpm. The extraction process can be improved when the friction generates heat and evaporates water during the process (Abdoulhdi, et al., 2021). Mechanical grinding is able to give high efficiency, low energy input and large capacity for nanocellulose extraction compared to the high-pressure homogenisation technique. Moreover, this method is less prone to the clogging of the system. However, the main concern of mechanical grinding is the fiber damage due to the strong mechanical force applied during the process. This will significantly decrease the physical strength of the nanocellulose produced (Xie, et al., 2018).

To summarise, mechanical extraction is simple to be operated but a special equipment is required which results in high energy consumption. Additionally, the diameter of the nanocellulose produced is relatively wide. Hence, it is recommended to combine mechanical extraction with other approaches in order to obtain high quality nanocellulose.

2.4.2 Enzymatic Hydrolysis

Enzymatic hydrolysis is a process of biological treatment in which enzymes are utilised as a catalyst to digest or modify the cellulose fibers in the biomass sources. Cellulase, a multicomponent enzyme system, is used in enzymatic hydrolysis to extract nanocellulose. According to Xie, et al. (2018), the components of cellulase include endoglucanases, cellobiohydrolases, and β-glucosidase. Among these enzymes, endoglucanases are widely used for extraction of nanocellulose as it preferentially reacts on the cellulose’s amorphous region while retaining the crystalline regions in the process.

Enzymatic hydrolysis is an environmental-friendly process that causes no pollution. It is also a low energy-intensive process as it is normally performed in mild thermal and pressure conditions (Ribeiro, et al., 2019). Furthermore, it can control the structural characteristics of nanocellulose accurately. Nonetheless, this extraction method is limited by its relatively long reaction time, low nanocellulose yield and low suspension stability (Yu, et al., 2021). Hence, a combination pathway that incorporates enzymatic hydrolysis with other methods is always used for production of nanocellulose.

2.4.3 Acid Hydrolysis

Among the extraction methods discussed, acid hydrolysis is the most widely used method to extract nanocellulose from biomass fibers. Since cellulose chains consist of a combination of ordered and disordered regions, acid is able to hydrolyse the disordered regions easily while leaving the ordered regions as remaining (Phanthong, et al., 2018). Typically, concentrated acids such as phosphoric acid, nitric acid, sulphuric acid and hydrochloric acid are being used for nanocellulose extraction. Sulphuric acid is the mostly employed acid for acid hydrolysis among them due to the negative surface charge on the particles which can increase the stability of the suspension (Xie, et al., 2018).

Nanocrystalline cellulose can be strongly isolated via acid hydrolysis. It is a simple method for nanocellulose extraction with a short reaction time. A major drawback of acid hydrolysis is the generation of acid wastewater during the washing process. Washing process is carried out to neutralise the pH value of nanocellulose products by using cold water or alkali such as sodium hydroxide (Phanthong, et al., 2018). In addition, acid hydrolysis is costly in terms of equipment and operating cost as it requires extensive recovery process and highly corrosion resistant reactor due to the corrosive and hazardous concentrated acid used. Thus, it is crucial to control the factors that will influence the nanocellulose yield such as acid concentration, reaction time, temperature and pH (Lee, Hamid and Zain, 2014). For instance, according to Xie, et al. (2018), 60 – 65 % sulphuric acid concentration, reaction temperature of 40 – 50 °C and reaction time of 30 – 60 minutes were required for acid hydrolysis to take place.

2.5 Pathways for Biodiesel Production

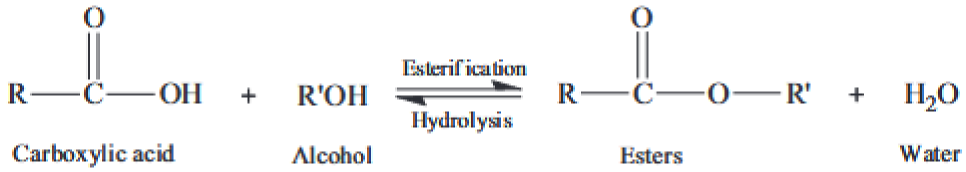
There are three pathways that can be conducted for biodiesel production, namely esterification, transesterification and interesterification. Conventionally, biodiesel is produced by transesterification. However, it is hardly produced if the oil feedstock consists of high FFA content. Table 2.4 shows some of the oil feedstocks that contain high FFA content. Hence, an acid-catalysed esterification pretreatment is usually carried out first, followed by alkali-catalysed transesterification while interesterification is a modification of transesterification to improve the process.

Table 2.4: FFA Content in Different Oil Feedstocks.

Feedstock	FFA Content (wt %)	References
Coconut oil	12.8	Nakpong and Wootthikanokkhan (2010)
Soybean oil	59.3	Haas, et al. (2003)
Rice bran oil	76	Zullaikah, et al. (2005)
Jatropha oil	15	Berchmans and Hirata (2008)
Mahua oil	19	Ghadge and Raheman (2005)
Waste chicken oil	13.45	Alptekin and Canakci (2010)

2.5.1 Esterification

Esterification is a reaction between free fatty acid and alcohol to produce ester and water in the presence of an acid catalyst. Figure 2.8 shows the general equation for esterification reaction. This process is essential to be carried out as a pretreatment step for oils with high FFA content in order to reduce the free acidity until a level below 1 wt % before undergoing transesterification reaction (Lucena, Silva and Fernandes, 2008). It is to avoid the occurrence of saponification of the fatty acids with the alkali used. Commonly, strong acid such as sulphuric acid is used as catalyst for esterification reaction as its activity is not influenced by the presence of FFA, but it can cause severe reactor corrosion problem. Hence, the development of alternative catalysts such as heterogenous acid catalysts has been studied to improve the esterification process.



$$R-\overset{O}{\overset{\|}{C}}-OH + R'OH \underset{\text{Hydrolysis}}{\overset{\text{Esterification}}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O$$

Figure 2.8: Esterification Reaction (Pereira, et al., 2014).

2.5.2 Transesterification

Biodiesel can be produced via conventional transesterification process which is the reaction of triglycerides from plant oils or animal fats and an alcohol in the existence of a catalyst to generate fatty acid alkyl esters (FAAE) and glycerol. This reaction can help to reduce the viscosity of triglycerides, thus producing a biodiesel with lower viscosity which is capable to replace petroleum diesel. The alcohols used are usually short carbon-chain alcohols such as methanol and ethanol. Since transesterification reaction is a reversible reaction, the conversion of triglycerides is promoted by using a catalyst to shift the equilibrium towards the formation of FAAE and glycerol (Koberg and Gedanken, 2013). In this context, the catalyst can be an acid or base catalyst, depending on the FFA content in the feedstock.

Figure 2.9 shows the transesterification reaction. There are three consecutive reactions taking place during transesterification of triglycerides. First of all, triglyceride reacts with the alcohol to form a diglyceride intermediate and FAAE molecule. After that, the diglyceride generated further reacts with the alcohol to generate a monoglyceride intermediate and another FAAE molecule. Again, monoglyceride reacts with the alcohol for the formation of glycerol and FAAE (Koberg and Gedanken, 2013). Eventually, three moles of FAAE and one mole of glycerol can be obtained in this process.

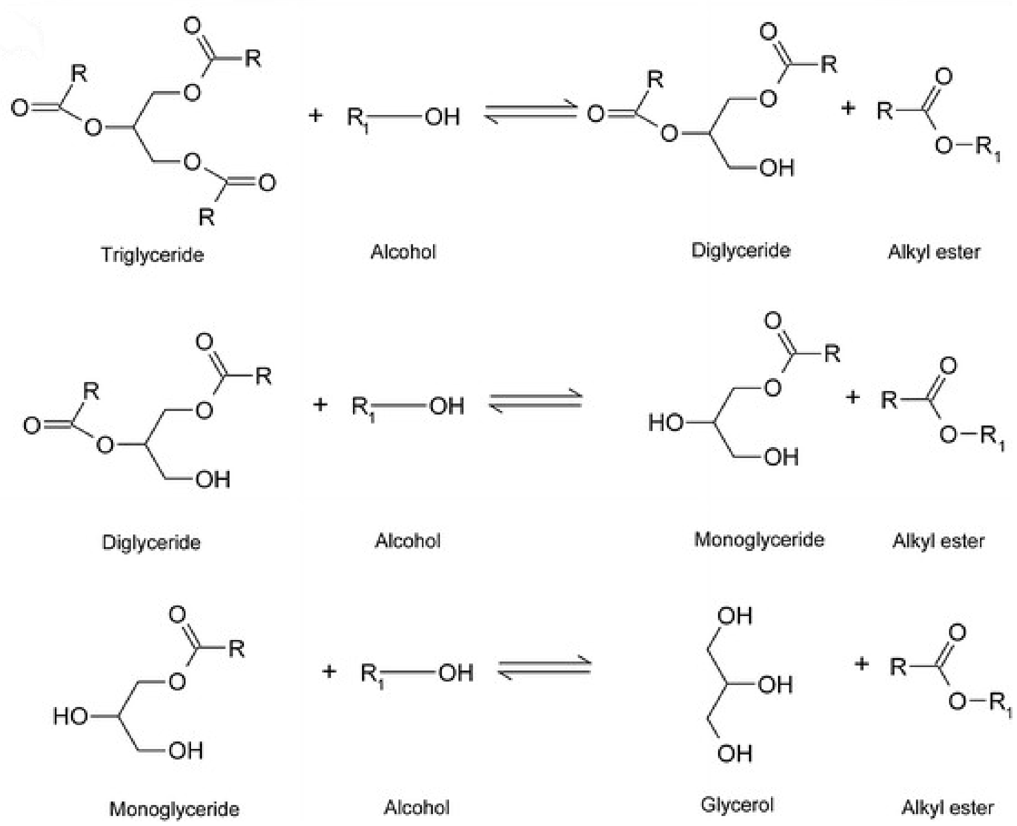


Figure 2.9: Transesterification Reaction (Lourinho and Brito, 2014).

2.5.3 Interesterification

In transesterification reaction, glycerol is usually formed as a waste product which has low economic value. To improve the process for biodiesel production, interesterification can be considered as a promising alternative to transesterification by replacing the alcohol by methyl acetate. Therefore, a higher value product, glycerol triacetate (triacetin) is formed instead of glycerol. For instance, triacetin can be used as plasticiser and gelatinizing agent in polymers and explosives. In addition, it also can be utilised as fuel additive in diesel engines due to the complete solubility of triacetin in biodiesel (Casas, Ramos and Pérez, 2013).

The interesterification reaction of triglyceride and methyl acetate is shown in Figure 2.10. This reaction also involves three consecutive procedures where triglyceride firstly react with methyl acetate to form FAME and monoacetindiglyceride. Then, the monoacetindiglyceride generated undergoes the same reaction to yield another FAME and diacetinmonoglyceride. Finally, the reaction of diacetinmonoglyceride and methyl acetate produces FAME and triacetin.

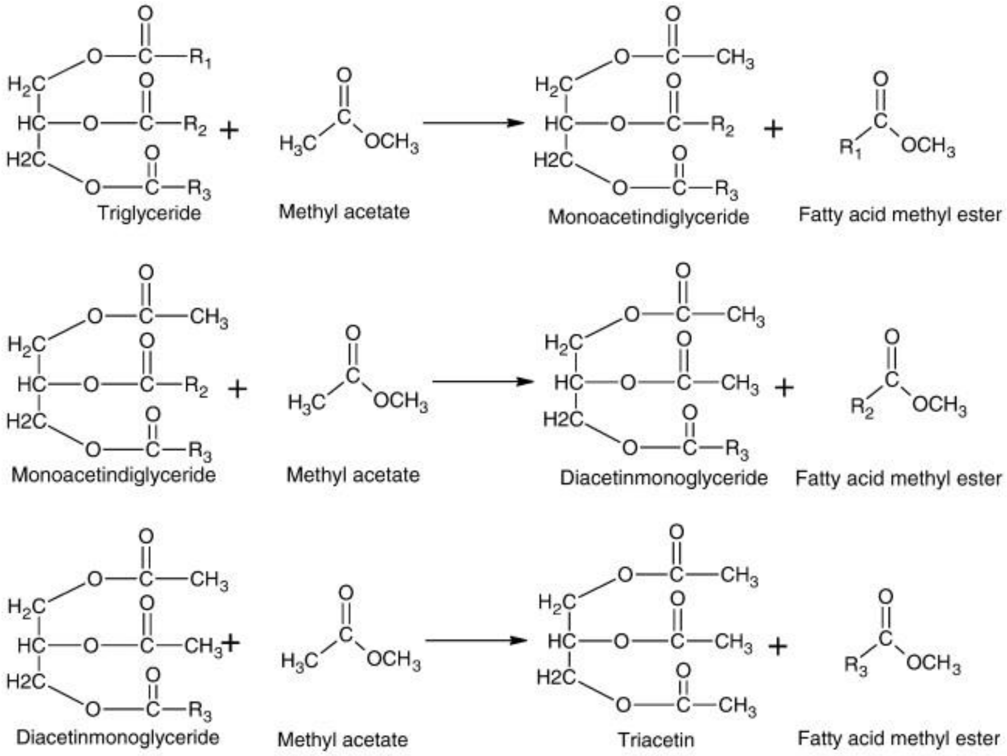


Figure 2.10: Interesterification Reaction (Maddikeri, Pandit and Gogate, 2013).

2.6 Effects of Transesterification Parameters on Biodiesel Yield

There are several process parameters that will affect the biodiesel yield, which are catalyst loading, reaction temperature, methanol-to-oil molar ratio and reaction duration. It is significant to investigate the effects of these process parameters in order to optimise the reaction conditions and achieve the maximum biodiesel yield.

2.6.1 Catalyst Loading

As known, the presence of catalyst can increase the rate of reaction, hence lead to higher yield of the products in shorter time. This is because the activation energy required for the reaction to occur can be further lower down by the increased amount of catalysts which give more active sites available on the catalyst surface for transesterification reaction. Thus, more reactant molecules can be activated for successive reactions to take place, thereby accelerating the reaction and producing more methyl esters. The biodiesel yield will be lower if the catalyst loading is low due to insufficient active sites for reactants to react.

According to Ayodele and Dawodu (2014), the effect of a variation of sulphonated microcrystalline cellulose catalyst concentration on the biodiesel yield was conducted at a range of 1.5-10 wt %. The FAME yield was found to increase when the catalyst loading was increased from 1.5 wt % to 5 wt %. However, the biodiesel yield started to drop when the catalyst loading was higher than 5 wt % due to a rise in the viscosity of the reaction mixture. High viscous mixture will lead to increased soap formation and mass transfer resistance in the reaction system which inhibits the biodiesel production (Xie and Zhao, 2014). Nevertheless, the optimum catalyst loading required for biodiesel yield depends on the catalyst type. Based on another study conducted by Al-Muhtaseb, et al. (2018), the transesterification reaction was run in the presence of carbon catalyst. The biodiesel yield was low at the catalyst loading of 1.5 wt %, but it was increased with the rise in catalyst amount. The optimal biodiesel yield of 98.2 % was found to be achieved at 4.5 wt % catalyst loading due to the presence of sufficient active sites for the reaction at this amount. A decrement in biodiesel yield was observed when further increasing the catalyst loading beyond 4.5 wt %.

2.6.2 Methanol-to-oil Molar Ratio

Methanol-to-oil molar ratio is one of the most significant aspects which will affect the biodiesel yield in the transesterification reaction. This parameter is crucial to be optimised in order to determine the amount of methanol required for transesterification reaction so that the biodiesel production is economically viable. Stoichiometrically, the molar ratio of methanol to oil required for transesterification is 3:1. Since transesterification reaction is reversible, it is usually required to apply higher methanol-to-oil molar ratio for shifting the equilibrium towards the formation of desired product, methyl ester. Additionally, the miscibility and contact between the alcohol molecule and the triglyceride can also be improved by employing higher methanol-to-oil molar ratio (Musa, 2016).

By referring to Helmiyati and Masriah (2019), the dependency of methanol-to-oil molar ratio on the biodiesel yield using cellulose/CaO-γ-Fe_2O_3

nanocomposite catalyst was conducted at a different ratio of 6:1; 8:1; 10:1; 12:1 and 14:1. An increase in FAME conversion was observed when the methanol-to-oil molar ratio is increased. In this case, the optimal methanol-to-oil molar ratio required for biodiesel production was found to be 12:1 which can yield 89.2 % FAME. A further increase in molar ratio beyond 12:1 was shown to decrease the biodiesel yield. Excessive use of methanol will cause the catalyst's active sites to become flooded, thus hindering the reaction of triglycerides at the active sites to form methyl esters (Lokman, et al., 2014). According to Jamil, et al. (2021), the molar ratio was varying at 6:1; 9:1; 12:1; 15:1 and 18:1 to investigate its influence on biodiesel yield using SrO-carbon catalyst. The yield was found to be increased as the amount of methanol increased and the maximum yield of 94.27 % can be achieved at 15:1 methanol-to-oil molar ratio. Further increasing the amount of methanol caused a slightly reduction in the biodiesel yield which may be attributed to the fact of dilution in the reaction system. Thus, there was less interactions between the reactants and the catalyst's active sites. Besides, the decreased biodiesel yield in the excess of methanol was also caused by the emulsion of the reaction mixture since the hydroxyl group of methanol is polar in nature.

2.6.3 Reaction Temperature

Generally, the reaction rate can be increased at higher reaction temperature which shortens the reaction period. Based on the kinetics of chemical reaction, the kinetic energy of the reactant molecules is raised by an increase in the reaction temperature which makes the molecules have adequate energy for effective collision and successive reaction to occur. Additionally, since transesterification reaction is an endothermic reaction, extra amount of heat is required to favour the forward reaction (Jamil, et al., 2021).

For instance, the influence of reaction temperature on the yield of biodiesel in the presence of a cellulose-derived catalyst was investigated by Gaikwad and Gogate (2015) to determine the optimum temperature for the reaction. It was reported that the conversion increased from 50 % to 77 % when there is an increase in reaction temperature from 45 °C to 60 °C due to more interactions of reactants to the catalyst's active sites. However, the biodiesel yield will be decreased if the reaction temperature exceeds the optimum temperature. Another research using SrO-carbon catalyst which was conducted by Jamil, et al. (2021) also indicated that the biodiesel yield increased rapidly with the temperature until reaching a maximum yield of 94.27 % at 65 °C. There was a slightly reduction in biodiesel yield when the temperature was further increased to 70 °C. This is because evaporation of alcohol may occur which affects the optimum alcohol-to-oil molar ratio for biodiesel production (Abbah, et al., 2016). Since the alcohol exists in the vapour phase at higher temperature, the amount of alcohol used for transesterification reaction is decreased. Nonetheless, the process is refluxing continuously which leads to lower yield. Hence, the reaction temperature is generally below the boiling point of the alcohol used in order to prevent the alcohol from being vaporised.

2.6.4 Reaction Duration

The conversion efficiency of transesterification reaction can be influenced by the reaction duration. Sufficient reaction time is required by the reactants to cross the energy barrier for complete conversion to methyl esters. The reaction rate is usually slower at the beginning of the reaction as methanol are being mixed and dispersed with the oil. When the duration increases, the reaction rate is expected to increase steadily until reaching a maximum yield (Bano, et al. 2020).

Azahra and Helmiyati (2020) studied the effect of reaction duration on biodiesel production using cellulose-Fe_3O_4/ZnO nanocomposite catalyst at different time intervals from 60 minutes, 120 minutes to 180 minutes. The results showed that the conversion was improved from 83.55 % to 90.60 % with an increase in the reaction duration from 60 minutes to 120 minutes. This is because the increased reaction time enhances the interactions between reactants and catalysts by means of collisions, thus increasing the biodiesel yield. Nevertheless, a reduction of biodiesel conversion was observed when the reaction duration was increased to 180 minutes. This phenomenon is probably due to the reverse reaction of transesterification when the reaction reaches its equilibrium with high product concentration. The esters produced are hydrolysed into fatty acids which undergo saponification reaction to form soaps in the product and eventually lead to lower biodiesel yield (Efavi, et al., 2018). Besides, catalyst deactivation may also occur due to accumulation of water by-product, hence inhibiting the reaction. Meanwhile, the influence of reaction duration on biodiesel yield was also investigated in another study by varying the reaction time from 30 minutes to 120 minutes with a 30-minute interval in the presence of *Jatropha curcas* biomass-derived carbon catalyst (Mardhiah, et al., 2017). A similar result with the above-mentioned study was obtained. It was observed that the biodiesel yield was low at the beginning of 30 minutes. With the increase in reaction time, the biodiesel yield increased significantly and the highest conversion yield of 99.13 % can be achieved when the reaction time reached 60 minutes. However, the yield was decreased for the reaction time beyond 60 minutes. Nevertheless, this optimum reaction duration of 60 minutes was shorter in comparison to other studies that used similar catalysts.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Research Methodology

This study comprises a series of methodology steps with biomass-derived cellulose catalyst for biodiesel production as the main focus. Figure 3.1 illustrates the overall summarised methodology used to manage the information for this study which includes five main steps, that are planning, searching, screening, data collection and data analysis.

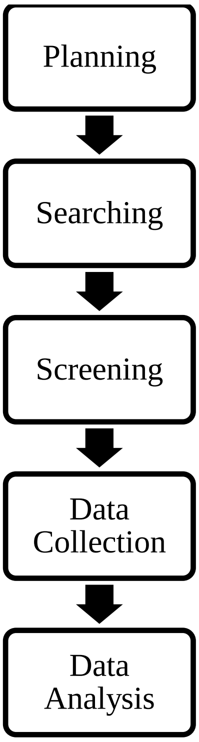


Figure 3.1: Research Methodology Steps.

3.1.1 Planning

The present study was started by identifying the problem statement, aims and objectives. The application of biomass-derived cellulose catalyst in biodiesel production was covered under this review study. Thus, several research questions were identified for the needs for this study which was shown as the follows:

i. What were the morphological characteristics of biomass-derived cellulose catalyst?
ii. What were the mechanical properties of biomass-derived cellulose catalyst?
iii. What were the thermal properties of biomass-derived cellulose catalyst?
iv. What were the functional properties of biomass-derived cellulose catalyst?
v. What were the catalytic activities of biomass-derived cellulose catalysts in biodiesel production?
vi. How were the kinetics and thermodynamics of biomass-derived cellulose catalyst in biodiesel production?
vii. What are the challenges and future prospects of the application of biomass-derived cellulose catalyst in biodiesel production?

3.1.2 Searching

Literatures were sourced through different online platforms in order to obtain informations for biomass-derived cellulose catalyst for biodiesel production. The search engine used in this paper was Scopus database which includes thousands of publishers such as the primary publisher, Elsevier and other publishers, Springer, Wiley, Emerald and Oxford University Press. Besides, database of ScienceDirect was also used to view the full text articles from journals and books of Elservier since Scopus only includes the abstracts and citation statistics. Literature searching also can be performed by utilising ResearchGate and Multidisciplinary Digital Publishing Institute (MPDI) as online journal sources.

In this context, several keywords were identified for literature searching to minimise the risk of bias from the topic. For instance, “cellulose catalyst”, “transesterification”, “biodiesel” and “FAME” were widely utilised. In the database of ScienceDirect, the articles were searched with these keyword terms. In Scopus database, the search option used were “title, abstract and keywords”. The use of Boolean operators such as AND and OR were applied in the search string of this review for more concentrated results. As such, biodiesel OR FAME could be used since FAME also referred to biodiesel. The articles published from 2011 to 2021 were included in this literature searching phase. The search strategy identified 982 potential titles for this topic.

3.1.3 Screening

To ensure the articles selected were eligible for this study, screening of research papers was conducted based on the abstract reading before choosing them as the relevant papers. In this context, titles and abstracts from 982 publications were evaluated based on the inclusion criteria and exclusion criteria to determine the relevancy and accuracy to the topic. The inclusion criteria for this review were shown as below:

i. Studies that relate to biodiesel production using biomass-derived cellulose catalyst.
ii. Articles published from 2011 to 2021.
iii. Articles presenting comprehensive data and information.

On the other hand, the exclusion criteria included:

i. Articles published in a language other than English.
ii. Studies whose full texts could not be found.
iii. Works dealing with biodiesel production using catalysts other than biomass-derived cellulose catalyst.
iv. Works dealing with biomass-derived cellulose catalyst used for other applications.
v. Editorial materials, reports, letters and conference papers.

To summarise, a total of 187 articles were found to meet the inclusion criteria of this study. These articles were included in the review, followed by full text reading.

3.1.4 Data Collection

Extraction of data including qualitative and quantitative data from the 187 selected articles were conducted. The data collected should be accurate, reliable and informative to ensure decisions can be made for the study based on data. In this matter, the data extracted included the article publications (authors or organisations, publication year, title and journal name) and the results (biodiesel yield produced by using biomass-derived cellulose catalyst, characterisation of biomass-derived cellulose catalyst, kinetics and thermodynamics of biomass-derived cellulose catalysts on biodiesel production).

3.1.5 Data Analysis

Data analysis was the most essential part of any research to ensure data integrity. In fact, data tabulation is useful in summarising and interpretation of findings during the analysis phase of the study. The important informations and data were processed and tabulated from the articles and journals to be used for report writing. These informations and data were then evaluated critically by using statistical and logical techniques to draw meaningful insights for the topic. Structuring and report writing was performed after completing data analysing and interpretation.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterisation of Biomass-Derived Cellulose Catalyst

It is significant to study the characteristics of biomass-derived cellulose catalyst as it could affect the catalytic activity in biodiesel production. In this regard, the catalytic activity depends on some important parameters such as catalyst surface area, crystallinity, thermal stability and functional groups. Throughout the study, several characterisation techniques have been used to study and analyse the morphology, mechanical, thermal and functional properties of biomass-derived cellulose catalyst for biodiesel production. The characterisation analyses include scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA) and fourier transform infrared spectroscopy (FTIR).

4.1.1 Morphology

The structural properties and surface morphology of biomass-derived cellulose catalyst were determined through SEM analysis. The SEM images of raw cellulose and sodium hydroxide (NaOH) treated cellulose samples derived from different biomass such as date palm, lemongrass and sugarcane bagasse are presented in the Figures 4.1 to 4.4.

Figure 4.1 and Figure 4.2 show the SEM images of the cellulose and NaOH treated cellulose derived from different parts of date palm biomass at 3000X magnification. The skeletal rod-like structures were observed in the celluloses of rachis and fiber as shown on Figure 4.1 (a) and (c). The structures were well-defined with distinguishable shape and similar intrafibrillar diameters. Nevertheless, the leaflet cellulose produced aggregated structures with undefined dimensions in the SEM images as shown in Figure 4.1 (b). Meanwhile, non-uniform shapes with intertwined distribution and agglomeration of nodules were found on the surfaces of NaOH treated celluloses from different parts of the date palm as shown in Figure 4.2.

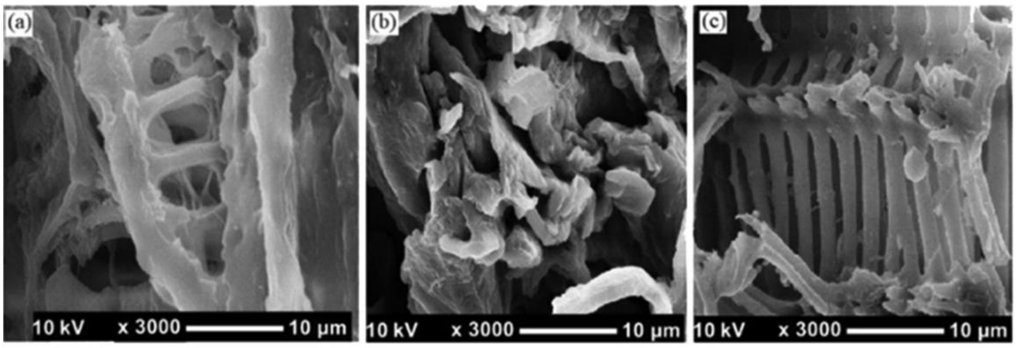


Figure 4.1: SEM Images of Celluloses Derived from Different Date Palm Biomass Parts, (a) Rachis, (b) Leaflet and (c) Fiber (Galiwango, et al., 2019).

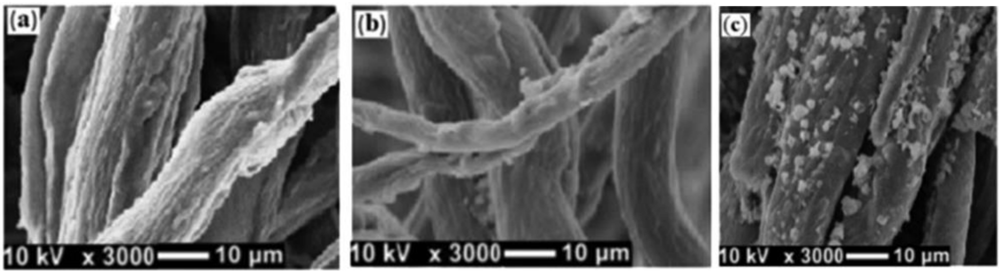


Figure 4.2: SEM Images of NaOH Treated Celluloses Derived from Different Date Palm Biomass Parts, (a) Rachis, (b) Leaflet and (c) Fiber (Galiwango, et al., 2019).

The morphology of lemongrass biomass-derived cellulose was observed at 20X magnification. Figure 4.3 illustrates the SEM images of lemongrass biomass-derived cellulose. As shown in Figure 4.3 (a), a clear bundle-like structure with small particles on the smooth surfaces was observed on the cellulose from lemongrass biomass. However, the pretreatment by NaOH had successfully removed the non-cellulosic layer such as hemicellulose and lignin because nano-dimension was founded in the SEM images of treated cellulose by referring to Figure 4.3 (b).

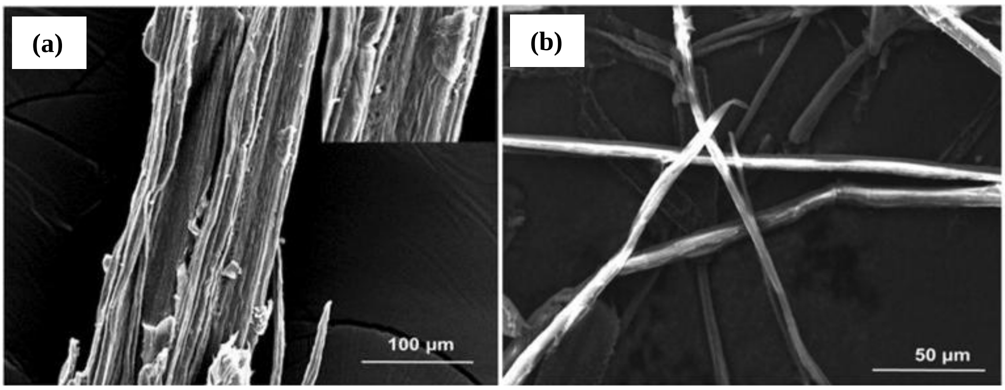


Figure 4.3: SEM Images of (a) Cellulose and (b) NaOH Treated Cellulose Isolated from Lemongrass Biomass (Kumari, et al., 2019).

The SEM images of sugarcane bagasse-derived cellulose before and after NaOH pretreatment are presented in Figure 4.4 at 2000X magnification. In Figure 4.4 (a), a rigid and compact fibrous structure with a continuous smooth layer was displayed on the surface of cellulose bundles. On the contrary, a disordered morphology of NaOH treated cellulose could be observed from Figure 4.4 (b) due to the removal of the non-cellulosic components and consequently destroyed the biomass structure and separated the bundles of fiber.

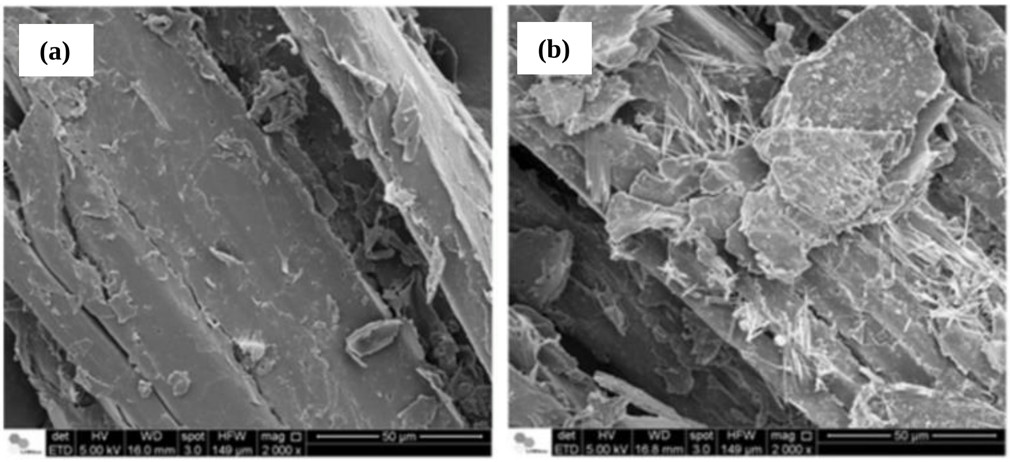


Figure 4.4: SEM Images of (a) Cellulose and (b) NaOH Treated Cellulose Isolated from Sugarcane Bagasse Biomass (Lima, et al., 2014).

By referring to the figures presented, it is clear that the structures of raw celluloses from date palm, lemongrass and sugarcane bagasse were similar which were rod-like structures with smooth surfaces. The long fibers of cellulose are usually held in place by hydrogen bonding between the hydroxyl groups of cellulose (Kumari, et al., 2019). However, rougher, more disorganised and microporous structures were formed after the pretreatment with NaOH. The cellulose structures were destroyed and loosened which signifies the removal of lignin, thus giving greater exposure of the cellulose fibers. In fact, larger surface area could increase the reaction rate as it could give more contacts between the reactants and catalyst. Moreover, a reduction of size could be observed for the treated celluloses derived from different biomass. When the cellulose was treated with NaOH, defibrillation was promoted which reduced the diameter of the cellulose fiber as a result of the removal of non-cellulosic components such as lignin, hemicelluloses, waxes and pectins. For example, the size of the cellulose fiber could be greatly decreased from the range of micrometer to nanometer which was typically less than 100 nm in diameter (Radakisnin, et al., 2020).

4.1.2 Crystallinity

The mechanical properties of the cellulose are depending on the crystalline characteristics (Trilokesh and Uppuluri, 2019). In this context, XRD is an analytical method used to determine the crystallinity of the cellulose catalyst according to the constructive interference of monochromatic beam of X-rays in the crystalline sample. The beams of X-ray only can be diffracted by a solid with crystalline structure. The crystallinity index for the cellulose samples are determined using the method by Segal, et al. (1959) as in Equation 4.1:

$$CrI\ (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\ \% \tag{4.1}$$

where

CrI = Crystallinity index, %

I_{002} = Peak intensity related to crystalline region

I_{am} = Peak intensity related to amorphous region

The XRD profile of the cellulose derived from rice husk is illustrated in Figure 4.5 (a). The diffractogram showed the peaks at 2θ of 17.12°, 22.26°

and 34.48° which were corresponded to the lattice planes (110), (200) and (004) of cellulose, respectively. The highest peak at the angle around 22.26° indicated the presence of crystalline cellulose structure. The rice husk-derived cellulose possessed a quite high crystallinity index of 58.73 % while its crystallite size was found to be 3.44 nm.

Similarly, XRD analysis have been conducted to evaluate the crystalline structure of cellulose derived from banana pseudo-stem biomass. Based on the XRD pattern in Figure 4.5 (b), this study had discovered similar crystalline peaks at 2θ of around 22.6° and 34.7° and an amorphous peak at about 16.7°. In comparison to rice husk-derived cellulose, the diffraction intensity of the cellulose derived from banana pseudo-stem at the primary crystalline peak of 22° increased, indicating a higher crystallinity which was in good agreement with the crystallinity index obtained. In this context, the crystallinity of the cellulose reached 71.54 % and the cellulose had a crystallite size of 4.02 nm. The cellulose sample exhibited high crystallinity in the lattice plane (200) due to the decrement of amorphous hemicellulose and lignin.

In another similar work, a higher crystallinity index at 83.42 % and a crystallite size of 2.80 nm were found for the cellulose derived from jackfruit peel biomass. According to the XRD pattern in Figure 4.5 (c), there were one primary peak and two secondary peaks found where the highest peak intensity was observed at 2θ values of 22.60° which was attributed to the crystalline structure of cellulose. On the other hand, the secondary peak at 15.78° was corresponded to the amorphous content of the cellulose.

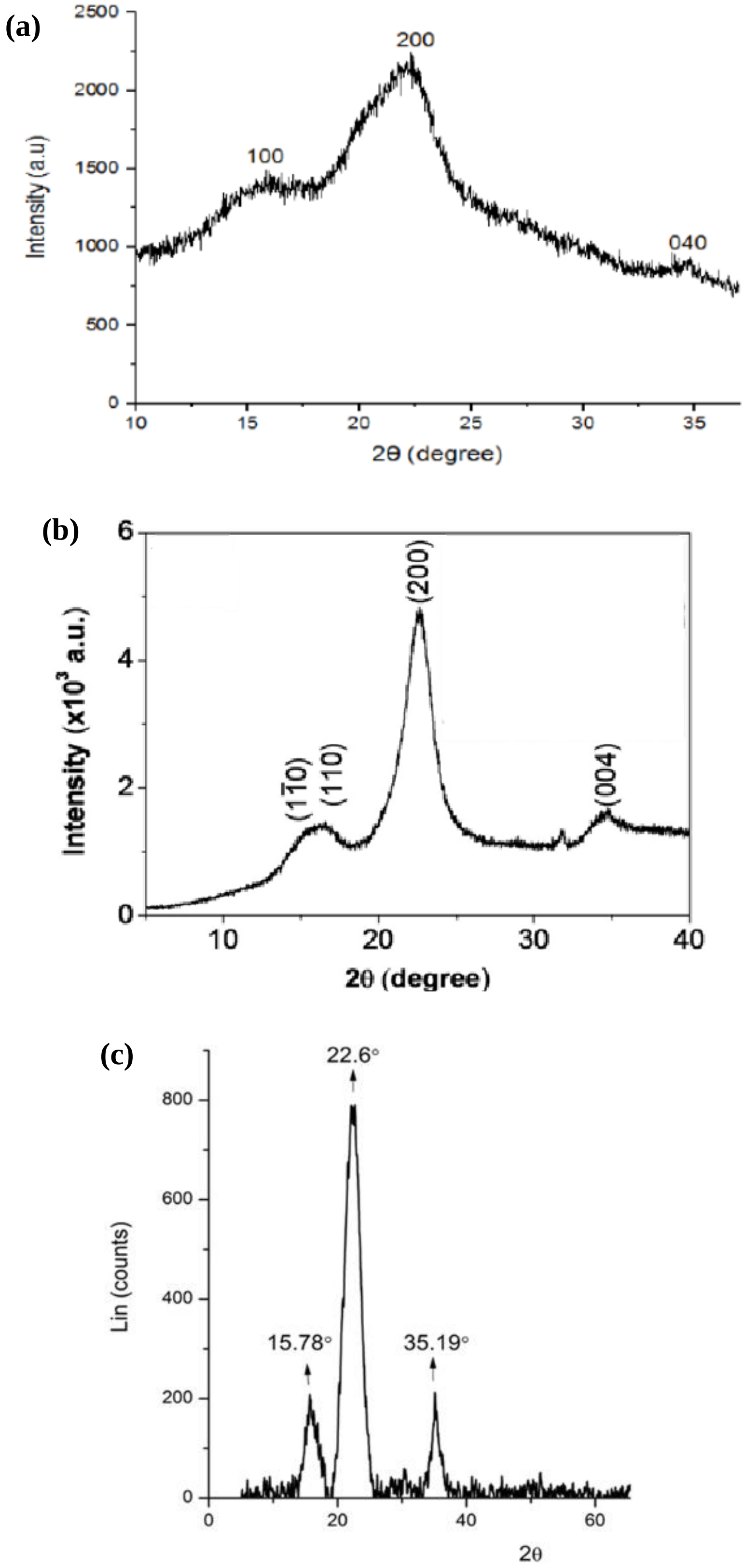


Figure 4.5: XRD Diffractogram of Cellulose Isolated from (a) Rice Husk (Yunus, et al., 2019), (b) Banana Pseudo-Stem (Das, et al., 2018) and (c) Jackfruit Peel (Trilokesh and Uppuluri, 2019).

Table 4.1 compares the degree of 2θ, crystallinity index and crystallite size of cellulose samples derived from different biomass sources. All the cellulose samples exhibited similar diffraction peaks where the highest peak appears at 2θ of around 22° to 23°. This peak was a characteristic peak of cellulose structure which was related to the crystal field of 200. Moreover, the low peak intensity at around 15° to 17° reflected the amorphous regions of the cellulose samples.

On the other hand, crystallinity index refers to the ratio of the crystalline regions to the crystalline and amorphous regions of cellulose. Therefore, the higher the crystallinity index, the greater the crystalline regions. The distribution of crystalline and amorphous parts varied in different cellulose samples as different feedstocks contain different amount of cellulose, hemicellulose and lignin. The crystallinity obtained from the cellulose samples were quite high as shown in Table 4.1. This was due to the effective removal of lignin and hemicellulose in the amorphous region of the cellulose during the cellulose extraction process. Typically, the crystalline structure of the cellulose was attributed to the interactions of hydrogen bonds of hydroxyl groups and Van der Waal forces between the adjacent molecules (Kumari, et al., 2019). Higher degree of crystallinity could improve the strength of the cellulose by increasing the stiffness and rigidity, thus improving the mechanical properties (Samuel and Adefusika, 2019). This was due to the enhancement of binding forces between the molecular chains and conducive fiber orientations (Li, et al., 2021).

Table 4.1: Comparison of Crystallinity Index and Crystal Size of Cellulose from Different Biomass Sources.

Cellulose Samples	**2θ (°)**			**CrI (%)**	**Crystallite Size (nm)**	**References**
	Plane 110	**Plane 200**	**Plane 004**			
Rice husk	17.12	22.26	34.48	58.73	3.44	Yunus, et al. (2019)
Banana pseudo-stem	16.70	22.60	34.70	71.54	4.02	Das, et al. (2018)
Jackfruit peel	15.78	22.60	35.19	83.42	2.80	Trilokesh and Uppuluri (2019)
Wheat bran	16.20	22.40	34.70	70.32	-	Xiao, et al. (2019)
Cotton fiber	16.50	22.80	34.00	91.20	-	Theivasanthi, et al. (2018)
Shwetark stem fiber	17.01	23.15	-	72.06	3.00	Raja, et al. (2020)
Jute fiber	15.30	23.20	-	82.22	-	Thomas, et al. (2015)
Corn stalk waste	16.28	22.12	-	69.70	5.30	Liu, et al. (2019)
Oil palm empty fruit bunches	16.00	22.50	-	70.00	9.80	Nazir, et al. (2013)
Date palm fruit bunch stalk	16.10	22.80	34.70	78.60	-	Alotaibi, et al. (2019)

4.1.3 Thermal Stability

TGA is applied to evaluate the thermal stability and decomposition characteristics of the cellulose catalyst by determining the weight loss of the samples as a function of temperature. The stages with significant weight loss at a certain temperature range can be determined through the TGA temperature profile.

Figure 4.6 (a) shows the thermograms of TGA and derivative thermogravimetric (DTG) analyses performed on cellulose derived from different oil palm biomass sources which are oil palm mesocarp fiber (OPMF), oil palm empty fruit bunch (OPEFB) and oil palm frond (OPF). The cellulose samples were subjected to TGA analysis where they were heated from 50 ℃ to 550 ℃ under the atmosphere of nitrogen with a heating rate of 10 ℃/min. By referring to Figure 4.6 (a), gradual weight loss was observed at temperature around 100 ℃, followed by a single-step degradation from 230 ℃ to 380 ℃. After 380 ℃, there was no significant weight loss for all samples. This could be further proved by the single peak shown in the DTG curves for all samples. The rate of degradation reached its peak at the temperature around 350 ℃.

In another similar study, cellulose derived from sugarcane bagasse and soft wood biomass were degraded into two steps with similar thermal stability. Based on Figure 4.6 (b), there was a small rate in weight loss at the first 100 ℃ and the samples were thermally stable until 250 ℃. The weight percent of the samples then started to drop drastically in the temperature range of 250 ℃ to 380 ℃. This was in agreement with the reported study using oil palm biomass for cellulose isolation. Similar degradation stages were also exhibited by cellulose derived from rice husk based on the TGA thermograms in Figure 4.6 (c). However, rice husk derived cellulose possessed a slightly higher thermal decomposition temperature where the second degradation step ended at the temperature of 400 ℃. The significant weight loss could be supported by the DTG curves where the greatest degradation of cellulose occurred at the temperature approximately 360 ℃ to 370 ℃.

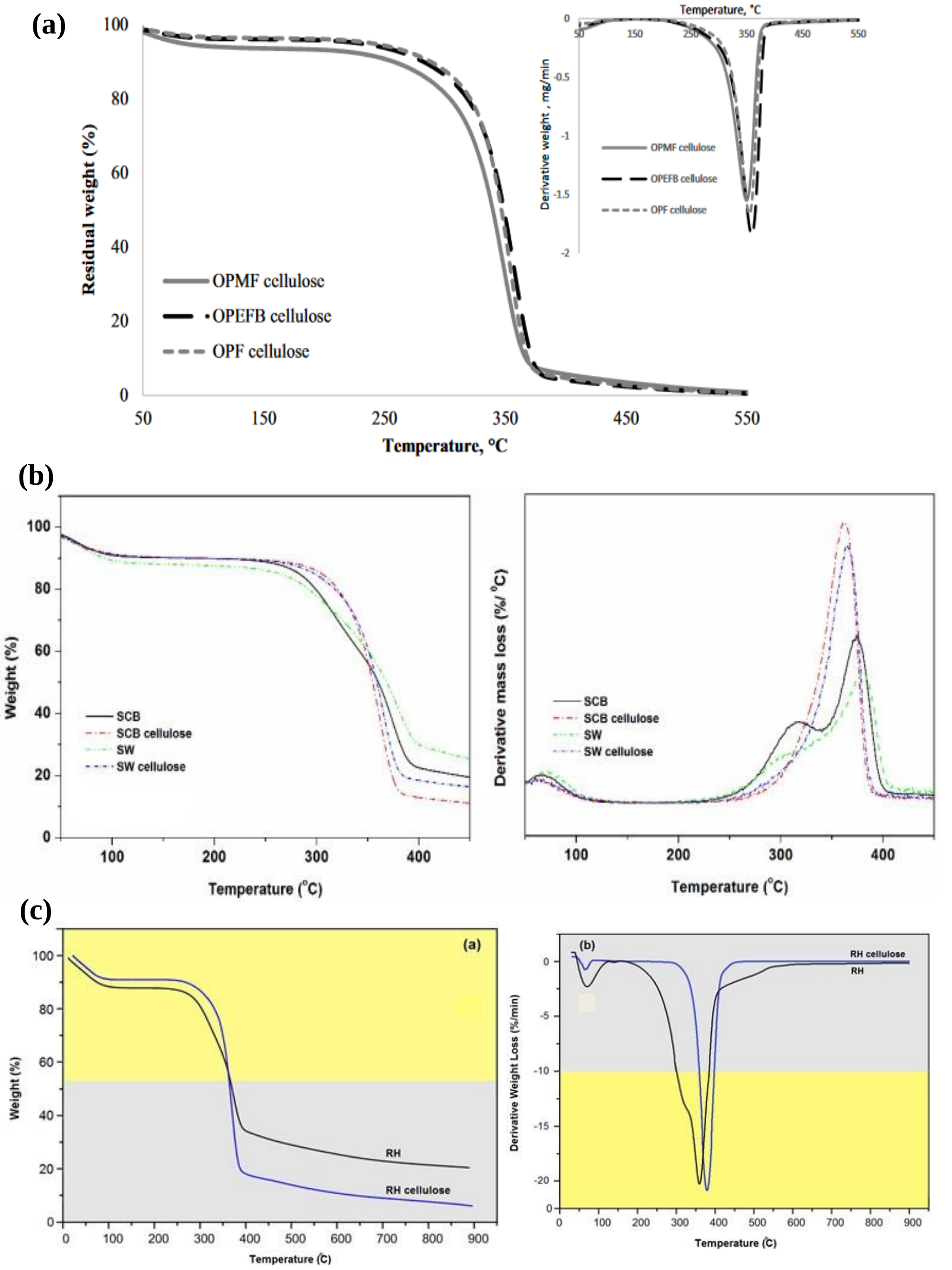


Figure 4.6: TG and DTG Thermograms of Cellulose from (a) Different Oil Palm Biomass (Megashah, et al., 2018), (b) Sugarcane Bagasse (SCB) and Soft Wood (SW) (Mohomane, Motaung and Revaprasadu, 2017) and (c) Rice Husk (RH) (Khandanlou, Ngoh and Chong, 2016).

Table 4.2 presents the thermal degradation temperature of cellulose obtained from different biomass sources. Based on the thermograms produced from different biomass-derived cellulose samples, it was concluded that the weight loss of the cellulose catalyst could be divided into two main stages. The first stage of the weight loss at the temperature range of 30 – 100 ℃ was related to the vaporisation of the absorbed moisture content from the catalyst surface. Besides, the second stage of degradation occurred at the temperature around 230 – 380 ℃ where the weight of the catalyst dropped dramatically. This reduction in weight was normally attributed to the degradation of cellulose such as depolymerisation, dehydration and decomposition of glycosidic units (Xiao, et al., 2019). This finding revealed that biomass-derived cellulose catalyst provided an excellent thermal stability up to 380 ℃. Thus, the catalyst was able to perform well if the reaction temperature did not go beyond the decomposition temperature of the catalyst. It was also reported by Díez, et al. (2020) that the cellulose decomposition normally occurred between the temperature range of 250 – 380 ℃, depending on the nature of the feedstock. In this regard, a more dense and compact cellulose structure could be produced after the elimination of non-cellulosic components as the orientation of the cellulose crystals were rearranged. This led to the increase in the degradation temperature, hence increasing the thermal stability (Mandal and Chakrabarty, 2011).

Table 4.2: Comparison of Themal Degradation Temperature of Cellulose from Different Biomass Sources.

Cellulose Samples	**Degradation Temperature (℃)**	**References**
Oil palm	350	Megashah, et al. (2018)
Sugarcane bagasse	370	Mohomane, Motaung and Revaprasadu (2017)
Soft wood	370	
Rice husk	360	Khandanlou, Ngoh and Chong (2016)
Shwetark stem fiber	350	Raja, et al. (2020)
Sisal fiber	378	Mariano, Cercená and Soldi (2016)
Wheat bran	352.97	Xiao, et al. (2019)
Sugarcane bagasse	370	Mandal and Chakrabarty (2011)
Kenaf bast	361	Karimi, et al. (2014)
Orange peel	350	Hideno, Abe and Yano (2014)

4.1.4 Functional Groups

FTIR analysis is used to identify the functional groups present on the surface of the catalysts by comparing the magnitude of the absorbed energy with the available database. In the FTIR analysis, the spectra of the cellulose derived from different biomass sources such as jackfruit peel, kelp and oil palm empty fruit bunch are shown in Figure 4.7.

Based on Figure 4.7, a broadening absorption band around 3 400 cm^{-1} to 3 500 cm^{-1} appeared in the FTIR spectra of all cellulose samples, indicating the stretching of O-H functional group in the cellulose molecules. In addition, C-H stretching vibrations could be found in the spectra of kelp, oil palm empty fruit bunch and jackfruit peel at 2 897 cm^{-1}, 2 900 cm^{-1} and 2 923 cm^{-1}, respectively. The spectra also displayed a peak near 1632 cm^{-1} to 1 645 cm^{-1}, which represented the bending of adsorbed water. Furthermore, there was an absorption peak at around 1 057 cm^{-1} to 1 164 cm^{-1} which was attributed to the C–O–C pyranose ring skeletal vibrations. The peak associated with the CH_2 symmetric bending vibrations which was usually being detected in the spectra of polysaccharides at 1 425 cm^{-1}, 1 430 cm^{-1} and 1 442 cm^{-1} for oil palm empty fruit bunch, kelp and jackfruit peel, respectively. Moreover, there was also a small peak between 896 cm^{-1} to 905 cm^{-1} which was an indicative of C-H rock vibrations.

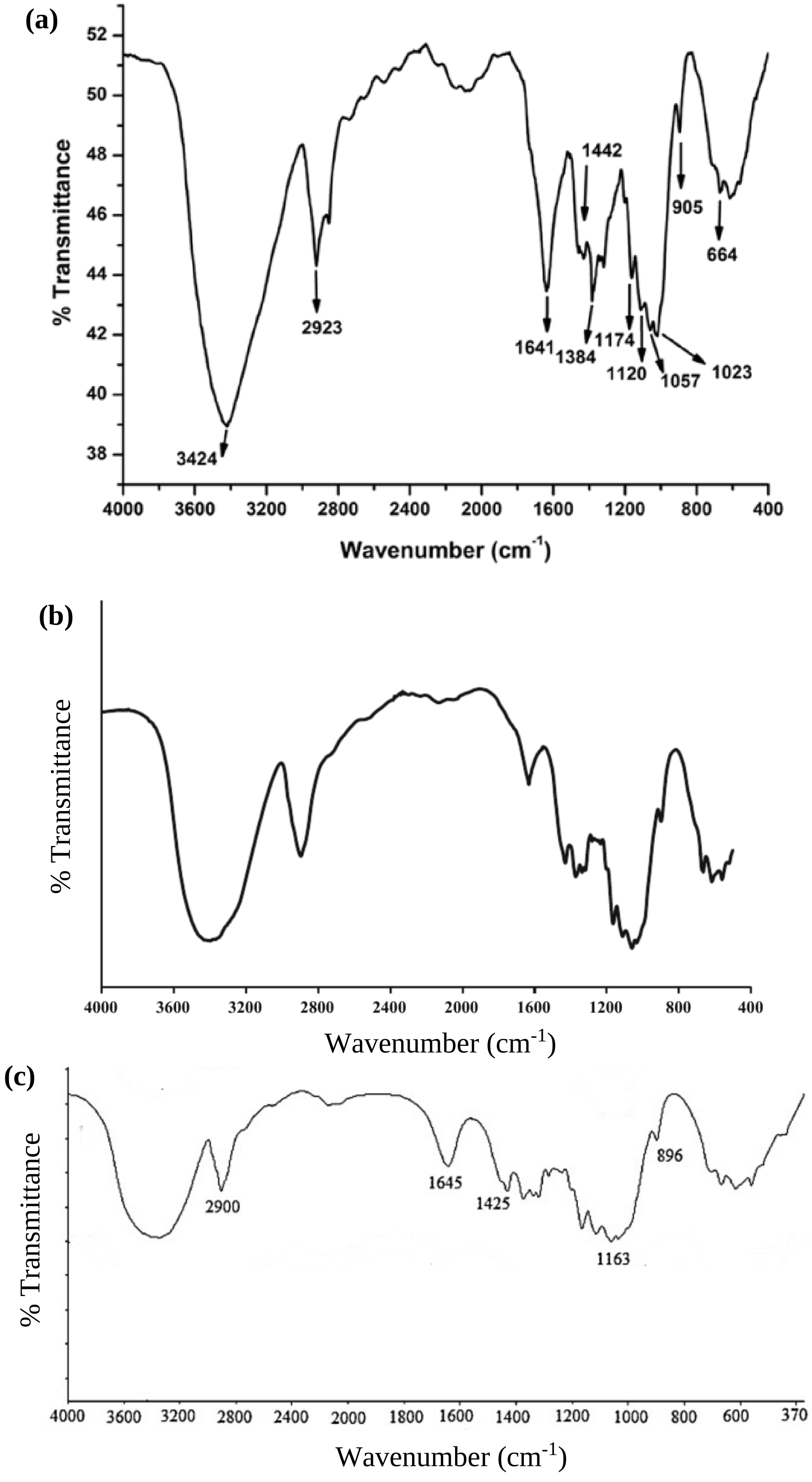


Figure 4.7: FTIR Spectra of Cellulose Isolated from (a) Jackfruit Peel (Trilokesh and Uppuluri, 2019), (b) Kelp (He, et al., 2018) and (c) Oil Palm Empty Fruit Bunch (Haafiz, et al., 2013).

Table 4.3 compares the vibrational frequencies of different types of biomass-derived cellulose samples from several biomass sources. The peaks and bands at certain wavenumbers indicated that the specific functional groups for cellulose were clearly visible such as O-H, C-H, CH_2, C-O-C and adsorbed water. Generally, the absorption bands associated with O-H bending and stretching would not exist in the FTIR spectrum of raw cellulose as the hydroxyl groups in the raw cellulose were covered by cementing materials such as hemicellulose, lignin and waxes (Thomas, et al., 2015). In this regard, the O-H stretching could be attributed to the intermolecular disruption of the hydrogen bonds of cellulose structure. Apart from that, the C-H rock vibration in the wavenumber range from 896 cm^{-1} to 905 cm^{-1} suggested that the β-glycosidic linkages in cellulose were disrupted which increased the surface area and porosity of the cellulose sample (Jin, et al., 2020). These linkages showed the typical structure of cellulose as they linked the anomeric carbon atoms of saccharides for the formation of polysaccharides. According to Haafiz, et al. (2013), the adsorbed water absorption band was due to the strong interaction between water and cellulose.

In addition, the absence of peak at 1 580 cm^{-1} showed the absence of C=C of the aromatic ring of lignin. There was also no C=O carbonyl functional group either acetyl or uronic ester group of the hemicellulose due to the absence of peak at around 1 700 cm^{-1} (Konwar, et al., 2014). Thus, these FTIR spectra indicated high purity of the cellulose catalyst and the successive removal of hemicellulose and lignin.

Table 4.3: Comparison of Vibration Frequencies of Cellulose from Different Biomass Sources.

Cellulose Samples	**Wavenumber (cm^{-1})**				**References**
	O-H Stretching	**C-H Stretching**	**Adsorbed H_2O**	**CH_2 Bending**	
Jackfruit peel	3 424	2 923	1 641	1 442	Trilokesh and Uppuluri (2019)
Kelp	3 420	2 897	1 632	1 430	He, et al. (2018)
Oil palm empty fruit bunch	3 400 – 3 500	2 900	1 645	1 425	Haafiz, et al. (2013)
Sugarcane bagasse	3 451	2 899	1 644	1 382	Wulandari, Rochliadi and Arcana (2016)
Wheat bran	3 415	2 914	1 642	-	Xiao, et al. (2019)
Jute fiber	3 320	2 895	1 631	-	Thomas, et al. (2015)
Oil palm mesocarp fiber	3 340	2 852	-	1 315	Chieng, et al. (2017)
Sugar beet pulp	3 340 – 3 367	2 924	1 630	1 371	Li, et al. (2014)
Rice husk	3 300 – 3600	2 916	1 580 – 1 640	-	Iorfa, et al. (2020)
Oil cake waste	-	-	-	-	Konwar, et al. (2014)

Table 4.3 (Continued)

Cellulose Samples	**Wavenumber (cm^{-1})**				**References**
	C-O-C Stretching	**C-H Rock**	**C=C Stretching**	**C=O Stretching**	
Jackfruit peel	1 057	905	-	-	Trilokesh and Uppuluri (2019)
Kelp	1 164	898	-	-	He, et al. (2018)
Oil palm empty fruit bunch	1 163	896	-	-	Haafiz, et al. (2013)
Sugarcane bagasse	1 060	-	-	-	Wulandari, Rochliadi and Arcana (2016)
Wheat bran	1 157	-	-	-	Xiao, et al. (2019)
Jute fiber	1 163	896	-	-	Thomas, et al. (2015)
Oil palm mesocarp fiber	1 035	896	-	-	Chieng, et al. (2017)
Sugar beet pulp	1 035	898	-	-	Li, et al. (2014)
Rice husk	1 021 – 1 262	983	-	-	Iorfa, et al. (2020)
Oil cake waste	-	-	1 580	1 700	Konwar, et al. (2014)

4.2 Kinetic Study

The performance of biomass-derived cellulose catalyst could be assessed by its kinetics. The kinetic behaviour of the reaction catalysed by biomass-derived cellulose catalyst to produce biodiesel was studied to determine the reaction rate constant and the activation energy of the process. These two parameters were the key parameters to be evaluated before scaling up the process.

4.2.1 Reaction Rate Constant

The reaction of transesterification is considered to be a first-order reaction based on the following assumptions (Nazir, et al., 2021):

i. Triglyceride is a limiting reactant.
ii. Methanol is in excessive concentration so that the transesterification reaction of the triglycerides to form biodiesel and glycerol is irreversible by shifting the reaction equilibrium towards the products.

Since the concentration of methanol is higher with respect to triglyceride, the methanol concentration can be considered as a constant parameter. Therefore, the reaction rate can be expressed as Equation (4.2) (Zik, Sulaiman and Jamal, 2020):

$$-r_A = -\frac{dC_{TG}}{dt} = kC_{TG} \tag{4.2}$$

where

r_A = Reaction rate, mol/L·min
k = Reaction rate constant, min^{-1}
C_{TG} = Concentration of triglyceride, mol/L
t = Time, min

At t = 0, C_{TG} is assumed to be 0, therefore the integration of Equation (4.2) gives Equation (4.3) (Zik, Sulaiman and Jamal, 2020):

$$ln\, C_{TG,0} - \ln C_{TG} = kt \tag{4.3}$$

The conversion of methyl ester (ME), X_{ME} is expressed as Equation (4.5):

$$C_{TG} = C_{TG,0}(1 - X_{ME}) \tag{4.4}$$

$$X_{ME} = 1 - \frac{C_{TG}}{C_{TG,0}} \tag{4.5}$$

Thus, Equation (4.3) is rearranged, resulting in Equation (4.6):

$$-\ln(1 - X_{ME}) = kt \tag{4.6}$$

The value of the reaction rate constant, k can be obtained by plotting a linear graph of $-\ln(1 - X_{ME})$ against t where the slope of the graph is the value of k.

The kinetic study of transesterification reaction using nano-crystal cellulose catalyst derived from coconut was reported by Zik, Sulaiman and Jamal (2020). The study was conducted at different reaction temperatures, 55 ℃, 60 ℃ and 65 ℃. By referring to the slope of the linear graph, the reaction rate constants obtained at 55 °C, 60 °C and 65 °C were 0.0092 min^{-1}, 0.0120 min^{-1} and 0.0151 min^{-1}, respectively. Meanwhile, Zhang, et al. (2016) performed the transesterification reaction by utilising cellulose beads as the catalyst at the temperature from 40 ℃ to 60 ℃. The reaction rate constants were found as 0.00146 min^{-1}, 0.00282 min^{-1} and 0.00597 min^{-1} at 40 ℃, 50 ℃ and 60 ℃, respectively. The range of reaction rate constant was lower than that of using coconut-derived nano-crystal cellulose catalyst which indiated a slower rate of reaction. Apart from that, Helmiyati and Anggraini (2019) had conducted a esterification reaction between oleic acid (OA) and methanol in the presence of nanocomposites of rice husk-derived cellulose catalysts in a temperature range of 40 °C to 70 °C. However, the reaction rate constant was identified by plotting a graph of ln C_{OA} against t according to Equation (4.7).

$$\ln C_{OA} = \ln C_{OA,0} + kt \tag{4.7}$$

The values of the reaction rate constant were reported at 0.0095 min^{-1}, 0.0112 min^{-1}, 0.0137 min^{-1} and 0.0165 min^{-1} for 40 °C, 50 °C, 60 °C and 70 °C, respectively. The reaction rate constants obtained in that study were consistent with the values reported by Zik, Sulaiman and Jamal (2020). Figure 4.8 presents an example of the linear graph of $-\ln(1 - X_{ME})$ against t which is the transesterification reaction catalysed by cellulose bead at different temperatures.

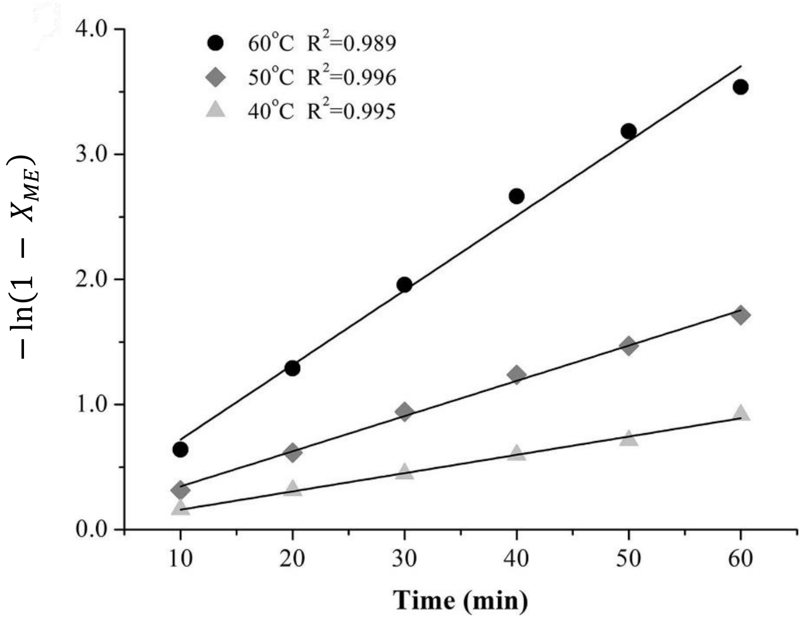


Figure 4.8: Graph of $-\ln(1 - X_{ME})$ against t for Reaction Using Cellulose Bead Catalyst (Zhang, et al., 2016).

Table 4.4 tabulates the results of reaction rate constants at different temperatures by using a variety of biomass-derived cellulose catalysts. It can be seen that the correlation coefficients, R^2 for the plots were above 0.9 which indicated that the results were best fitted with the linear equation. Therefore, the kinetic study followed the prediction of the reaction order, which was pseudo first-order reaction.

Table 4.4: Reaction Rate Constants Using Different Cellulose Catalysts.

Catalysts	***T*** **(°C)**	***k*** **($\min^{-1}$)**	R^2	**References**
Coconut-derived nano-crystal cellulose	55	0.0092	0.9075	Zik, Sulaiman and Jamal (2020)
	60	0.0120	0.9025	
	65	0.0151	0.9409	
Cellulose beads	40	0.00146	0.9950	Zhang, et al. (2016)
	50	0.00282	0.9960	
	60	0.00597	0.9890	
Rice husk-derived cellulose nanocomposites	40	0.0095	-	Helmiyati and Anggraini (2019)
	50	0.0112	-	
	60	0.0137	-	
	70	0.0165	-	
Date seed-derived cellulose	55	0.0080	0.9829	Jamil, et al. (2021)
	60	0.0090	0.9094	
	65	0.0150	0.9020	
Mango peel-derived cellulose	40	0.0098	0.8883	Memon, et al. (2021)
	50	0.0144	0.9806	
	60	0.0199	0.9434	
	70	0.0254	0.9758	
Sugarcane bagasse-derived cellulose	45	0.0046	-	Basumatary, et al. (2021)
	55	0.0065	-	
	65	0.0092	-	
	75	0.0091	-	
Potato peel-derived cellulose	40	0.0064	0.9500	Hussein, et al. (2021)
	60	0.0133	0.9600	
	80	0.0293	0.9900	
Coconut-derived cellulose	55	0.0184	-	Sulaiman, Talha and Balqis (2017)
	60	0.0205	-	
	65	0.0142	-	

From the reaction rate constants obtained, it was clear that the rates of both transesterification and esterification reactions for biodiesel production increased when increasing the reaction temperature. According to the theory of collision, an increment in temperature could supply more energy into the reaction system and raise the collision probability between molecules, thereby accelerated the reaction towards product formation (LibreTexts, 2021). Besides, the methanol solubility in the oily phase could be improved when raising the reaction temperature, led to a higher methyl ester conversion (Chaos-Hernández, et al., 2022). Thus, the kinetic reaction of the biomass-derived cellulose catalyst could be enhanced by raising the temperature of the reaction.

However, the rate of a chemical reaction could be affected by various factors such as temperature, pressure, physical state and concentration of the reactants which could cause a crucial impact on the reaction kinetics (Chaos-Hernández, et al., 2022). For instance, according to the study reported by Sulaiman, Talha and Balqis (2017) as shown in Table 4.4, the reaction rate constant dropped significantly when increasing temperature to 65 °C. This was probably because the temperature had reached its optimum value. The reaction rate decreased when the reaction temperature increased beyond its optimum value.

4.2.2 Activation Energy

Activation energy is the minimum amount of energy essential for a reaction to happen. Hence, the data of activation energy is imperative to evaluate the energy potential of using biomass-derived cellulose catalyst to produce biodiesel. Based on the reaction rate constants, activation energy for the transesterification reaction can be determined through the Arrhenius equation as shown in Equation (4.8) (Nazir, et al., 2021):

$$k = Ae^{\frac{-E_A}{RT}} \tag{4.8}$$

where

k = Reaction rate constant, min^{-1}

A = Arrhenius constant, min^{-1}

E_A = Activation energy, J/mol

R = Ideal gas constant, 8.314 J/mol·K

T = Temperature, K

Taking the natural logarithm of Equation (4.8) to give Equation (4.9):

$$\ln k = \ln A - \frac{E_A}{RT} \tag{4.9}$$

The value of activation energy, E_A can be determined by plotting a straight line graph of $\ln k$ against $1/T$ where the slope of the plot is $\frac{-E_A}{R}$. The results of the kinetic study conducted by using biomass-derived cellulose catalysts are compared with similar works from other researchers that used non-cellulose catalysts, as shown in Table 4.5.

Table 4.5: Kinetic Study Performed by Using Different Catalysts.

Catalysts		**E_A (kJ/mol)**	**References**
Cellulose	Coconut-derived nano-crystal cellulose	45.72	Zik, Sulaiman and Jamal (2020)
	Cellulose beads	14.68	Zhang, et al. (2016)
	Rice husk-derived cellulose nanocomposites	16.56	Helmiyati and Anggraini (2019)
	Date seed-derived cellulose	29.64	Jamil, et al. (2021)
	Mango peel-derived cellulose	15.42	Memon, et al. (2021)
	Sugarcane bagasse-derived cellulose	22.12	Basumatary, et al. (2021)
	Potato peel-derived cellulose	32.90	Hussein, et al. (2021)
	Coconut-derived cellulose	33.88	Sulaiman, Talha and Balqis (2017)
Others	CaO	78.80	Maneerung, et al. (2016)
	Al–Sr nanocatalyst	72.86	Feyzi and Shahbazi (2017)
	NaOH	53.90	Reyero, et al. (2015)

Based on Table 4.5, the activation energy for the reaction to produce biodiesel using different biomass-derived cellulose catalysts were found in the range of 14.68 kJ/mol to 45.72 kJ/mol. In comparison, the activation energy was much lower than that of other non-cellulose catalysts which obtained the values higher than 70 kJ/mol although there was significant variation in the experimental conditions for these research works. Typically, the value of activation energy can be affected by the activity of the catalyst as various catalysts provide different alternative reaction routes with different lower activation energy. This kinetic study revealed that the catalysis using biomass-derived cellulose catalyst was able to lower the activation energy which increased the rate and efficiency of the reaction. Hence, this indicates the transesterification reaction to produce biodiesel is not an energy-intensive process so that the commercial-scale biodiesel production can be more economical. In a nutshell, biomass-derived cellulose catalyst exhibits great catalytic activity and it can be utilised as an efficient biocatalyst in the near future.

Apart from that, the values of activation energy could be used to determine whether the nature of the reaction was diffusion-limited or reaction-limited. The reaction was diffusion-limited if the activation energy was ranged between 10 kJ/mol to 15 kJ/mol while the reaction with activation energy of more than 25 kJ/mol was reaction-limited (Hussein, et al., 2021). From the values obtained in Table 4.5, the biodiesel production processes using cellulose catalysts derived from coconut, date seeds and potato peel were reaction-limited since the activation energy values were higher than 25 kJ/mol. In other words, the reactions were chemically-controlled instead of mass transfer-controlled under the conditions used in their respective studies. In contrast, the transesterification reaction catalysed by cellulose beads was a diffusion-limited process. This indicated that it was necessary to overcome the barriers for the mixing of reactants in order to initiate the production of methyl ester (Chaos-Hernández, et al., 2022). For the catalytic reactions by cellulose catalysts derived from rice husk, mango peel and sugarcane bagasse, it could be found that the reactions were neither mass transfer-controlled nor chemically-controlled.

4.3 Thermodynamics Study

The thermodynamic parameters such as change in enthalpy (ΔH°), change in entropy (ΔS°) and change in Gibbs free energy (ΔG°) for transesterification reaction catalysed by biomass-derived cellulose catalyst can be determined based on Eyring-Polanyi equation as shown in Equation (4.10) (Nautiyal, Subramanian and Dastidar, 2014):

$$k = \frac{k_b T}{h} \exp\left(-\frac{\Delta G}{RT}\right) \tag{4.10}$$

$$\Delta G = \Delta H - T\Delta S \tag{4.11}$$

where

k = Reaction rate constant, s^{-1}

k_b = Boltzmann constant, 1.38×10^{-23} J/K

h = Planck constant, 6.626×10^{-34} J·s

R = Ideal gas constant, 8.314 J/mol·K

T = Temperature, K

ΔG = Change in Gibbs free energy, J/mol

ΔH = Change in enthalpy, J/mol

ΔS = Change in entropy, J/mol·K

Taking the natural logarithm of Equation (4.10) and substituting Equation (4.11) to give Equation (4.12) (Basumatary, et al., 2021):

$$\ln\frac{k}{T} = -\frac{\Delta H}{RT} + \left[\ln\frac{k_b}{h} + \frac{\Delta S}{R}\right] \tag{4.12}$$

Based on Equation (4.12), the values of ΔH°, ΔS° and ΔG° can be calculated from the slope ($-\frac{\Delta H}{R}$) and intercept ($\ln\frac{k_b}{h} + \frac{\Delta S}{R}$) of the plot of $ln\ k/T$ versus $1/T$. Figure 4.9 presents the Eyring-Polanyi plots for biodiesel production using coconut-derived nano-crystal cellulose catalyst, cellulose bead catalyst and rice husk-derived cellulose nanocomposite catalyst.

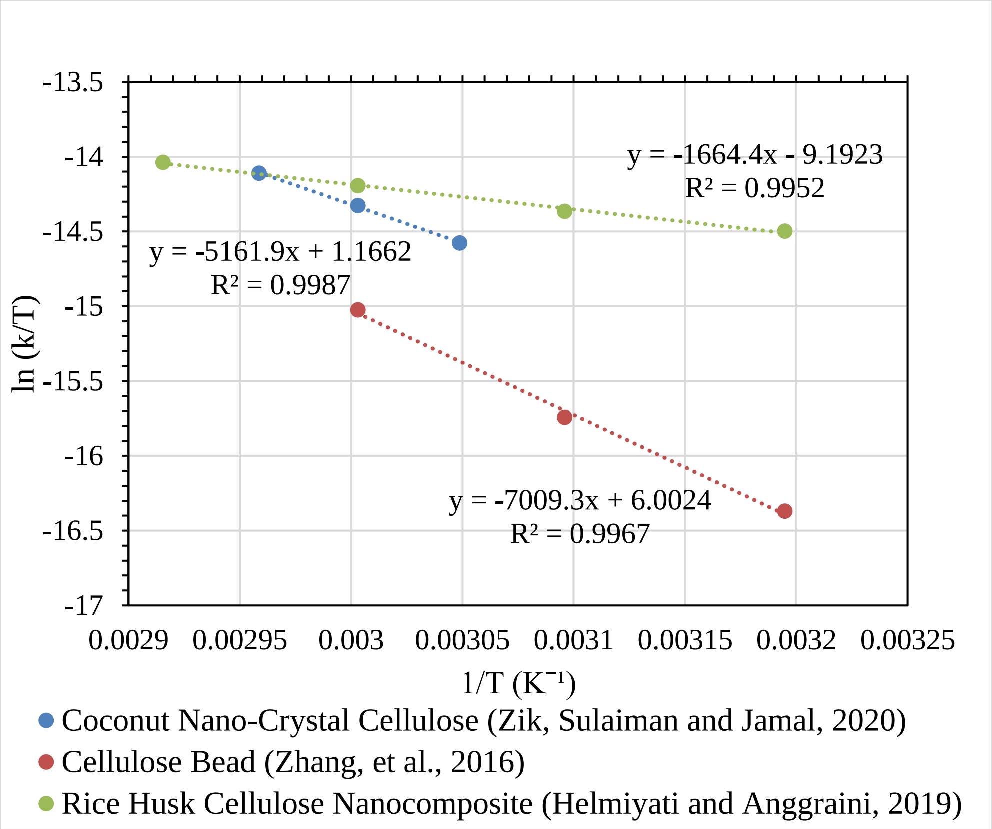


Figure 4.9: Graph of $ln\ k/T$ versus $1/T$ for Reaction Using Coconut-Derived Nano-Crystal Cellulose Catalyst, Cellulose Bead Catalyst and Rice Husk-Derived Cellulose Nanocomposite Catalyst.

Table 4.6 tabulates the calculated values of the thermodynamic parameters of transesterification reaction by using different biomass-derived cellulose catalysts. It could be determined that the transesterification reaction was an endothermic reaction based on the positive values of ΔH° (Sarve, Varma and Sonawane, 2016). The positive values of ΔG° also represented the cellulose-catalysed transesterification reaction was non-spontaneous and endergonic in nature (Nautiyal, Subramanian and Dastidar, 2014). Therefore, both values of ΔH° and ΔG° reflected that an external energy input was required to boost the energy level of reactants to their transition state so as to form the products. Furthermore, the negative values of ΔS° indicated that there was a more ordered structure of the transition state compared to the reactants in the ground state. The reactant molecules interacted with each other to form activated complexes during the reaction through associative mechanism (Zainol, Amin and Asmadi, 2019).

Table 4.6: Thermodynamic Parameters of Reaction Catalysed by Different Cellulose Catalysts.

Catalysts	**ΔH° (kJ/mol)**	**ΔS° (kJ/mol·K)**	**T (℃)**	**ΔG° (kJ/mol)**
Coconut-derived nano-crystal cellulose	42.92	-0.1878	55	104.53
			60	105.47
			65	106.41
Cellulose beads	58.28	-0.1476	40	104.48
			50	105.96
			60	107.44
Rice husk-derived cellulose nanocomposites	13.84	-0.2740	40	99.59
			50	102.33
			60	105.07
			70	107.81
Date seed-derived cellulose	54.99	-0.1528	55	105.10
			60	105.87
			65	106.63

Table 4.6 (Continued)

Catalysts	**ΔH° (kJ/mol)**	**ΔS° (kJ/mol·K)**	**T (℃)**	**ΔG° (kJ/mol)**
Mango peel-derived cellulose	25.73	-0.2354	40	99.41
			50	101.77
			60	104.12
			70	106.47
Sugarcane bagasse-derived cellulose	19.45	-0.2626	45	102.94
			55	105.57
			65	108.19
			75	110.82
Potato peel-derived cellulose	32.11	-0.2190	40	100.64
			60	105.02
			80	109.40
Coconut-derived cellulose	16.88	-0.2615	55	102.65
			60	103.96
			65	105.27

The thermodynamic parameters also possessed similar trends with the works by other researchers that utilised other non-cellulose catalysts to produce biodiesel. According to Roy, Sahani and Sharma (2020), the transesterification reaction was catalysed by potassium modified ceria oxide and the values of ΔH°, ΔS° and ΔG° were found to be 47.35 kJ/mol, -0.1287 kJ/mol·K and 90.85 kJ/mol, respectively. Wu, et al. (2016) investigated the biodiesel production in the presence of NaOH catalyst which obtained 28.33 kJ/mol for ΔH°, -0.18 kJ/mol·K for $\Delta S^{\circ}$and 83.30 – 87.69 kJ/mol for ΔG°. In addition, the values of ΔH°, ΔS° and ΔG° were 50.62 kJ/mol, -0.105 kJ/mol·K and 82.44 – 85.55 kJ/mol, respectively as reported by Sarve, Varma and Sonawane (2016) when using barium hydroxide as the catalyst for transesterification reaction. As could be observed, the values of each thermodynamic parameter reported were comparable with the corresponding values reported by the biomass-derived cellulose catalysts, thus making them as a competitive and more trustworthy catalyst for biodiesel production.

The values of thermodynamic parameters were varied due to the influence of the biodiesel feedstocks, production methods, reaction parameters as well as the catalytic activity. A more reactive catalytic system was exhibited by nanocomposites of rice husk-derived cellulose catalyst compared to other catalysts as it had lower ΔH° values and hence a smaller amount of energy was necessary to break down the chemical bonds in order to form the transition state. However, the value of ΔS° was slightly more negative which signified the degree of ordered geometry for transition state was slightly higher (Zainol, Amin and Asmadi, 2019). Therefore, the formation of transition state along the reaction pathway was greater than that of other catalysts.

On the other hand, as the temperature increased, the values of ΔG° for all catalysts as shown in Table 4.6 also increased and were always positive. This indicated the reactions were non-spontaneous at all temperatures. Thus, an external driving force was required to make the reaction to be spontaneous in order to favour the product formation. Typically, the energy level in the transition state was always higher than that of the reactants or products. This resulted the value of activation energy was always positive, regardless of exergonic or endergonic reaction. In the case of endergonic reaction, the transition state was similar to exergonic reaction but with higher activation energy (Khan Academy, 2022). Hence, more energy was required to reach the transition state so that the reaction can proceed.

4.4 Catalyst Reusability

The reusability of biomass-derived cellulose catalysts was studied to assess the stability of the catalysts in the process of biodiesel production at optimum reaction conditions. Several studies reported that biomass-derived cellulose catalysts display good reusability for production of biodiesel. Figure 4.10 illustrates the comparison of catalyst reusability between various biomass-derived cellulose catalysts and non-cellulose catalysts.

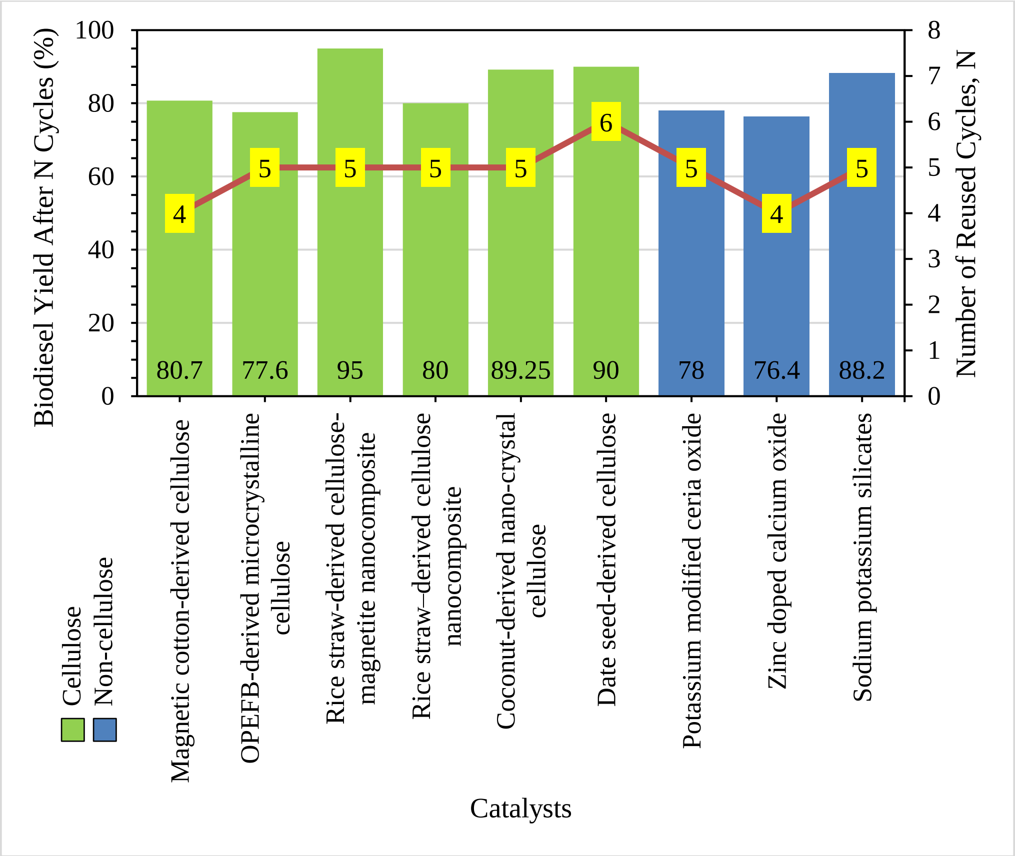


Figure 4.10: Comparison of Catalyst Reusability between Biomass-Derived Cellulose Catalysts and Non-Cellulose Catalysts (Han, et al., 2016; El-Nahas, et al., 2017; Naveenkumar and Baskar, 2019; Roy, Sahani and Sharma, 2020; Zik, Sulaiman and Jamal, 2020; Helmiyati, et al., 2021; Jamil, et al., 2021; Krishnan, Pua and Zhang, 2022; Oliveira, et al., 2022).

In a study conducted by Han, et al. (2016), the transesterification reaction was catalysed by magnetic cotton-derived cellulose based catalyst. The results indicated that the catalyst remained stable at the first three runs of experiment which could obtain biodiesel yield above 85 %. However, the biodiesel yield decreased quickly to 80.7 % at the subsequent run. Thus, it was clear that the catalyst could be reused up to four reaction cycles. The decrement of the catalytic activity was mainly due to the deactivation of the catalyst.

On top of that, Krishnan, Pua and Zhang (2022) had conducted an esterification reaction using microcrystalline cellulose based magnetic acid catalyst which was isolated from oil palm empty fruit bunch. It was found that the catalyst could be reused up to five cycles as the rate of esterification started to drop significantly to 77.6 % at the fifth run. The leaching of the catalyst's active sites was the main factor that resulted in the gradual reduction of biodiesel yield. Based on the leachability test, the catalyst had a high leaching phase up to 58.8 %, causing the leaching of iron and sulphur ions during the reaction.

According to El-Nahas, et al. (2017), functionalised cellulose-magnetite nanocomposite catalyst derived from rice straw biomass was used in the production of biodiesel. From the reusability test, the catalyst appeared to be highly reusable without significant change in biodiesel yield. The biodiesel yield remained high at 95 % at the fifth cycle. The high catalytic performance of this catalyst was related to high dispersion of the Brönsted acid sites on the nanocellulose surface and the Lewis acid sites of magnetite species. Meanwhile, another rice straw–derived cellulose nanocomposite catalyst was applied on coconut oil for biodiesel production and it showed similar recyclability of five cycles but with yield of 80 % (Helmiyati, et al., 2021).

In another study, the reusability of five cycles was also observed in the coconut-derived nano-crystal cellulose to convert the waste cooking oil into methyl ester (Zik, Sulaiman and Jamal, 2020). Apart from that, date seed-derived cellulose catalyst was able to remain its catalytic activity up to six reaction cycles. The biodiesel yield was high at 90 % for the sixth run and decreased to a large extent for the seventh run (Jamil, et al., 2021).

Based on Figure 4.10, it could be observed that biomass-derived cellulose catalysts were competitive with other non-cellulose catalysts. For instance, potassium modified ceria oxide catalyst used for converting waste cooking oil to biodiesel displayed recyclability of five cycles (Roy, Sahani and Sharma, 2020). Moreover, the effect of reusability was investigated on zinc doped calcium oxide nanocatalyst in which the biodiesel yield was decreased to 76.4 % at the fourth run (Naveenkumar and Baskar, 2019). In addition, it was also found that sodium potassium silicates were able to produce biodiesel yield of 88.2 % at the fifth cycle (Oliveira, et al., 2022).

Therefore, it was concluded that biomass-derived cellulose catalysts possessed a great catalytic performance for biodiesel production due to their comparable product yield and reusability of four to six reaction cycles. The reusability of catalyst was significant as it could help to reduce the cost of raw material for overall production. Overall, the catalyst deactivation was due to the leaching of species from the catalyst's active sites into the reaction medium, resulting in product contamination and reduction in catalytic activity (Helmiyati, et al., 2021). Another factor of catalyst deactivation was due to the binding of the crude glycerol or other remaining particles from the reaction medium to the active sites of the catalyst, leading to the blockage of the catalyst pores (Zhang, et al., 2017). In addition, the aggregation of catalyst during the reaction might also contribute to the loss of active sites for the substrates (Wang, et al., 2015).

4.5 Challenges and Future Prospects

The utilisation of biomass-derived cellulose catalysts for biodiesel production has captured extensive attention in these recent years due to their great catalytic activity and environment-friendly properties. These catalysts can significantly reduce the high production cost of biodiesel since they are derived from biodegradable raw materials and easy to handle. They are also eco-friendly as they do not result in any environmental hazard for large disposal of these catalysts after use. Furthermore, the addition of nanocellulose could enhance the catalytic activity for biodiesel production (Helmiyati, et al., 2021). The cellulose catalyst exhibited adequate porosity which gave high adsorption capacity for the substrates to catalyse the reaction (Zhang, et al., 2016). The Brönsted acid sites on the nanocellulose surface was also found to contribute to high catalytic activity towards the formation of methyl ester (El-Nahas, et al., 2017).

Nevertheless, the investigation on using biomass-derived cellulose catalysts to produce biodiesel is limited. Therefore, future efforts must be made on the further development of biomass-derived cellulose catalyst to validate the capability of these catalysts for large-scale biodiesel production and improve their catalytic performance in the process.

The exploration of biomass waste as the catalyst source must be promoted because the catalysts prepared based on the reported literature consist only of little amount of cellulose biomass compared to other chemical substances added. There were several catalysts have been synthesised for biodiesel production by using inorganic substances supported by cellulose. For instance, Azahra and Helmiyati (2020) had prepared a green catalyst by combining Fe_3O_4/ZnO composites on the cellulose catalyst support. Another catalyst was also synthesised by Helmyati and Suci (2019) through the combination of cellulose and ZnO/SiO_2 composites. Moreover, organic compounds were also used in the synthesis of cellulose catalyst for biodiesel production. A heterogeneous catalyst had been developed by isolating cellulose from coconut residue and using polyvinyl alcohol as a support (Zik, Sulaiman and Jamal, 2020). In this context, the catalyst could be incorporated more biomass wastes as much as possible. Therefore, research on catalyst performance is required to provide new applications for the wastes in order to create sustainability and reduce the dependence on using conventional chemicals during catalyst preparation.

In addition, there are several problems encountered by solid catalysts such as the number of active sites, specific surface area, porosity and leaching problem. It is necessary to make further improvement on the catalytic properties of biomass-derived cellulose catalyst, namely specific surface area, pore diameter, strength of active sites, catalyst stability and reaction rate. The decrement in the reaction rate and production yield are generally caused by the catalyst deactivation after repeated use. Hence, one of the research focuses should be on synthesising biomass-derived cellulose catalysts that are more stable and durable.

In this regard, another challenges reported for these catalysts include the deactivation and reusability of the catalyst. The catalyst deactivation is usually due to leaching of active species and clogging of active sites by impurities, which will contaminate the final product and reduce the catalytic activity. Typically, it is tedious and time-consuming for the recovery of catalysts. For example, huge amount of water and energy are necessary for the catalyst washing procedures. Thus, further research should focus on the recyclability and deactivation of biomass-derived cellulose catalysts to synthesise catalysts with effective recovery in order to reduce the preparation time and cost while increasing the yield and selectivity of the desired products.

From the perspective of economics, the use of biomass-derived cellulose catalysts appears to be economically feasible for biodiesel production. However, economic analysis should be conducted deeply before commercialising the cellulose catalyst in biodiesel industry. This is because the equipment and maintenance costs are insignificant in a lab scale of catalyst preparation. To implement the use of biomass-derived cellulose catalysts on an industrial scale, there will be an increase in operation cost. Hence, it is necessary to have more study on economic aspect before scaling up the catalyst production.

Moreover, life-cycle assessment also should be performed on the biodiesel production using biomass-derived cellulose catalyst although this catalyst is well known as an environmentally benign catalyst. It is important to investigate the environmental impacts of utilising cellulose catalyst to produce biodiesel in order to make sure it does not pose a hazard to the environment and to be more environmentally friendly.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The present research study focused on the development of biomass-derived cellulose catalyst in biodiesel production. A variety of biomass could be utilised to generate biomass-derived catalysts which were able to catalyse the transesterification reaction. It was found that biomass-derived catalysts had a high surface area and greater amount of active sites, hence enhanced the rate of the reaction and produced high biodiesel yield. From the study, the biodiesel production using biomass-derived cellulose catalysts showed a remarkable methyl ester yield above 85 % under optimum reaction conditions.

Several characterisation studies such as SEM, XRD, TGA and FTIR were conducted for the analysis of biomass-derived cellulose catalyst. SEM micrographs showed that the catalysts could increase the binding of reactant molecules as they exhibited a disordered, rough and porous structure. In addition, XRD diffractograms revealed that the peaks at around 16°, 22° and 34° were the characteristic peaks of cellulose where the highest peak at 22° was attributed to the crystalline structure of cellulose. The catalysts also showed great crystallinity with the percentage above 58 % which could improve the mechanical properties. Based on the TGA results, the catalysts went through two stages of degradation where the first weight drop was corresponded to the removal of absorbed moisture from the catalyst surface while the second weight drop was caused by the decomposition of cellulose. The main finding of this analysis indicated that biomass-derived cellulose catalyst was thermally stable up to 380 ℃. On the other hand, a typical FTIR spectra of cellulose was displayed which included functional groups of O-H, C-H, CH_2, C-O-C and adsorbed water. This finding was further proven in which the C=C and C=O stretchings were not found in the spectra, indicating the absence of functional groups of hemicellulose and lignin on the catalysts. The analysis also showed the disruption of the cellulose linkages which could increase the surface area of the cellulose catalyst.

For the investigation on the kinetic and thermodynamic characteristics, it was identified that the activation energy of the reaction to produce biodiesel using biomass-derived cellulose catalyst was much lower compared to other catalysts. It has provided the important insight that less energy is required to catalyse the reaction using biomass-derived cellulose, thus improving the efficiency of the reaction. Moreover, the thermodynamic parameters of biomass-derived cellulose catalyst in biodiesel production were also studied with the following results obtained: $\Delta H^{\circ} > 0$, $\Delta S^{\circ} < 0$ and $\Delta G^{\circ} > 0$. The positive values of ΔH° and ΔG° showed that the reaction was endothermic and endergonic while the reduction in randomness during the reaction was indicated by the negative values of ΔS°.

Overall, the planned objectives were achieved in this research where the biodiesel production using biomass-derived cellulose catalyst and characterisation studies of biomass-derived cellulose catalysts were reviewed thoroughly. The kinetics and thermodynamics of the catalyst in biodiesel production were also studied and discussed as well. The presented results were remarkable as they highlighted the biomass-derived cellulose as one of the useful catalyst for biodiesel production since it is renewable, abundantly available and economically viable. Nevertheless, there is always a room for improvement. Further research is still required to ensure the accuracy of data and information collected.

5.2 Recommendations for Future Work

Since the analysis of this research was conducted based on the data and information obtained from various research studies and journals, the result comparisons were influenced by different catalyst preparation methods and operating conditions. Moreover, the available data and information for biomass-derived cellulose catalyst was limited in order to demonstrate the effectiveness of the catalyst in biodiesel production with sufficient evidence. Hence, several recommendations were made to improve the accuracy and reliability of the results in the future related research work. The suggested recommendations are listed in the following.

i. Preparation of biomass-derived cellulose catalyst should be derived from the same raw materials to make the comparison of results more accurate.
ii. Each type of characterisation techniques of biomass-derived cellulose should be carried out under same operating conditions to ensure the accuracy of the comparison.
iii. Any equipment used such as scanning electron microscope, thermogravimetric analyser, X-ray diffractometer and fourier transform infrared spectrometer should be consistent to minimise discrepancies.
iv. The kinetics and thermodynamics of transesterification reaction catalysed by biomass-derived cellulose should be investigated under the same reaction parameters such as reaction temperature, catalyst loading, methanol-to-oil molar ratio and reaction duration.
v. Pilot-scale testing can be conducted to determine the stability and validate the capability of biomass-derived cellulose catalyst to produce biodiesel on an industrial scale.

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