

1. Submitted to the journal “ANNALES DE CHIMIE – SCIENCE DES MATERIAUX”
(28-05-2023)
2. First revision: Accepted (16-08-2024)
3. Revised version received (04-09-2024)
 - Revisions and Amends
 - Revised version with highlights
4. Paper accepted (18-09-2024)
5. Paper published (01-11-2024)
 - Final paper

1. Submitted to the journal “INTERNATIONAL JOURNAL OF INDUSTRIAL ENGINEERING & PRODUCTION RESEARCH” (29-11-2023)



D.N. Dian Retno Sari Dewi P. , ST., MT. <dianretnosd@ukwms.ac.id>

Paper submission: Biodiesel synthesis from calophyllum inophyllum utilizing modified zeolite and bentonite catalysts

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Biodiesel synthesis from calophyllum inophyllum utilizing modified zeolite and bentonite catalysts

Herman Hindarso^{1*}, Aning Ayucitra², Dian Retno Sari Dewi³, Nyoman Puspa Asri⁴

^{1,2} Department of Chemical Engineering, Widya Mandala Catholic University, Kalijudan 37, Indonesia

³ Department of Industrial Engineering, Widya Mandala Catholic University, Kalijudan 37, Indonesia

⁴ Department of Food Technology, Ciputra University, Citraland CBD Boulevard, Indonesia

Corresponding Author Email: herman@ukwms.ac.id

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<https://doi.org/10.18280/acsm.xxxxxx>

ABSTRACT

Received:
Revised:
Accepted:
Available online:

Keywords:

Calophyllum inophyllum oil; Transesterification; Modified zeolite; Modified bentonite; Biodiesel

Biodiesel serves as a renewable, eco-friendly alternative fuel. Its production relies on converting triglyceride sources into methyl esters through transesterification. These triglycerides can be sourced from vegetable oils and animal fats. Previous studies often relied on acids and bases as catalysts. However, there's a lack of research exploring the use of modified zeolite and bentonite as catalysts, which hold the promise of higher yields compared to previous studies. In this study, biodiesel was derived from calophyllum inophyllum via esterification and transesterification processes. Characterization of these catalysts was done using XRD and FTIR analyses. Transesterification to produce biodiesel occurred at temperatures ranging from 50 to 70°C over a reaction period of 5 hours. The largest yield of biodiesel was obtained at 60°C, with 88.19% using modified zeolite catalyst, 78.84% using modified bentonite catalyst, and 82.36% using a blend of modified zeolite and bentonite catalysts in a 1:1 ratio. Biodiesel resulting from the highest yield using modified zeolite catalyst underwent characteristic testing in accordance with SNI standards. The findings revealed a density of 887 kg/m³, viscosity of 5.633 mm²/s, cetane number of 53, flash point at 121°C, and methyl ester content of 94.55%.

1. INTRODUCTION

At present, the reserves of fossil fuels like crude oil, coal, and natural gas are dwindling due to escalating usage and their non-renewable nature [1]. Consequently, there is a pressing need for the development of alternative and renewable fuel sources [2]. Indonesia, as a nation, boasts a diverse range of natural resources, encompassing both renewable and non-renewable ones.

The demand for crude oil as the world's primary fuel source is substantial. However, this demand is not accompanied by an awareness that the combustion of processed crude oil products such as gasoline, diesel, and others has negative impacts on the environment and tends to harm the Earth in the long term [3]. The adverse effects of excessive fossil fuel usage include climate change due to global warming, often referred to as global warming [4–6].

Nowadays, the ongoing and swift consumption of crude oil as a fuel is leading to its diminishing reserves. Therefore, there is a demand for alternative energy sources and fuels that can evolve and hold promise for the future [4]. Biodiesel is a renewable alternative fuel for diesel engines derived from renewable sources such as vegetable oil, animal fats, and algae [7]. It exhibits combustion properties remarkably similar to diesel fuel, hence holds potential for substituting petroleum diesel [8–11].

Calophyllum inophyllum, a thick brown-colored vegetable oil with a strong caramel-like scent [12], finds various uses among farmers in Kebumen and Cilacap, Central Java, Indonesia. It serves as a coating for roof tiles, aids in batik making, and is utilized in embalming [13]. In West Java, some fishermen rely on calophyllum inophyllum as a fuel for their boats during maritime activities [14]. This oil is rich in unsaturated fatty acids, notably oleic acid, and contains unsaponifiable components like fatty alcohols, sterols, xanthenes, coumarin derivatives, phytols, isophytols, isophthalates, capillary acids, pseudobrasileic acid, and triterpenoid compounds, ranging from 0.5% to 2%, which possess medicinal properties [13].

Advantages of using Calophyllum inophyllum as a source of biofuel include its high oil content (up to 74%) and its non-competition with food production [15]. Calophyllum inophyllum offers various benefits for biodiesel production and development: it naturally grows abundantly across Indonesia, easily regenerates, and bears fruit throughout the year, indicating its resilience to environmental conditions. It can be cultivated with ease either in single-crop fields or mixed forests and thrives in dry climates [16]. Nearly all parts of the calophyllum inophyllum plant are valuable, yielding various economically significant products. Using calophyllum inophyllum biofuel can also help reduce deforestation for firewood, given its high seed productivity compared to other plants [13].

Biodiesel derived from calophyllum inophyllum also offers advantages, including its comparatively high oil yield (40-73%) when compared to other plants like jatropha and palm oil [17]. Some quality parameters already meet Indonesian standards, and calophyllum inophyllum burns twice as long as kerosene. Additionally, it holds future potential as a blending component. Compared to fossil fuels, biodiesel has several benefits, such as renewability, higher energy efficiency, emissions reduction, and the possibility of using it as a complete diesel substitute with advanced processing technology [18]. It also offers better emission quality than diesel and can serve as a bio-kerosene alternative [19].

The rationale for this study lies in the limited utilization of calophyllum inophyllum oil, despite its considerable potential as a replacement for fossil fuels. Previous investigations commonly utilized acids and bases as catalysts, whereas there's limited research on employing modified zeolite and bentonite in calophyllum inophyllum oil production. Despite their potential for higher yields compared to acids and bases, these modified catalysts are rarely explored in prior studies. An additional advantage of modified heterogeneous catalysts is the ease of separating the catalyst after the reaction, enabling its reuse and preventing any waste generation from the catalyst. This differs from the biodiesel production process using acid-base catalysts, which produces waste acids and bases during the separation of biodiesel products from the leftover catalyst. Hence, our research identifies a gap in the extant research in utilizing modified zeolite and bentonite as promising catalysts for achieving greater yields.

2. LITERATURE REVIEW

Calophyllum inophyllum can be obtained through several stages of processing [9].

1. Peeling the seeds from their hard shells.
2. Slicing them thinly.
3. Sun-drying for two days.
4. Crushing and steaming for 2 hours.
5. Pressing with a manual hydraulic machine or extruder, resulting in dark-colored oil due to impurities from the skin and chemical compounds like alkaloids, phosphatides, carotenoids, chlorophyll, and others. Pressing 2.5 kg of dried seed material without skins yields 1 liter of calophyllum inophyllum oil.
6. Removal of latex, which involves separating latex and impurities from the oil using a 1% phosphoric acid solution.
7. Filtration, which separates oil from impurities to obtain clear oil.

The characteristics of calophyllum inophyllum before and after latex removal are shown in Table 1 [20].

Tabel 1. The physical and chemical properties of calophyllum inophyllum oil

Parameter	Before latex removal	After latex removal
Mositure content (%)	0,25	0,41
Density 20 °C (g/mL)	0,944	0,940
Viskositiy (cP)	56,7	53,4
Acid number (mg KOH/g)	198,1	194,7

Parameter	Before latex removal	After latex removal
Iod number	86,42	85,04
Refraktif index	1,447	1,478
Appearance	Dark green, thick, and pungent odor	Thick reddish-yellow

The composition of fatty acids constituting calophyllum inophyllum can be seen in Table 2 [21].

Table 2. The fatty acid composition of calophyllum inophyllum oil

Fatty acid	Composition
Palmitoleat acid (C16:1)	0,5 – 1 %
Palmitat acid (C16)	15 – 17 %
Oleat acid (C18:1)	30 – 50 %
Linoleat acid (C18:0)	25 – 40 %
Stearat acid (C18:0)	8 – 16 %
Arachidat acid (C20)	0,5 – 1 %
Gadoleat acid (C19:1)	0,5 – 1 %

The free fatty acid content of calophyllum inophyllum before latex removal is very high. This is due to the fact that calophyllum inophyllum comes from seeds that have aged, where the oxidation process of the oil has already begun while they are still in seed form. Through the latex removal process, the free fatty acid content will decrease, as will the values of several other parameters [22].

The decline in viscosity and density values occurs because of the elimination of latex and impurities from the oil solution. The drop in saponification number is due to the introduction of phosphoric acid, while the decrease in iodine number is linked to the reduction in the quantity of unsaturated fatty acids resulting from the latex removal process. The outcome of the latex removal process manifests in a distinct color change of the oil, transitioning from dark green to shades of yellow and red.

After the latex removal process, calophyllum inophyllum undergoes further processing, such as neutralization with NaOH, to transform it into biokerosene, which serves as a substitute for kerosene oil and is highly beneficial for heating purposes in rural communities [23]. As a fuel, it is evident that calophyllum inophyllum exhibits a longer burning duration compared to kerosene oil, as experiments show that 1 ml of calophyllum inophyllum burns for 11.8 minutes, while 1 ml of kerosene oil burns for only 5.6 minutes. Furthermore, during water boiling tests, it was found that 0.9 mL of kerosene oil was required, whereas only 0.4 mL of calophyllum inophyllum was needed. These results indicate that calophyllum inophyllum can be utilized as a household fuel source, providing significant benefits for daily use by communities.

Calophyllum inophyllum falls into the category of oils containing a mixture of saturated and unsaturated fatty acids with lengthy carbon chains. Its main components consist of

oleic acid at 37.57%, linoleic acid at 26.33%, and stearic acid at 19.96%. The remainder includes myristic acid, palmitic acid, linolenic acid, arachidic acid, and erucic acid in smaller proportions [24].

Biodiesel can be produced from both vegetable and animal oils. Vegetable oil and biodiesel belong to the same large group of organic compounds, namely the fatty acid ester group. Vegetable oil is a triglyceride of fatty acids with glycerol or triglyceride, while biodiesel is a fatty acid monoester with methanol. This difference in molecular structure has important consequences in assessing them as candidates for diesel engine fuel [25].

1. Vegetable oil (triglycerides) has a much larger molecular weight than biodiesel (methyl esters). This property causes triglycerides to relatively easily undergo cracking into various smaller molecules when heated without contact with air.
2. Vegetable oil has a much higher viscosity than diesel or kerosene as well as biodiesel, making it difficult for fuel injection pumps in diesel engines to produce good atomization when vegetable oil is sprayed into the combustion chamber.
3. Vegetable oil molecules are relatively more branched than fatty acid methyl esters, resulting in a lower cetane number for vegetable oil compared to methyl esters.
4. The cetane number is a measure of the ease of ignition or combustion of a fuel in a diesel engine.

Esterification is the process of converting free fatty acids into esters. This reaction involves combining fatty oils with alcohol. A suitable catalyst for this process is a substance with strong acidic properties, such as sulfuric acid, organic sulfonic acid, or strong acid cation exchange resin, which are commonly used catalysts in industrial applications [26].

To ensure that the reaction proceeds to complete conversion at low temperatures, an excess of methanol reactant must be added (usually greater than 10 times the stoichiometric ratio), and any water produced in the reaction must be removed from the oil phase. Through the appropriate combinations of reaction conditions and methods for removing water, the complete conversion of fatty acids to their methyl esters can be achieved within a few hours. The esterification reaction can be seen in the reaction below [21].



Figure 1. Esterification reaction of calophyllum inophyllum

Esterification is often used to create biodiesel from oils with high levels of free fatty acids (acid value of 5 mg-KOH/g). During this phase, free fatty acids are transformed into methyl esters. Following esterification, the next step is typically transesterification. However, prior to transferring the esterification products to the transesterification phase, it's essential to remove any water and the majority of the acid catalyst present [21].

Transesterification, commonly known as alcoholysis, is the process of converting triglycerides (vegetable oil) into alkyl esters by reacting with alcohol, resulting in glycerol as a by-product. Among monohydric alcohols considered as alkyl group suppliers, methanol is predominantly used due to its affordability and high reactivity (thus, referred to as methanolysis). Therefore, biodiesel is essentially fatty acid methyl esters. The transesterification reaction of triglycerides

into methyl esters is depicted in Figure 2 (Kustanto et al., 2022).

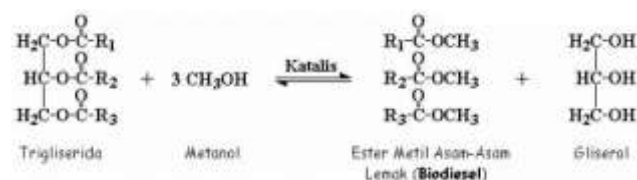


Figure 2. Transesterification reaction from triglycerides to methyl esters

Transesterification also involves the use of catalysts during its reaction phase. The presence of a catalyst maximizes the conversion attained, although the reaction proceeds slowly. Base catalysts are commonly employed in transesterification reactions because they accelerate the reaction. The objective of the transesterification reaction is to obtain fatty acid methyl esters. According to the principle of equilibrium reactions, there are various methods to shift the reaction equilibrium towards the products [27]:

1. Adding excess methanol to the reaction.
2. Separating glycerol immediately.
3. Lowering the reaction temperature (transesterification is an exothermic reaction).

Research into the production of biodiesel from calophyllum inophyllum is increasingly undertaken by various researchers. Ilminafik and Sugara [28] conducted a study on biodiesel production from calophyllum inophyllum using microwave heating, employing solid CaO catalyst at concentrations ranging from 2-6% of the oil weight. The objective of the research was to synthesize biodiesel from calophyllum inophyllum through transesterification, with varying ratios of oil to methanol at 1:9 and 1:12, and microwave power levels at 100, 264, and 400 W. The study identified the optimal conditions for biodiesel yield to be 94% with a microwave heating power of 100 W, 4% catalyst concentration, and an oil to methanol molar ratio of 1:9 [28].

Atabani [29] conducted research on nyamplung seeds utilizing an esterification process with phosphoric acid to remove latex, yielding 85% calophyllum inophyllum. This calophyllum inophyllum was then converted into biodiesel through transesterification using ethanol and NaOH catalyst at 1% of the oil weight. Experimental conditions included a reaction temperature of 60°C and a reaction time of 60 minutes. The biodiesel obtained amounted to 80.89%, and its specifications met the SNI parameters. The subsequent study conducted by Demirbas et al. [21] utilized calophyllum inophyllum and employed transesterification with methanol and 1.25% KOH catalyst, yielding biodiesel at 88.27% under reaction conditions of 60°C temperature and a reaction time of 121 minutes. The produced biodiesel met the specifications according to the SNI parameters [21].

Arumugam and Ponnusami [30] also conducted experiments on producing biodiesel from calophyllum inophyllum using 1% solid KOH catalyst in a microwave reactor. The study aimed to explore the impact of microwave power, reaction time, and temperature on biodiesel yield. Transesterification was performed with varying microwave power levels of 100, 200, and 400 W, reaction times from 5 to 15 minutes, and temperatures from 50 to 70°C. The research identified the most favorable conditions at 200 W power, 65°C reaction temperature, and 5 minutes reaction time, resulting in a biodiesel yield of 84.62%. Quality testing confirmed that the

biodiesel met the SNI 04-7182-2006 standard. This investigation revealed that microwave irradiation could significantly accelerate the transesterification reaction, reducing the reaction time to 1/6 of the conventional method [30].

Subsequent research on biodiesel from calophyllum inophyllum utilized a microwave reactor under reaction conditions of 60°C temperature and a duration of 60 minutes. The catalyst used was a liquid 1-butyl-3-methyl imidazolium hydrogensulphate (BMIMHSO₄) with an ion content of 15% of the oil weight. The study yielded biodiesel at 81.2%, and its specific characteristics met the SNI parameters [31].

The various studies on biodiesel production from calophyllum inophyllum mentioned above utilized both liquid and solid catalysts without any catalyst modification. The novelty of the research lies in the utilization of catalysts derived from natural materials that were subsequently modified. The modification of these catalysts aims to enhance the yield of biodiesel and ensure that its specifications meet the SNI test parameters.

In this study, the biodiesel production process from calophyllum inophyllum was conducted using the transesterification process, which occurred in the liquid phase with heterogeneous catalysts zeolite and bentonite that were modified with acid and calcination. The resulting biodiesel was then analyzed for its characteristics according to SNI standards, including density, viscosity, cetane number, flash point, and methyl ester content.

3. METHODS

This study involves several phases: preparation of catalysts, extraction of Calophyllum inophyllum seeds using n-hexane solvent to obtain calophyllum inophyllum and subsequent analysis of its characteristics, esterification stage to reduce the free fatty acid content in calophyllum inophyllum, and transesterification stage to produce biodiesel. The yield of the resulting biodiesel is then calculated. The biodiesel with the highest product yield is further analyzed for its characteristics according to the American Society for Testing and Materials (ASTM) procedures and follows the requirements of the Indonesian National Standard (SNI) for biodiesel (SNI 04-7182-2006), including viscosity, density, cetane number, flash point, and methyl ester content. Below are the research steps:

- **Materials**

The primary materials used in this study include Calophyllum inophyllum fruit obtained from the Ampel area of Surabaya, natural zeolite and bentonite obtained from Pacitan. The reagents used include n-hexane, hydrochloric acid (purity 33%), and methanol Merck (purity 99.9%), sourced from PT. Kurniajaya, Surabaya.

- **Preparation of modified catalysts**

The modified heterogeneous catalysts used were zeolite and bentonite. For the preparation of zeolite catalyst, 100 g of natural zeolite powder was weighed and placed into a three-neck flask. Then, 400 mL of 0.5 M HCl solution was added until all the zeolite powder was submerged. The mixture was then heated to 100°C and stirred for 24 hours. Subsequently, the mixture was filtered, and the resulting zeolite solid was calcined for 4 hours at 550°C. The same procedure was carried out for bentonite.

- **Calophyllum inophyllum extraction**

The extraction process of dried Calophyllum inophyllum seeds was conducted to obtain calophyllum inophyllum using n-hexane solvent with a ratio of 1:4 (weight:volume). The extract was separated from the solvent mixture by distillation to obtain pure calophyllum inophyllum [31].

- **Analysis of free fatty acid content in calophyllum inophyllum**

A total of 10 g of calophyllum inophyllum was weighed and mixed with 25 mL of neutral 96% alcohol. The mixture was heated in a water bath until boiling, then cooled to room temperature and 2 drops of phenolphthalein indicator were added. This solution was then titrated using 0.1 N NaOH solution until it turned pink, and then the content of free fatty acids in the calophyllum inophyllum was calculated. This testing was also conducted on the oil resulting from the esterification process [31].

- **Esterification**

The esterification process aims to decrease the free fatty acid content by reacting calophyllum inophyllum with methanol at a molar ratio of 1:20 using a potent acid catalyst, specifically concentrated HCl. Calophyllum inophyllum is combined with 370 mL of methanol in a three-necked flask, and concentrated HCl, acting as the catalyst, is added at a quantity equivalent to 10% of the oil volume. The mixture undergoes a 2-hour reaction at 60°C. Upon completion of the reaction, the resulting methyl esters are separated from the mixture using a separating funnel, and the product is then analyzed to determine its free fatty acid level [32].

- **Transesterification**

The transesterification reaction is carried out by adding modified catalysts, namely zeolite and bentonite. The molar ratio used between calophyllum inophyllum and methanol is 1:6, with the catalyst amounting to 10% of the oil's weight. In this study, 100 mL of calophyllum inophyllum resulting from esterification is placed in a three-necked flask and mixed with 24.3 mL of methanol and 10% of the weight of modified zeolite or bentonite catalyst. The mixture is then stirred using a magnetic stirrer, and the reaction takes place for 5 hours at various temperatures, namely 50, 60, 65, and 70°C. After the reaction is completed, the mixture is filtered using a Buchner funnel to separate the catalyst from the biodiesel and glycerol mixture. The biodiesel and glycerol are then separated using a separating funnel. The resulting biodiesel is subsequently dried in a rotary evaporator to remove its water content. The yield and characteristics of the resulting biodiesel are then calculated.

- **Characterization of biodiesel and catalyst**

The biodiesel product obtained is subjected to characterization testing under conditions of maximum biodiesel yield, following SNI parameters, including density, viscosity, flash point, cetane number, and methyl ester content. Density testing is performed using a pycnometer, viscosity testing with a Brookfield

Viscometer spindle no.21 at 100 rpm, flash point with a Pensky Marten Closed Tester according to ASTM D93, cetane number with a Cetane Number Tester GD-R3035 following ASTM D613 and D6887, while the methyl ester content is analyzed using Gas Chromatography (GC). These tests are conducted at the Pertamina laboratory in Jagir, Surabaya. The characterization of modified zeolite and bentonite catalysts includes X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) tests conducted at the Energy Laboratory, Sepuluh Nopember Institute of Technology, Surabaya. XRD testing utilizes a Philips X-pert with an X-ray diffractometer at 30 kV and 15 mA, while FTIR employs an Invenio-Bruker Corp. spectrometer.

4. RESULTS AND DISCUSSIONS

4.1 Calophyllum inophyllum analysis

The extracted calophyllum inophyllum used as the raw material for biodiesel production exhibits characteristics as shown in Table 3.

Table 3. Calophyllum inophyllum characteristics

Parameter	Unit	Value
Density	g/cm ³	0,92
Kinematic viscosity	cP (on 25,6 °C)	98
Free fatty acid	(%)	26,27

The calophyllum inophyllum does not meet the criteria as a raw material for biodiesel production because its free fatty acid content exceeds 2%. Therefore, an esterification process is required for the calophyllum inophyllum to meet the criteria as a raw material for biodiesel production, which is to reduce the free fatty acid content to the appropriate range for transesterification in biodiesel production. The requirement for oil to be used as a biodiesel feedstock is to have a maximum free fatty acid content of 2% [32].

Table 4 below presents the charactéristis of calophyllum inophyllum after undergoing the esterification process. From the results of the esterification stage conducted on the calophyllum inophyllum, a decrease in the free fatty acid content to 1.71% was obtained. Therefore, the calophyllum inophyllum resulting from the esterification process can be used as a raw material for biodiesel production to be further processed by transesterification.

Table 4. Calophyllum inophyllum after esterification

Parameter	Unit	Value
Density	g/cm ³	0,90
Kinematic viscosity	cP (on 25,6 °C)	45
Free fatty acid	%	1,71

4.2 Modified catalysts characteristics

The modified catalysts were analyzed using X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) for characterization. XRD was employed to identify the Si/Al (Silica/Aluminum) compound content in both catalyst types. The XRD characterization results are depicted in the figure below.

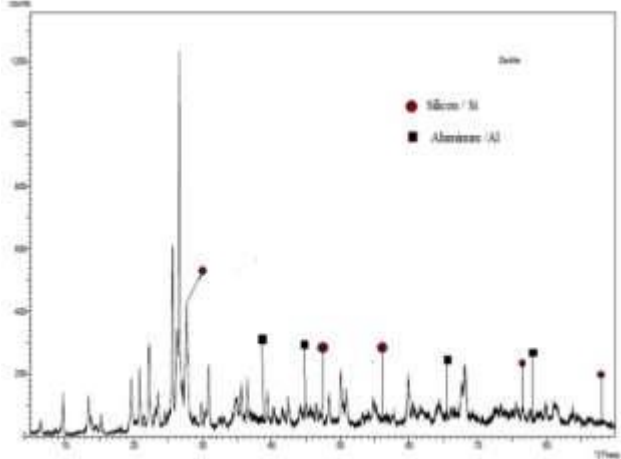


Figure 3. XRD results of natural zeolite

Figures 3 and 4 depict the XRD analysis results for natural zeolite and after modification with acid, respectively.

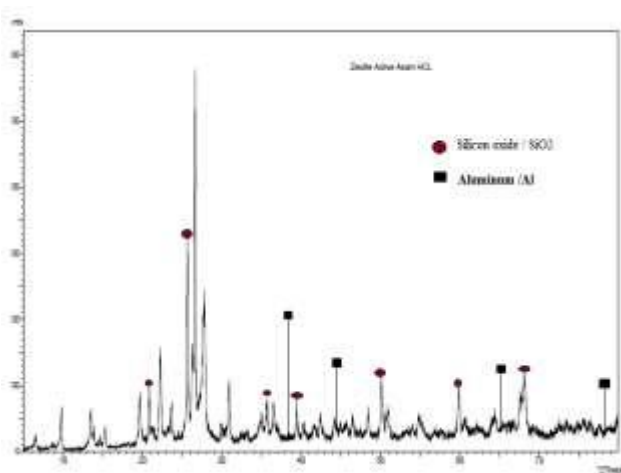


Figure 4. XRD results of modified zeolite

Subsequently, Figures 5 and 6 show the XRD analysis results for natural bentonite and after modification with acid.

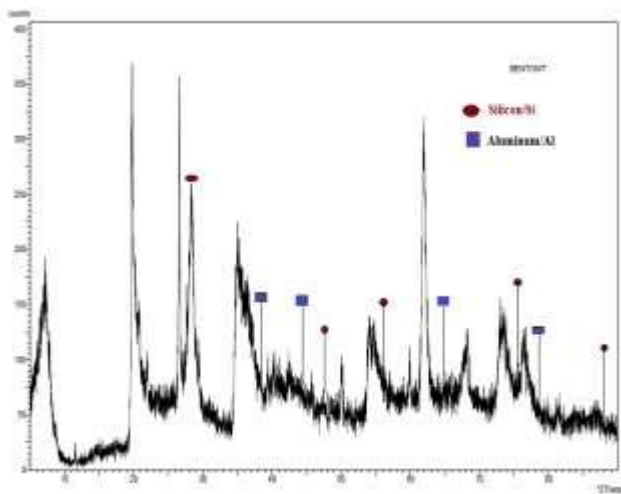


Figure 5. XRD results of natural bentonite.

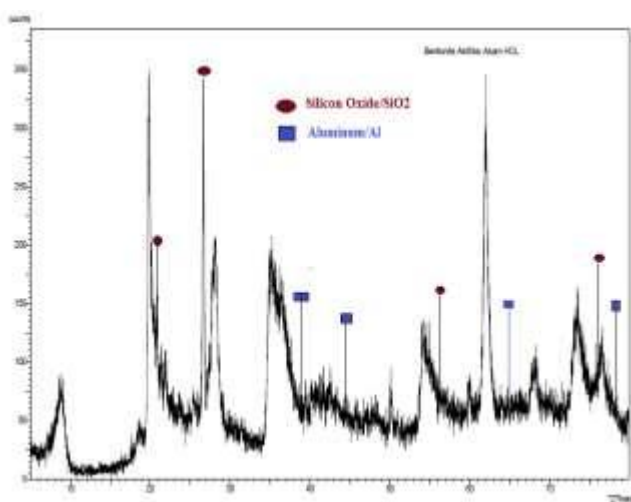


Figure 6. XRD results of modified bentonite

The XRD characterization analysis results indicate a change in the characteristics of both catalysts before and after modification. This can be observed in Figures 3 and 4 for Zeolite. A comparison of these two figures shows a change in the Si content, with more SiO₂ compound formed, while the Al compound decreases. This is consistent with the principle of catalyst activation with acid, which involves releasing Al atoms to optimize the aluminum content in the catalyst, thereby enhancing its catalytic properties and absorption.

A similar trend is evident in Figure 5 and Figure 6 regarding the bentonite catalyst, showing an augmentation in SiO₂ content following the modification process. However, the alterations resulting from the modification of both catalysts are not prominently observable due to the relatively low acid concentration utilized for the catalyst modification.

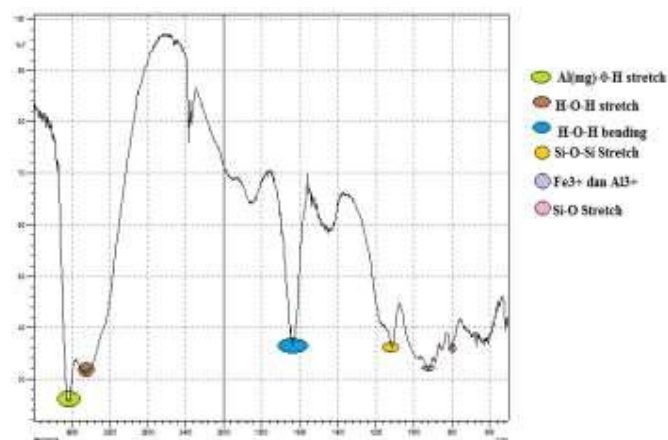


Figure 7. FTIR results of natural bentonite

Figures 7 and 8 depict the FTIR analysis results for natural bentonite and its modified form.

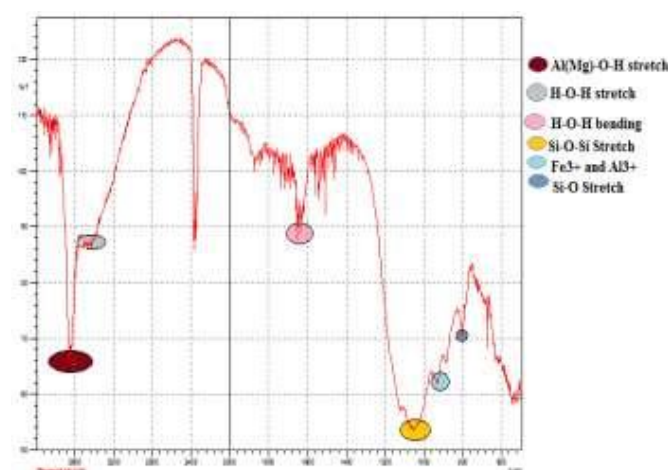


Figure 8. FTIR results of modified bentonite

Next, Figures 9 and 10 show the FTIR analysis results for natural zeolite and its modified form. Catalyst characterization with FTIR aims to identify the functional groups present in both types of catalysts before and after the acid modification process.

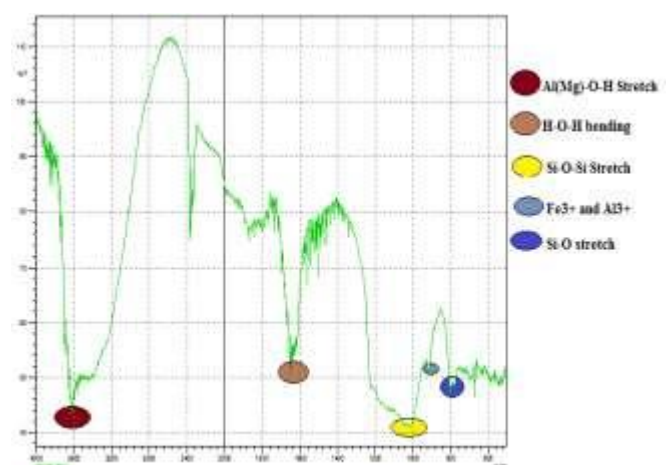


Figure 9. FTIR results of natural zeolit

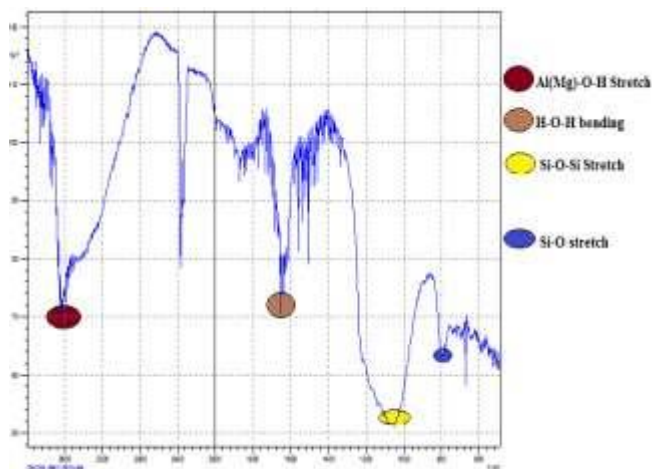


Figure 10. FTIR results of modified zeolite

Based on the FTIR analysis results, it is observed that no new functional groups are formed on the catalyst. Modification using acid causes an increase in bond strength, as indicated by the increase in transmittance percentage at certain wavelengths from the FTIR analysis results. However, this increase is not significantly visible due to the relatively low concentration of acid used.

4.3 The effect of reaction temperature on the yield of biodiesel production

The influence of reaction temperatures of 50, 60, 65, and 70°C on the yield of biodiesel produced using modified zeolite catalysts, modified bentonite, and a mixture of modified zeolite and bentonite in a 50:50 ratios is shown in Table 5.

Tabel 5. Biodiesel yield produced using modified catalysts

The type of catalyst and the ratio of catalyst amounts.	The yield of biodiesel based on reaction temperature.			
	50°C	60°C	65°C	70°C
Modified Zeolit (100:0)	78,36	88,19	83,19	81,15
Modified Bentonit (100:0)	67,73	78,84	72,09	70,58
Modified Zeolit and Bentonit (50:50)	70,83	82,36	75,49	73,11

Based on the data, it appears that increasing the transesterification reaction temperature from 50°C to 60°C leads to an increase in the yield of biodiesel. However, further increases in the transesterification reaction temperature above 60°C to 70°C result in a decrease in biodiesel yield.

At a temperature of 60°C, the highest yield of biodiesel was obtained for the three types of catalysts used. The highest biodiesel yield achieved was 88.19% with modified zeolite catalyst, 78.84% with modified bentonite catalyst, and 82.36% with a mixture of modified zeolite and modified bentonite catalysts in a 1:1 ratio.

4.4 The influence of modified catalyst type on the yield of biodiesel production.

The experiment results indicate that the type of modified catalyst used in the transesterification process influences the yield of biodiesel obtained, as shown in Table 5. The use of modified zeolite catalysts yields a greater amount of biodiesel compared to modified bentonite catalysts and a mixture of modified zeolite and bentonite at a 50:50 ratio. This trend is observed across various transesterification reaction temperatures ranging from 50, 60, 65, to 70°C. This phenomenon occurs due to the differences in properties and characteristics among the three types of modified catalysts used in the transesterification process.

One distinguishing feature of zeolite, functioning as an adsorbent, is its expansive surface area and micro-sized pores. Bentonite, another adsorbent, possesses a surface area smaller than zeolite, with macro-sized pores. These qualities play a crucial role in the transesterification reaction, especially since the oil used often contains high levels of fatty acids due to its elevated water content. Zeolite's adsorbent nature significantly aids in water absorption during the transesterification process, leading to a higher biodiesel yield compared to bentonite. This aspect underscores bentonite's drawback, resulting in its comparatively lesser influence on biodiesel yield when compared to zeolite catalysts.

4.5 The analysis results of biodiesel characteristics at the highest yield.

The biodiesel produced under conditions yielding the highest output is analyzed for its characteristics according to the Indonesian National Standard (SNI) requirements for biodiesel. The parameters include density, viscosity, flash point, cetane number, and methyl ester content analysis using GC, as shown in Table 6.

Table 6. The characteristics of the biodiesel produced at the highest yield using modified zeolite catalyst at a reaction temperature of 60°C.

Parameter	Test results	SNI
Flash point, °C	121	Min 100
Viscosity, mm ² /s	5,633	2,3-6
Density, kg/m ³	887	850-887
Cetane number	53	Min 51

Density testing is performed to ascertain its compliance with biodiesel standards and is juxtaposed against the SNI benchmark. The analysis reveals a density of 0.887 g/cm³ (887 kg/m³). The SNI specifies a density range for biodiesel of 850-887 kg/m³, confirming that the biodiesel derived from this study aligns with SNI regulations for biodiesel products.

The viscosity of the produced biodiesel is analyzed to ensure its compliance with the criteria for being declared as methyl ester according to the SNI standards. The viscosity of a fuel affects flow profile, atomization, and lubrication effectiveness. The analysis results indicate that the viscosity of the biodiesel obtained at a measurement temperature of 40°C is 5.633 mm²/s, while the benchmark according to the SNI standards ranges from 2.3 to 6.0 mm²/s. Therefore, the biodiesel product meets the SNI standards.

The next test is the cetane number, which is essential because it indicates the diesel engine fuel's spontaneity to combust

after being injected into the combustion chamber [27]. The cetane number obtained for biodiesel from *Calophyllum inophyllum* is 53, while the SNI parameter for biodiesel cetane number is a minimum of 51. Hence, the biodiesel product meets the SNI requirements.

The flash point test on biodiesel is conducted to determine its ignition temperature when applied as fuel. A high flash point makes fuel storage easier as it is less prone to ignite at room temperature [27]. The test results indicate that the biodiesel derived from *Calophyllum inophyllum* under conditions yielding the highest output has a flash point of 121°C. The test results show that the biodiesel product meets the SNI criteria, which stipulates a minimum flash point of 100°C.

Another test is to measure the methyl ester content in biodiesel. This test is conducted to determine the amount of fatty acids converted into methyl esters. Methyl ester analysis is carried out using a GC instrument [27]. The result of the methyl ester content analysis for biodiesel produced from *calophyllum inophyllum* is 94.55%.

5. CONCLUSION

The study indicates that *Calophyllum inophyllum* oil can effectively be transformed into biodiesel through esterification and transesterification processes using modified zeolite and bentonite catalysts. The biodiesel yield achieved with these modified catalysts is 88.19%, matching that of biodiesel produced with acid and base catalysts, which is 88.27%. The advantage of using these modified catalysts is their easy separation and ability to be reused in the biodiesel production process, making them eco-friendly. In contrast, traditional acid-base catalysts are difficult to separate and cannot be reused, resulting in industrial waste that requires management. The use of modified catalysts offers potential for advancing biodiesel science and industry by reducing waste and lowering separation costs in the future. The resulting biodiesel meets the specifications outlined by the Indonesian National Standard (SNI), confirming its viability as a renewable fuel option. Recommendations for further research include exploring biodiesel production from other non-edible oils and testing catalysts derived from other environmentally friendly natural materials to improve biodiesel yield.

ACKNOWLEDGMENT

This work is supported by the Directorate of Research and Community Service, Directorate General of Higher Education, Ministry of Research and Technology, Republic of Indonesia, for funding this research through the Competency-Based Research (PBK) Grant in the fiscal year 2019 based on Contract No. 011/SP2H/AMD/LT/MULTI/L7/2019.

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2. First revision: Accepted (17-08-2024)



D.N. Dian Retno Sari Dewi P. , ST., MT. <dianretnosd@ukwms.ac.id>

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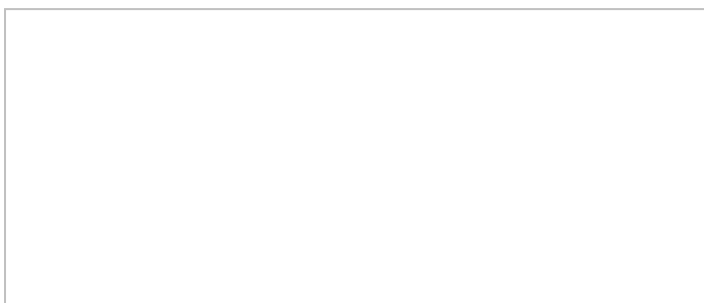
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Review Comments Regarding ACSM 28394

1. Comprehensiveness and Modernity of Literature Review

The literature review on the use of modified zeolite and bentonite as biodiesel catalysts seems incomplete. The authors are advised to reference and incorporate more recent studies, especially from the last five years concerning innovations in solid material science and biodiesel catalysts. This will enhance the modernity and relevance of the research.

2. Experimental Design and Methodology

The current description of the experimental design lacks detail in some critical parameters, such as the specific methods and conditions for catalyst modification. Detailed experimental conditions are crucial for the reproducibility of the results.

3. Interpretation and Data Analysis of Results

Although the study provides biodiesel yield data using different catalysts, there is a lack of detailed scientific explanation behind the data. For example, analyses on how modified zeolite and bentonite affect the reaction mechanism and yields are missing. Add more discussion on the relationship between the catalyst's surface characteristics and its reactivity, possibly including the catalyst's surface acidity, pore structure, and their specific impacts on the reaction.

4. Innovation and Contribution

Comment: The paper has some innovative aspects in using modified zeolite and bentonite as catalysts, but the description of its unique contributions is not highlighted enough. Clearly point out the innovations in the field of solid material science, such as unique catalyst modification methods or new application mechanisms, and how these innovations advance biodiesel technology.

5. Sustainability and Environmental Impact

Although the paper emphasizes the environmental benefits of biodiesel, there is insufficient discussion on the environmental impacts of catalyst production and usage. Include results from a Life Cycle Analysis (LCA) of the catalysts, discussing the energy consumption and environmental emissions during their production and use, and how these processes can be optimized to reduce environmental impacts.

6. Depth and Prospective of Conclusions

The conclusion section is currently simplistic and lacks in-depth discussion on future research directions. Enhance the conclusions with discussions on potential future research directions, such as further optimization of the catalysts, possibilities for scale-up applications, and the technical and economic challenges involved.

I hope my comments will be helpful in your research.

Dear Author,

I have reviewed the manuscript carefully focusing on the cutting-edge innovations in solid material science. I have the following comments from at least 6 perspectives:

- Introduction

1. The introduction should highlight the most recent advances that motivate this work to better frame its significance.
2. A brief critique of limitations of existing biodiesel production methods is needed to establish knowledge gaps.

- Catalyst Design

1. More details are required on the specific activation mechanisms in modifying the zeolite and bentonite catalysts.
2. Advanced characterization techniques like XPS could provide insights into changes in surface chemistry after modification.
3. The effect of varying acid concentration for catalyst modification should be analyzed.

- Biodiesel Analysis

1. The fuel properties of the produced biodiesel should be benchmarked against state-of-the-art biofuels to highlight advantages.
2. A comparison of combustion performance and emissions with petroleum diesel is needed through engine testing.
3. An evaluation of long-term storage stability can ascertain biodiesel quality over time.

- Process Optimization

1. Statistical design of experiments could identify optimal parameters like catalyst loading, temperature, etc. for maximum yield.
2. Techno-economic analysis and life cycle assessment can determine process viability and environmental impact.

- Commercialization Potential

1. Scalability of the proposed method should be analyzed considering practical limitations and requirements.
2. Design of portable mini-reactors suited for on-site biodiesel generation could aid adoption.

- Alternative Feedstocks

Applicability of the method for other non-edible oils besides *Calophyllum inophyllum* should be explored.

I hope these suggestions help strengthen your manuscript. Please feel free to contact me if you need any clarification. Wish you the very best!

3. Revised version received (04-09-2024)

- Revisions and Amends

- Revised version



D.N. Dian Retno Sari Dewi P. , ST., MT. <dianretnosd@ukwms.ac.id>

Fwd: Revision Results ACSM 28394

Herman ., ST., MT. <herman@ukwms.ac.id>
To: dianretnosd@ukwms.ac.id

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Aning Ayucitra : 0000-0002-6838-9396

Nyoman Puspa Asri : [0000-0003-2779-6195](https://orcid.org/0000-0003-2779-6195)

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Department of Chemical Engineering

Widya Mandala Surabaya Catholic University

Kalijudan 37 Surabaya 60114 Indonesia

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Biodiesel synthesis from calophyllum inophyllum utilizing modified zeolite and bentonite catalysts

Herman Hindarso^{1*}, Aning Ayucitra², Dian Retno Sari Dewi³, Nyoman Puspa Asri⁴

^{1,2} Department of Chemical Engineering, Widya Mandala Catholic University, Kalijudan 37, Indonesia

³ Department of Industrial Engineering, Widya Mandala Catholic University, Kalijudan 37, Indonesia

⁴ Department of Food Technology, Ciputra University, Citraland CBD Boulevard, Indonesia

Corresponding Author Email: herman@ukwms.ac.id

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<https://doi.org/10.18280/acsm.xxxxxx>

ABSTRACT

Received:

Revised:

Accepted:

Available online:

Keywords:

Calophyllum inophyllum oil;
Transesterification; Modified zeolite;
Modified bentonite; Biodiesel

Biodiesel serves as a renewable, eco-friendly alternative fuel. Its production relies on converting triglyceride sources into methyl esters through transesterification. These triglycerides can be sourced from vegetable oils and animal fats. Previous studies often relied on acids and bases as catalysts. However, there's a lack of research exploring the use of modified zeolite and bentonite as catalysts, which hold the promise of higher yields compared to previous studies. In this study, biodiesel was derived from calophyllum inophyllum via esterification and transesterification processes. Characterization of these catalysts was done using XRD and FTIR analyses. Transesterification to produce biodiesel occurred at temperatures ranging from 50 to 70°C over a reaction period of 5 hours. The largest yield of biodiesel was obtained at 60°C, with 88.19% using modified zeolite catalyst, 78.84% using modified bentonite catalyst, and 82.36% using a blend of modified zeolite and bentonite catalysts in a 1:1 ratio. Biodiesel resulting from the highest yield using modified zeolite catalyst underwent characteristic testing in accordance with SNI standards. The findings revealed a density of 887 kg/m³, viscosity of 5.633 mm²/s, cetane number of 53, flash point at 121°C, and methyl ester content of 94.55%.

1. INTRODUCTION

At present, the reserves of fossil fuels like crude oil, coal, and natural gas are dwindling due to escalating usage and their non-renewable nature [1]. Consequently, there is a pressing need for the development of alternative and renewable fuel sources [2]. Indonesia, as a nation, boasts a diverse range of natural resources, encompassing both renewable and non-renewable ones.

The demand for crude oil as the world's primary fuel source is substantial. However, this demand is not accompanied by an awareness that the combustion of processed crude oil products such as gasoline, diesel, and others has negative impacts on the environment and tends to harm the Earth in the long term [3]. The adverse effects of excessive fossil fuel usage include climate change due to global warming, often referred to as global warming [4–6].

Nowadays, the ongoing and swift consumption of crude oil as a fuel is leading to its diminishing reserves. Therefore, there is a demand for alternative energy sources and fuels that can evolve and hold promise for the future [4]. Biodiesel is a renewable alternative fuel for diesel engines derived from renewable sources such as vegetable oil, animal fats, and algae [7]. It exhibits combustion properties remarkably similar to

diesel fuel, hence holds potential for substituting petroleum diesel [8–11].

Calophyllum inophyllum, a thick brown-colored vegetable oil with a strong caramel-like scent [12], finds various uses among farmers in Kebumen and Cilacap, Central Java, Indonesia. It serves as a coating for roof tiles, aids in batik making, and is utilized in embalming [13]. In West Java, some fishermen rely on calophyllum inophyllum as a fuel for their boats during maritime activities [14]. This oil is rich in unsaturated fatty acids, notably oleic acid, and contains unsaponifiable components like fatty alcohols, sterols, xanthenes, coumarin derivatives, phytols, isophytols, isophthalates, capillary acids, pseudobasilic acid, and triterpenoid compounds, ranging from 0.5% to 2%, which possess medicinal properties [13].

Advantages of using Calophyllum inophyllum as a source of biofuel include its high oil content (up to 74%), its non-competition with food production and its availability is abundant in tropical countries like Indonesia [15]. Calophyllum inophyllum offers various benefits for biodiesel production and development: it naturally grows abundantly across Indonesia, easily regenerates, and bears fruit throughout the year, indicating its resilience to environmental conditions. It can be cultivated with ease either in single-crop fields or mixed forests and thrives in dry climates [16]. Nearly all parts

of the calophyllum inophyllum plant are valuable, yielding various economically significant products. Using calophyllum inophyllum biofuel can also help reduce deforestation for firewood, given its high seed productivity compared to other plants [13].

Biodiesel derived from calophyllum inophyllum also offers advantages, including its comparatively high oil yield (40-73%) when compared to other plants like jatropha and palm oil [17]. Some quality parameters already meet Indonesian standards, and calophyllum inophyllum burns twice as long as kerosene. Additionally, it holds future potential as a blending component. Compared to fossil fuels, biodiesel has several benefits, such as renewability, higher energy efficiency, emissions reduction, and the possibility of using it as a complete diesel substitute with advanced processing technology [18]. It also offers better emission quality than diesel and can serve as a bio-kerosene alternative [19].

Recent developments in biodiesel production from nyamplung oil (Calophyllum inophyllum) have advanced in several areas, including improved processing technology, the use of more efficient and eco-friendly catalysts, and better purification methods. Future progress is expected to focus on further reducing production costs through innovations and optimizations in the production process, as well as the introduction of new, more cost-effective and efficient catalysts. The importance of producing biodiesel from nyamplung oil lies in diversifying energy sources, fostering local economic growth, benefiting the environment, and providing a sustainable renewable energy option. Energy diversification is achieved by utilizing nyamplung oil as a feedstock for biodiesel, offering an alternative renewable energy source, decreasing reliance on fossil fuels, and strengthening energy security [15].

Local economic development is facilitated by the creation of economic opportunities, such as jobs for farmers and communities in tropical regions, through the planting and cultivation of nyamplung trees, which in turn boosts community income. Environmentally, biodiesel produced from nyamplung oil offers the advantage of reducing greenhouse gas emissions when compared to fossil fuels. Moreover, cultivating nyamplung trees can enhance soil quality and aid in carbon absorption. Nyamplung is a renewable and sustainable energy source, as it is a non-food plant that is easy to cultivate, grows rapidly, and requires minimal operational costs [17, 18].

The rationale for this study lies in the limited utilization of calophyllum inophyllum oil, despite its considerable potential as a replacement for fossil fuels. Previous investigations commonly utilized acids and bases as catalysts, whereas there's limited research on employing modified zeolite and bentonite in calophyllum inophyllum oil production. Despite their potential for higher yields compared to acids and bases, these modified catalysts are rarely explored in prior studies. An additional advantage of modified heterogeneous catalysts is the ease of separating the catalyst after the reaction, enabling its reuse and preventing any waste generation from the catalyst. This differs from the biodiesel production process using acid-base catalysts, which produces waste acids and bases during the separation of biodiesel products from the leftover catalyst. Hence, our research identifies a gap in the extant research in utilizing modified zeolite and bentonite as promising catalysts for achieving greater yields. In addition to these factors, the use of modified zeolite and bentonite as catalysts for producing biodiesel from nyamplung oil offers various

innovative aspects that can enhance the efficiency and sustainability of the process. Here are some of the innovative aspects of this approach. [15, 17-19] :

1. Use of Nature-Based Materials
 - Zeolite: Zeolite is a natural mineral with an excellent porous structure, allowing it to function as a catalyst with high absorption and selectivity capabilities. By modifying zeolite, we can enhance its catalytic activity in the transesterification of nyamplung oil.
 - Bentonite: Bentonite is a clay rich in montmorillonite, which can be modified to improve its catalytic properties. This modification often involves changes to the surface structure or the addition of active materials.
2. Catalyst Modification
 - Metal Addition: Modifying zeolite and bentonite with transition metals or other active metals can enhance their catalytic capabilities for the transesterification reaction. These metals can act as active centers for the chemical reaction.
 - Enhancing Acid/Base Properties: Chemical or physical modifications to zeolite and bentonite can improve the acid or base properties of the catalyst, which are crucial for speeding up the transesterification process.
3. Energy Efficiency
 - Low-Temperature Reaction Process: By using modified catalysts, the transesterification process of nyamplung oil can be carried out at lower temperatures compared to conventional catalysts, reducing energy consumption and operational costs.
 - Reusable Catalysts: Modified zeolite and bentonite generally exhibit good stability and can be reused across multiple reaction cycles without significant loss of catalytic activity.
4. Use of Renewable Resources
 - Nyamplung Oil: Nyamplung oil is a renewable raw material, and utilizing modified zeolite and bentonite-based catalysts supports an environmentally friendly biodiesel production process.
5. Improvement in Biodiesel Quality
 - Purification and Product Quality: Modified catalysts can enhance the conversion of oil into biodiesel, resulting in higher quality biodiesel, including improved purity and physical characteristics that meet standards.
6. Waste Reduction
 - Minimized By-Products: The use of efficient catalysts can reduce the amount of by-products and waste, making the process cleaner and more environmentally friendly.
7. Availability and Cost
 - Affordable Catalysts: Zeolite and bentonite are relatively inexpensive materials that are abundantly available in Indonesia, so modifying them for use as catalysts in biodiesel production can reduce raw material and operational costs.
8. Adaptive Catalyst Design
 - Customizable Catalysts: Modifying zeolite and bentonite allows for adjustments to meet specific needs in the transesterification process, such as tailoring pore size or surface properties to enhance reactivity with nyamplung oil.

Overall, the innovation in using modified zeolite and bentonite as catalysts for producing biodiesel from nyamplung oil offers great potential to enhance process efficiency, reduce costs, and support sustainability in biodiesel production [17, 18]. The modification of zeolite and bentonite for catalytic applications in biodiesel production involves several unique and innovative aspects that can provide significant benefits for the advancement of biodiesel production technology. Here is a description of the uniqueness of these modifications, their application mechanisms, and innovations.

Uniqueness of Zeolite and Bentonite Modifications

1. Porous Structure and Catalytic Properties

- Zeolite: Zeolite features a crystalline structure with regular pores and specific pore sizes, allowing it to act as a catalyst with high absorption capacity and good reaction selectivity. Modifying zeolite can enhance its acid or base properties, increase pore size, or add active metals to accelerate transesterification reactions.
- Bentonite: Bentonite is a clay with a laminar structure providing a large surface area for chemical interactions. Modifications typically involve changes in chemical composition or the addition of active materials to improve catalytic capacity [12–14].

2. Chemical and Physical Modifications

- Zeolite: Chemical modifications, such as ion exchange and the addition of transition or other active metals, can enhance catalytic properties. Zeolites modified with active metals (e.g., Cu, Ni) can improve catalytic activity in transesterification reactions.
- Bentonite: Modifications may include altering the structure or surface properties by adding activating agents or using techniques like filtering or precipitation to change acid/base properties and enhance catalytic activity [13, 14, 17].

Mechanisms of Catalyst Modification with Hydrochloric Acid

Specific Activation of Zeolite and Bentonite Catalysts Using Hydrochloric Acid (HCl) The modification of zeolite and bentonite catalysts with hydrochloric acid aims to improve the catalytic properties of these materials through several key mechanisms:

1. Removal of Impurity Cations

- Mechanism: HCl interacts with alkali or alkaline earth metal cations trapped in the structure of zeolite or bentonite. These cations include sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}).
- Reaction: HCl ionizes and releases H^+ ions, which replace the cations in the material's structure, resulting in the release of these cations as dissolved chlorides (e.g., NaCl, KCl).
- Outcome: This process enhances the acidity of active sites in zeolite or bentonite and improves their catalytic activity.

2. Dealumination

- Mechanism: Dealumination is the removal of aluminum (Al) from the crystalline framework of zeolite or bentonite. Under certain conditions, H^+ ions from HCl can attack and extract Al^{3+} from the framework, which is then carried away as AlCl_3 or related compounds.
- Reaction: The process can be described by the reaction: $\text{Al-O-Si} + 3\text{H}^+ \rightarrow \text{H-O-Si} + \text{Al}^{3+}$, where the released Al^{3+} forms complexes with Cl^- ions from HCl.
- Outcome: Removal of aluminum increases the number of Bronsted acid sites on the material's surface, enhancing acid properties and catalytic ability, particularly for reactions requiring high acidity.

3. Increased Surface Area

- Mechanism: HCl can remove amorphous material or unstructured components covering the pore surfaces of zeolite or bentonite. This process opens up more access to active sites within the material's pores.
- Reaction: HCl dissolves metal oxides or other unstructured components that might obstruct the pores.
- Outcome: The specific surface area of the material increases, enhancing its ability to act as a catalyst.

4. Modification of Crystal Structure

- Mechanism: Under certain conditions, acid treatment can cause changes in the crystal structure of zeolite or bentonite, such as in pore size or distribution.
- Reaction: This can occur through delamination or recrystallization due to the high acidity of HCl.
- Outcome: These changes can produce materials with an optimal structure for specific catalytic applications, such as cracking or isomerization.

5. Removal of Organic Impurities

- Mechanism: HCl can also help remove organic impurities present in zeolite or bentonite, which might affect catalytic efficiency.
- Reaction: HCl reacts with organic compounds, especially if they are basic, forming salts that dissolve in the acid solution.
- Outcome: Removal of these impurities improves catalyst activity by preventing blockage of active sites.

Based on the above description, modifying zeolite and bentonite with hydrochloric acid significantly enhances acidity, surface area, and catalytic activity, making them more effective for various catalytic applications [12, 15, 17–19]. Variations in HCl concentration during modification significantly affect the physical and chemical properties of the resulting catalysts. Factors influenced by HCl concentration include acidity, structural stability, surface area, adsorption capacity, and overall catalytic properties. Low concentrations of HCl moderately increase acidity without damaging the

structure, while higher concentrations significantly enhance acidity and surface area but risk damaging the material's structure. Therefore, optimizing HCl concentration is necessary to balance increased acidity with structural stability for specific catalytic applications. The optimal HCl concentration for modifying zeolite is typically between 0.1 M and 2 M, while for bentonite, it ranges from 0.5 M to 3 M. Adjustments should consider material type, modification goals, and treatment conditions (time and temperature) to balance catalytic activity enhancement with maintaining material structural stability. In this study, zeolite and bentonite were modified using a 0.5 M HCl solution, which represents the optimum concentration for modifying both zeolite and bentonite.

Modification Application Mechanisms

1. Modification Processes
 - Zeolite:
 - Ion Exchange: This process replaces sodium ions in zeolite with active metal ions such as K^+ , Ca^{2+} , or other transition metals to enhance catalytic activity.
 - Metal Impregnation: Involves adding active metals to zeolite, which can improve catalytic capability for specific reactions.
 - Bentonite:
 - Addition of Catalytic Agents: Adding active materials such as metals or acids/bases to the surface of bentonite to improve catalytic activity.
 - Activation or Treatment: Methods like heating or using chemicals to alter the surface properties of bentonite, enhancing its catalytic ability [16–18].
2. Application in Biodiesel Production
 - Transesterification: Modified zeolite and bentonite are used in the transesterification process to convert nyamplung oil into biodiesel. These catalysts help accelerate the reaction between triglycerides and methanol or ethanol, producing methyl or ethyl esters (biodiesel) and glycerol.
 - Batch and Continuous Processes: Modified catalysts can be applied in both batch and continuous processes. They can be adapted for different reactor types, such as flow reactors or batch reactors [17–19].

Innovations for Technological Advancement

1. Energy Efficiency and Cost
 - Low-Temperature Processes: Modified catalysts enable reactions to occur at lower temperatures, reducing energy consumption and operational costs.
 - Recovery and Reusability: Modified catalysts generally have good durability and can be reused across multiple reaction cycles, reducing the need for new materials and lowering production costs [17–19].
2. Improved Biodiesel Quality

- Purification: Modified catalysts enhance the conversion of oil to biodiesel, resulting in high-quality biodiesel that meets stringent quality standards [13, 14].
- 3. Waste Reduction and Environmental Impact
 - Minimized By-Products: Efficient catalysts reduce the amount of by-products and waste, making the process cleaner and more environmentally friendly.
- 4. Adaptation for Various Feedstocks
 - Flexibility: Modifications to zeolite and bentonite allow adaptation to various types of feedstocks, not just nyamplung oil but also other vegetable oils, expanding the technology's application and flexibility [14, 15].
- 5. Integrated Catalyst Design
 - Multi-Functional Catalysts: Development of catalysts with multifunctional capabilities, such as those that can perform multiple reactions simultaneously (e.g., transesterification and free fatty acid removal), improves process efficiency and reduces additional processing steps [18, 19].

Overall, modifying zeolite and bentonite for catalytic applications in biodiesel production offers significant advantages in efficiency, cost, and environmental impact. This innovative approach has the potential to drive technological progress in the biodiesel industry and enhance the sustainability of renewable energy production.

Life Cycle Assessment (LCA) Results for Zeolite and Bentonite Catalysts Modified with Acid

The Life Cycle Assessment (LCA) for zeolite and bentonite catalysts modified with acid involves a thorough evaluation of environmental impact, energy consumption, and emissions throughout the entire life cycle of these catalysts. Below are the analysis and strategies to optimize the process to reduce environmental impact:

1. Energy Consumption
 - a. Production Stage
 - Extraction and Processing of Raw Materials: The energy required to mine and process zeolite and bentonite includes activities such as drilling, grinding, and drying. These activities require significant energy consumption.
 - Acid Modification: The acid modification process, including heating and chemical use, requires additional energy. Chemical reactions and separation processes also contribute to energy consumption.
 - b. Usage Stage
 - Catalyst Activation: If catalysts need to be activated before use, for example through heating, this also adds to energy consumption. However, this stage is usually lower compared to production.
 - Process Efficiency: Efficient catalysts allow biodiesel transesterification to occur at lower temperatures, reducing energy requirements in biodiesel production.
 - c. Optimization Strategies

- Energy Efficiency: Apply energy-efficient technologies in the modification and activation processes, such as using high-efficiency heaters or heat recovery systems.
 - Renewable Energy Use: Consider using renewable energy sources, such as solar or geothermal energy, in the production and modification processes [15–17].
2. Environmental Impact
- a. Production Stage
- Chemical Use: Acid modification involves chemicals that can potentially be hazardous. Proper handling and effective waste management methods are needed to minimize environmental impact.
 - Environmental Degradation: Mining and processing raw materials can cause environmental damage such as habitat disruption and soil or water pollution.
- b. Usage Stage
- Catalyst Efficiency: More efficient catalysts reduce the amount of raw materials needed and decrease by-product production, which positively impacts the environment.
 - Recycling and Reuse: Catalysts that can be recycled or reused reduce waste and the environmental impact of biodiesel production.
- c. Optimization Strategies
- Green Chemistry: Use less hazardous acids and chemicals in the modification process. Develop effective waste management solutions.
 - Sustainable Mining Practices: Implement environmentally friendly mining practices to reduce the environmental impact of raw material extraction [13–15, 17].
3. Emissions
- a. Production Stage
- Air Emissions: The acid modification process can produce emissions such as volatile organic compounds (VOCs) and hazardous gases. Effective emission control and ventilation systems are required.
 - Water Pollution: The use of acids and other chemicals can generate liquid waste that needs treatment to prevent pollution.
- b. Usage Stage
- Emissions During Use: Efficient catalysts produce fewer emissions during the biodiesel production process compared to conventional catalysts.
- c. Optimization Strategies
- Emission Control: Implement effective emission control technologies to capture and treat gases and pollutants from the production process.
 - Waste Treatment: Apply efficient waste treatment systems to manage liquid and solid waste from the modification process [13, 15–18].
4. Overall Process Optimization
- a. Environmentally Conscious Design
- Sustainable Catalyst Design: Design catalysts with a focus on efficiency, durability, and recyclability. Choose materials and processes that minimize environmental impact.
 - Recyclability: Ensure that catalysts can be recycled or reused efficiently to reduce waste.
- b. Ongoing Evaluation and Improvement
- Periodic Assessment: Conduct Life Cycle Assessments (LCA) regularly to identify areas for improvement in the catalyst life cycle.
 - Technological Innovation: Invest in research and development to create cleaner and more efficient modification and production processes.
- c. Stakeholder Engagement
- Collaboration: Work with stakeholders such as suppliers, customers, and regulators to promote environmentally friendly practices and sustainability in catalyst production [17–20].

By implementing these strategies, the environmental impact of producing and using zeolite and bentonite catalysts modified with acids can be minimized, contributing to a more sustainable and environmentally friendly biodiesel production process.

2. LITERATURE REVIEW

Calophyllum inophyllum can be obtained through several stages of processing [9].

1. Peeling the seeds from their hard shells.
2. Slicing them thinly.
3. Sun-drying for two days.
4. Crushing and steaming for 2 hours.
5. Pressing with a manual hydraulic machine or extruder, resulting in dark-colored oil due to impurities from the skin and chemical compounds like alkaloids, phosphatides, carotenoids, chlorophyll, and others. Pressing 2.5 kg of dried seed material without skins yields 1 liter of calophyllum inophyllum oil.
6. Removal of latex, which involves separating latex and impurities from the oil using a 1% phosphoric acid solution.
7. Filtration, which separates oil from impurities to obtain clear oil.

The characteristics of calophyllum inophyllum before and after latex removal are shown in Table 1 [20].

Tabel 1. The physical and chemical properties of calophyllum inophyllum oil

Parameter		Before latex removal	After latex removal
Mositure	content	0,25	0,41
Density	20 °C (g/mL)	0,944	0,940
Viscosity	(cP)	56,7	53,4
Acid number	(mg KOH/g)	198,1	194,7

Parameter	Before latex removal	After latex removal
Iod number	86,42	85,04
Refraktif index	1,447	1,478
Appearance	Dark green, thick, and pungent odor	Thick reddish-yellow

The composition of fatty acids constituting calophyllum inophyllum can be seen in Table 2 [21].

Table 2. The fatty acid composition of calophyllum inophyllum oil

Fatty acid	Composition
Palmitoleat acid (C16:1)	0,5 – 1 %
Palmitat acid (C16)	15 – 17 %
Oleat acid (C18:1)	30 – 50 %
Linoleat acid (C18:0)	25 – 40 %
Stearat acid (C18:0)	8 – 16 %
Arachidat acid (C20)	0,5 – 1 %
Gadoleat acid (C19:1)	0,5 – 1 %

The free fatty acid content of calophyllum inophyllum before latex removal is very high. This is due to the fact that calophyllum inophyllum comes from seeds that have aged, where the oxidation process of the oil has already begun while they are still in seed form. Through the latex removal process, the free fatty acid content will decrease, as will the values of several other parameters [22].

The decline in viscosity and density values occurs because of the elimination of latex and impurities from the oil solution. The drop in saponification number is due to the introduction of phosphoric acid, while the decrease in iodine number is linked to the reduction in the quantity of unsaturated fatty acids resulting from the latex removal process. The outcome of the latex removal process manifests in a distinct color change of the oil, transitioning from dark green to shades of yellow and red.

After the latex removal process, calophyllum inophyllum undergoes further processing, such as neutralization with NaOH, to transform it into biokerosene, which serves as a substitute for kerosene oil and is highly beneficial for heating purposes in rural communities [23]. As a fuel, it is evident that calophyllum inophyllum exhibits a longer burning duration compared to kerosene oil, as experiments show that 1 ml of calophyllum inophyllum burns for 11.8 minutes, while 1 ml of kerosene oil burns for only 5.6 minutes. Furthermore, during water boiling tests, it was found that 0.9 mL of kerosene oil was required, whereas only 0.4 mL of calophyllum inophyllum was needed. These results indicate that calophyllum inophyllum can be utilized as a household fuel source, providing significant benefits for daily use by communities.

Calophyllum inophyllum falls into the category of oils containing a mixture of saturated and unsaturated fatty acids with lengthy carbon chains. Its main components consist of

oleic acid at 37.57%, linoleic acid at 26.33%, and stearic acid at 19.96%. The remainder includes myristic acid, palmitic acid, linolenic acid, arachidic acid, and erucic acid in smaller proportions [24].

The availability of nyamplung (*Jatropha*) raw materials for biodiesel production is quite promising, especially in Indonesia, where the nyamplung tree is widely spread across Java, Sumatra, Kalimantan, Sulawesi, and Nusa Tenggara. The Indonesian government has shown interest in the development of biofuels as part of its national energy strategy. The development of nyamplung as a biodiesel source can be supported through structured development, including enhanced cultivation, seed processing, and government policies, including incentives for farmers and industries to grow and process nyamplung. With these measures, nyamplung can become a sustainable raw material source for biodiesel production in Indonesia [24-25].

Biodiesel can be produced from both vegetable and animal oils. Vegetable oil and biodiesel belong to the same large group of organic compounds, namely the fatty acid ester group. Vegetable oil is a triglyceride of fatty acids with glycerol or triglyceride, while biodiesel is a fatty acid monoester with methanol. This difference in molecular structure has important consequences in assessing them as candidates for diesel engine fuel [25].

1. Vegetable oil (triglycerides) has a much larger molecular weight than biodiesel (methyl esters). This property causes triglycerides to relatively easily undergo cracking into various smaller molecules when heated without contact with air.
2. Vegetable oil has a much higher viscosity than diesel or kerosene as well as biodiesel, making it difficult for fuel injection pumps in diesel engines to produce good atomization when vegetable oil is sprayed into the combustion chamber.
3. Vegetable oil molecules are relatively more branched than fatty acid methyl esters, resulting in a lower cetane number for vegetable oil compared to methyl esters.
4. The cetane number is a measure of the ease of ignition or combustion of a fuel in a diesel engine.

Esterification is the process of converting free fatty acids into esters. This reaction involves combining fatty oils with alcohol. A suitable catalyst for this process is a substance with strong acidic properties, such as sulfuric acid, organic sulfonic acid, or strong acid cation exchange resin, which are commonly used catalysts in industrial applications [26].

To ensure that the reaction proceeds to complete conversion at low temperatures, an excess of methanol reactant must be added (usually greater than 10 times the stoichiometric ratio), and any water produced in the reaction must be removed from the oil phase. Through the appropriate combinations of reaction conditions and methods for removing water, the complete conversion of fatty acids to their methyl esters can be achieved within a few hours. The esterification reaction can be seen in the reaction below [21].



Figure 1. Esterification reaction of calophyllum inophyllum

Esterification is often used to create biodiesel from oils with high levels of free fatty acids (acid value of 5 mg-KOH/g). During this phase, free fatty acids are transformed into methyl esters. Following esterification, the next step is typically

transesterification. However, prior to transferring the esterification products to the transesterification phase, it's essential to remove any water and the majority of the acid catalyst present [21].

Transesterification, commonly known as alcoholysis, is the process of converting triglycerides (vegetable oil) into alkyl esters by reacting with alcohol, resulting in glycerol as a by-product. Among monohydric alcohols considered as alkyl group suppliers, methanol is predominantly used due to its affordability and high reactivity (thus, referred to as methanolysis). Therefore, biodiesel is essentially fatty acid methyl esters. The transesterification reaction of triglycerides into methyl esters is depicted in Figure 2.

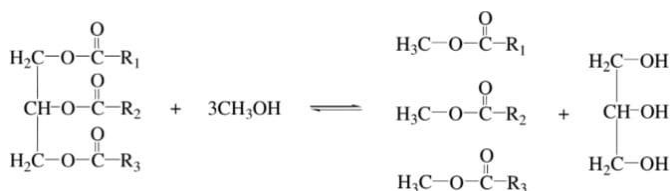


Figure 2. Transesterification reaction from triglycerides to methyl esters

Transesterification also involves the use of catalysts during its reaction phase. The presence of a catalyst maximizes the conversion attained, although the reaction proceeds slowly. Base catalysts are commonly employed in transesterification reactions because they accelerate the reaction. The objective of the transesterification reaction is to obtain fatty acid methyl esters. According to the principle of equilibrium reactions, there are various methods to shift the reaction equilibrium towards the products [27]:

1. Adding excess methanol to the reaction.
2. Separating glycerol immediately.
3. Lowering the reaction temperature (transesterification is an exothermic reaction).

Research into the production of biodiesel from calophyllum inophyllum is increasingly undertaken by various researchers. Ilminafik and Sugara [28] conducted a study on biodiesel production from calophyllum inophyllum using microwave heating, employing solid CaO catalyst at concentrations ranging from 2-6% of the oil weight. The objective of the research was to synthesize biodiesel from calophyllum inophyllum through transesterification, with varying ratios of oil to methanol at 1:9 and 1:12, and microwave power levels at 100, 264, and 400 W. The study identified the optimal conditions for biodiesel yield to be 94% with a microwave heating power of 100 W, 4% catalyst concentration, and an oil to methanol molar ratio of 1:9 [28].

Atabani [29] conducted research on nyamplung seeds utilizing an esterification process with phosphoric acid to remove latex, yielding 85% calophyllum inophyllum. This calophyllum inophyllum was then converted into biodiesel through transesterification using ethanol and NaOH catalyst at 1% of the oil weight. Experimental conditions included a reaction temperature of 60°C and a reaction time of 60 minutes. The biodiesel obtained amounted to 80.89%, and its specifications met the SNI parameters. The subsequent study conducted by Demirbas et al. [21] utilized calophyllum inophyllum and employed transesterification with methanol and 1.25% KOH catalyst, yielding biodiesel at 88.27% under reaction conditions of 60°C temperature and a reaction time of

121 minutes. The produced biodiesel met the specifications according to the SNI parameters [21].

Arumugam and Ponnusami [30] also conducted experiments on producing biodiesel from calophyllum inophyllum using 1% solid KOH catalyst in a microwave reactor. The study aimed to explore the impact of microwave power, reaction time, and temperature on biodiesel yield. Transesterification was performed with varying microwave power levels of 100, 200, and 400 W, reaction times from 5 to 15 minutes, and temperatures from 50 to 70°C. The research identified the most favorable conditions at 200 W power, 65°C reaction temperature, and 5 minutes reaction time, resulting in a biodiesel yield of 84.62%. Quality testing confirmed that the biodiesel met the SNI 04-7182-2006 standard. This investigation revealed that microwave irradiation could significantly accelerate the transesterification reaction, reducing the reaction time to 1/6 of the conventional method [30].

Subsequent research on biodiesel from calophyllum inophyllum utilized a microwave reactor under reaction conditions of 60°C temperature and a duration of 60 minutes. The catalyst used was a liquid 1-butyl-3-methyl imidazolium hydrogensulphate (BMIMHSO₄) with an ion content of 15% of the oil weight. The study yielded biodiesel at 81.2%, and its specific characteristics met the SNI parameters [31].

The experiment conducted by Sema Aslan [32] for biodiesel production from rapeseed oil used a natural bentonite catalyst modified through calcination at 500°C for 2 hours, followed by impregnation with lithium acetate at 60°C for 24 hours, and then calcination at 500°C for 5 hours. The experiment results showed that the biodiesel yield was 98.80%. This result is better than that obtained with unmodified bentonite catalyst.

In another experiment, Marso et al. [33] used a modified graphene oxide (GO/metal) composite catalyst containing Al³⁺ and Fe³⁺ ions for the pre-esterification of Calophyllum inophyllum oil. The results achieved a conversion of stearic acid to methyl stearate of 92.72% and a reduction in free fatty acid (FFA) content in Calophyllum inophyllum oil of 95.37%. This process also resulted in a decrease in acid number of 65.75% using non-surfactant materials, and a reduction of 95.37% with the help of surfactants.

Another study on biodiesel production from nyamplung (Calophyllum inophyllum) oil was conducted by Trisunaryanti et al. [34]. This experiment used Ni and Pt catalysts with an active carbon support derived from coconut shell. The results with the Pt catalyst produced the highest liquid yield of 84.77 wt%, with the best hydrocarbon selectivity of 91 wt%, obtained at a hydrotreatment temperature of 550°C for 2 hours with a Pt catalyst to nyamplung oil ratio of 1:300. Using the Ni catalyst resulted in a lower liquid yield of 78.83 wt%, containing 86.2 wt% hydrocarbons under hydrotreatment conditions of 550°C for 2 hours and a Ni to oil ratio of 1:200. This study provided an alternative, cost-effective, and environmentally friendly process for producing high-quality biofuel from the abundant Calophyllum inophyllum oil, which could be explored for future development [35].

An interesting subsequent study for biodiesel production from nyamplung oil used a catalyst made from coconut sawdust impregnated with Ni. The catalyst was created by carbonizing coconut sawdust at 700°C for 2 hours under a nitrogen flow at a rate of 20 mL/min. It was then impregnated with nickel nitrate solution and calcined at 550°C. Using this catalyst for biodiesel production from nyamplung oil with a hydrotreatment process at 550°C for 2 hours resulted in a

liquid yield of over 74% and a hydrocarbon content of 65% [36].

The next study on biodiesel production from nyamplung (*Calophyllum inophyllum*) oil used Ni and Pt catalysts with an active carbon support from coconut wood sawdust. The catalyst preparation was conducted both conventionally and using microwave heating. In the conventional method, the carbonization stage was performed at 700°C for 2 hours under inert nitrogen gas conditions with a flow rate of 20 mL/min, followed by physical activation with carbon dioxide gas at a flow rate of 10 mL/min, a heating temperature of 500°C, and a time of 2 hours. In the microwave method, carbonization was done at 800 W for 10 minutes, followed by activation at 500°C for 1 hour under carbon dioxide flow conditions at a rate of 10 mL/min. Using monometallic Ni catalysts with microwave carbonization and activation for biofuel production resulted in a hydrocarbon yield of 15.85%, while monometallic Pt catalysts yielded less than 15.85% hydrocarbons. The use of bimetallic catalysts (2.5% Ni and 2.5% Pt) with microwave carbonization and activation yielded 33.1% hydrocarbons and a selectivity of 99.99% [36].

The various studies on biodiesel production from *calophyllum inophyllum* mentioned above utilized both liquid and solid catalysts without any catalyst modification. The novelty of the research lies in the utilization of catalysts derived from natural materials that were subsequently modified. The modification of these catalysts aims to enhance the yield of biodiesel and ensure that its specifications meet the SNI test parameters.

In this study, the biodiesel production process from *calophyllum inophyllum* was conducted using the transesterification process, which occurred in the liquid phase with heterogeneous catalysts zeolite and bentonite that were modified with acid and calcination. The resulting biodiesel was then analyzed for its characteristics according to SNI standards, including density, viscosity, cetane number, flash point, and methyl ester content.

3. METHODS

This study involves several phases: preparation of catalysts, extraction of *Calophyllum inophyllum* seeds using n-hexane solvent to obtain *calophyllum inophyllum* and subsequent analysis of its characteristics, esterification stage to reduce the free fatty acid content in *calophyllum inophyllum*, and transesterification stage to produce biodiesel. The yield of the resulting biodiesel is then calculated. The biodiesel with the highest product yield is further analyzed for its characteristics according to the American Society for Testing and Materials (ASTM) procedures and follows the requirements of the Indonesia National Standard (SNI) for biodiesel (SNI 04-7182-2006), including viscosity, density, cetane number, flash point, and methyl ester content. The types of modified catalysts (i.e., zeolite, bentonite, and a mixture of zeolite and bentonite) and the transesterification reaction temperature were chosen as factors in this study.

Below are the research steps:

- **Materials**
The primary materials used in this study include *Calophyllum inophyllum* fruit obtained from the Ampel

area of Surabaya and moisture of crushed seeds was removed under natural sunlight, natural zeolite and bentonite obtained from Pacitan, East Java, Indonesia. The reagents used include n-hexane, hydrochloric acid (purity 33%), and methanol Merck (purity 99.9%), sourced from PT. Kurniajaya, Surabaya.

- **Preparation of modified catalysts**
The modified heterogeneous catalysts used were zeolite and bentonite. Prior to use, natural zeolite and bentonite was crushed using a JUNKE and KUNKEL micro hammer mill to obtain zeolite and bentonite with particle size of 170/240 mesh. Subsequently, the zeolite and bentonite was treated with 30% of hydrogen peroxide solution to remove the organic impurities. Excess of hydrogen peroxide solution was removed by gently heating in a water bath and the solution was separated from the zeolite and bentonite. The purified zeolite and bentonite was repeatedly washed and dispersed in distilled water. After the water have been separated from zeolite and bentonite, the purified zeolite and bentonite was then dried in an oven at 110 °C for 24 hours to remove moisture content from its structure. The dried zeolite and bentonite was finally crushed in a micro hammer mill to obtained powder zeolite with particle size of 170/240 mesh. Modification of zeolite and bentonite were prepared with HCl solution. A brief procedure of catalyst preparation is as follows : 100 g of natural zeolite powder was weighed and placed into a three-neck flask. Then, 400 mL of 0.5 M HCl solution was added until all the zeolite powder was submerged. The mixture was then heated to 100°C and stirred for 24 hours. Subsequently, zeolite and HCl solution was separated by filtration using a vacuum filter system. The zeolite catalyst was then oven-dried at 110 °C for 24 hours and the resulting zeolite solid was calcined at 550°C for 4 hours. The same procedure was carried out for bentonite.
- **Calophyllum inophyllum extraction**
The extraction process of dried *Calophyllum inophyllum* seeds was conducted to obtain *calophyllum inophyllum* oil using n-hexane solvent with a ratio of 1:4 (weight:volume) by the soxhlet method. The extracted oil was separated from the solvent mixture by distillation at 110 °C for an hour to obtain *calophyllum inophyllum* oil [31].
- **Analysis of free fatty acid content in calophyllum inophyllum**
A total of 10 g of *calophyllum inophyllum* was weighed and mixed with 25 mL of neutral 96% alcohol. The mixture was heated in a water bath until boiling, then cooled to room temperature and 2 drops of phenolphthalein indicator were added. This solution was then titrated using 0.1 N NaOH solution until it turned pink, and then the content of free fatty acids in the *calophyllum inophyllum* was calculated. This testing was also conducted on the oil resulting from the esterification process [31].
- **Esterification**

The esterification process aims to decrease the free fatty acid content by reacting calophyllum inophyllum with methanol at a molar ratio of 1:20 using a potent acid catalyst, specifically concentrated HCl. Calophyllum inophyllum is combined with 370 mL of methanol in a three-necked flask, and concentrated HCl, acting as the catalyst, is added at a quantity equivalent to 10% of the oil volume. The mixture undergoes a 2-hour reaction at 60°C. Upon completion of the reaction, the resulting methyl esters are separated from the mixture using a separating funnel, and the product is then analyzed to determine its free fatty acid level [37].

- Transesterification

Transesterification of Calophyllum inophyllum oil into biodiesel was carried out in a 500 mL three-neck flask equipped with reflux condenser, temperature indicator, and controlled water bath heater. The transesterification reaction is carried out by adding modified catalysts, namely zeolite and bentonite. The molar ratio used between calophyllum inophyllum oil and methanol is 1:6, with the catalyst amounting to 10% of the oil's weight. In this study, 100 mL of calophyllum inophyllum oil resulting from esterification is placed in a three-necked flask and mixed with 24.3 mL of methanol and 10% of the weight of modified zeolite or bentonite catalyst. The mixture is then stirred using a magnetic stirrer, and the reaction takes place for 5 hours at various temperatures, namely 50, 60, 65, and 70°C. After the reaction is completed, the mixture is filtered using a Buchner funnel **under vacuum condition** to separate the catalyst from the biodiesel and glycerol mixture. The biodiesel and glycerol are then separated using a separating funnel. The resulting biodiesel is subsequently dried in a vacuum rotary evaporator to remove its water content and **the excess methanol. Biodiesel product was then repeatedly washed using warm distilled water (60 °C). The fatty acid methyl ester or FAME layer (upper layer) was separated from water layer (bottom layer) using a separating funnel. The yield and characteristics of the resulting biodiesel are then analysed and calculated.**

- Characterization of biodiesel and catalyst

The biodiesel product obtained is subjected to characterization testing under conditions of maximum biodiesel yield, following SNI and ASTM parameters, including density, viscosity, flash point, cetane number, and methyl ester content. Density testing is performed using a pycnometer **according to ASTM D1298**, viscosity testing with a Brookfield Viscometer spindle no.21 at 100 rpm **according to ASTM D445-10, 2010**, flash point with a Pensky Marten Closed Tester according to ASTM D93, cetane number with a Cetane Number Tester GD-R3035 following ASTM D613 and D6887, while the fatty acid methyl ester content is analyzed using Gas Chromatography (GC Shimadzu 2014). **The GC was equipped with a DB-wax Capillary column (30 m x 0.25 mm i.d. x 0.1 μm film thickness, Agilent JW Scientific) and flame ionization detector**

(FID). Helium was employed as carrier gas at 40 cm/s. The injector temperature was 250 °C at splitless condition. The FID was set at 300 °C. The initial oven temperature was set at 50 °C with equilibration time of 3 min. After isothermal period, oven temperature was increased to 250 °C at heating rate of 10 °C/min and held for 8 min. Peaks of methyl esters were identified by comparing them with the reference standard. The yield of biodiesel was determined by the following equation :

$$\text{Yield(\%)} = (\text{weight of biodiesel} \times \% \text{FAME in sample}) \times 100\% / (\text{weight of Calophyllum inophyllum oil})$$

These FAME tests are conducted at the Pertamina laboratory in Jagir, Surabaya. **The limitations of this research are the characterization of modified zeolite and bentonite catalysts includes X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) tests conducted at the Energy Laboratory, Sepuluh Nopember Institute of Technology, Surabaya. Characterization analysis using X-ray Photoelectron Spectroscopy (XPS) was not employed. XRD testing utilizes a Philips X-pert Powder Analytical diffractometer with an X-ray diffractometer operating at 30 kV and 15 mA, with 2θ measurements ranging from 5° to 90°.while FTIR employs an Invenio-Bruker Corp. spectrometer.**

4. RESULTS AND DISCUSSIONS

4.1 Calophyllum inophyllum oil analysis

The physical and chemical properties of Calophyllum inophyllum oil were determined using standard test methods. These include density (ASTM D1298, 2005), kinematic viscosity (ASTM D445-10, 2010) and free fatty acid content (ASTM D93, 2010).

The extracted calophyllum inophyllum oil used as the raw material for biodiesel production exhibits characteristics as shown in Table 3.

Table 3. Calophyllum inophyllum characteristics

Parameter	Unit	Value
Density	g/cm ³	0,92
Kinematic viscosity	cP (on 25,6°C)	98
Free fatty acid	(%)	26,27

The calophyllum inophyllum oil does not meet the criteria as a raw material for biodiesel production because its free fatty acid content exceeds 2%. Therefore, an esterification process is required for the calophyllum inophyllum oil to meet the criteria as a raw material for biodiesel production, which is to reduce the free fatty acid content to the appropriate range for transesterification in biodiesel production. The requirement for oil to be used as a biodiesel feedstock is to have a maximum free fatty acid content of 2% [37].

Table 4 below presents the characteristics of calophyllum inophyllum oil after undergoing the esterification process. From the results of the esterification stage conducted on the calophyllum inophyllum oil, a decrease in the free fatty acid content to 1.71% was obtained. Therefore, the calophyllum inophyllum oil resulting from the esterification process can be used as a raw material for biodiesel production to be further processed by transesterification.

Table 4. Calophyllum inophyllum oil after esterification

Parameter	Unit	Value
Density	g/cm ³	0,90
Kinematic viscosity	cP (on 25,6 °C)	45
Free fatty acid	%	1,71

4.2 Modified catalysts characteristics

The modified catalysts were analyzed using X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) for characterization. XRD diffraction analysis was performed to identify the internal structure, bulk phase and crystallinity of the catalyst. XRD was employed to identify the Si/Al (Silica/Aluminum) compound content in both catalyst types. The XRD characterization results are depicted in the figure below.

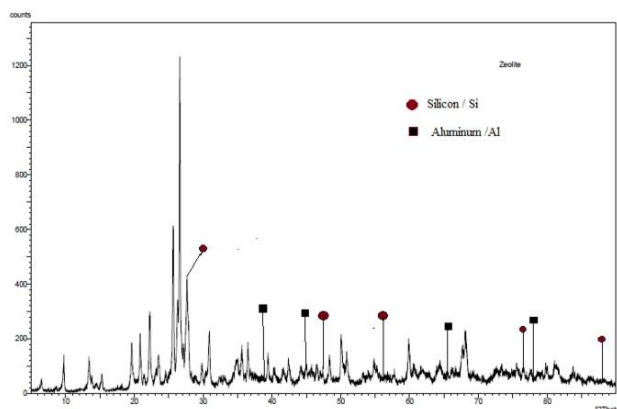


Figure 3. XRD results of natural zeolite

Figures 3 and 4 depict the XRD analysis results for natural zeolite and after modification with acid, respectively.

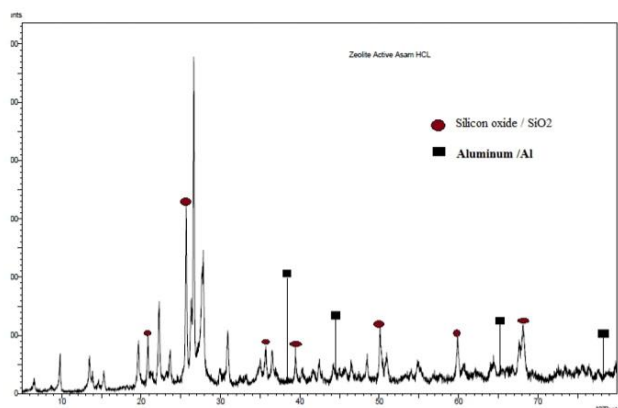


Figure 4. XRD results of modified zeolite

Subsequently, Figures 5 and 6 show the XRD analysis results for natural bentonite and after modification with acid.

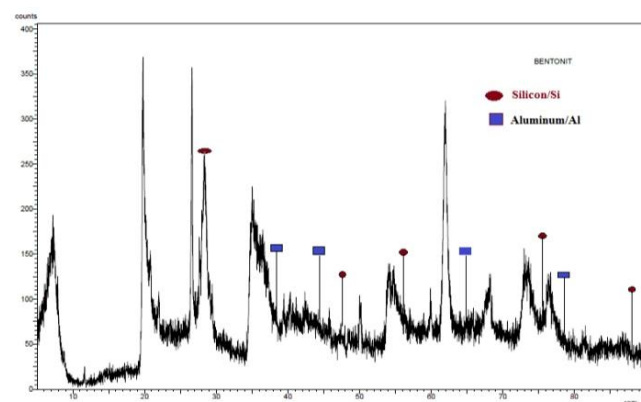


Figure 5. XRD results of natural bentonite.

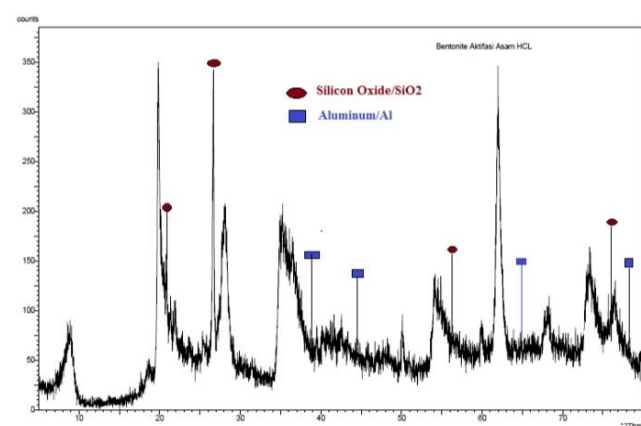


Figure 6. XRD results of modified bentonite

The XRD characterization analysis results indicate a change in the characteristics of both catalysts before and after modification. This can be observed in Figures 3 and 4 for Zeolite. A comparison of these two figures shows a change in the Si content, with more SiO₂ compound formed, while the Al compound decreases. This is consistent with the principle of catalyst activation with acid, which involves releasing Al atoms to optimize the aluminum content in the catalyst, thereby enhancing its catalytic properties and absorption. Silicon oxide and aluminium oxide is believed to play an important role during the transesterification of oil into fatty acid methyl esters since it has high catalytic activity.

A similar trend is evident in Figure 5 and Figure 6 regarding the bentonite catalyst, showing an augmentation in SiO₂ content following the modification process. However, the alterations resulting from the modification of both catalysts are not prominently observable due to the relatively low acid concentration utilized for the catalyst modification.

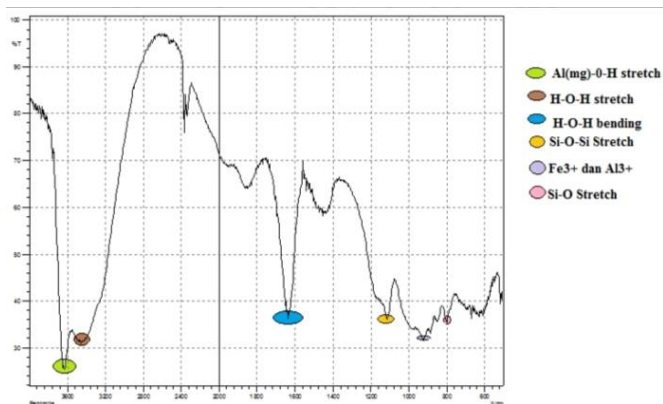


Figure 7. FTIR results of natural bentonite

Figures 7 and 8 depict the FTIR analysis results for natural bentonite and its modified form.

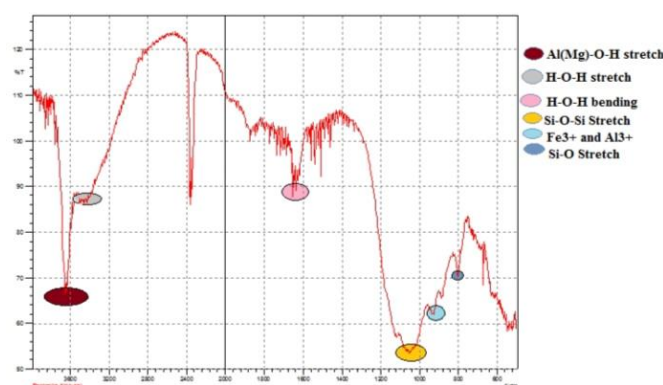


Figure 8. FTIR results of modified bentonite

Next, Figures 9 and 10 show the FTIR analysis results for natural zeolite and its modified form. Catalyst characterization with FTIR aims to identify the functional groups present in both types of catalysts before and after the acid modification process.

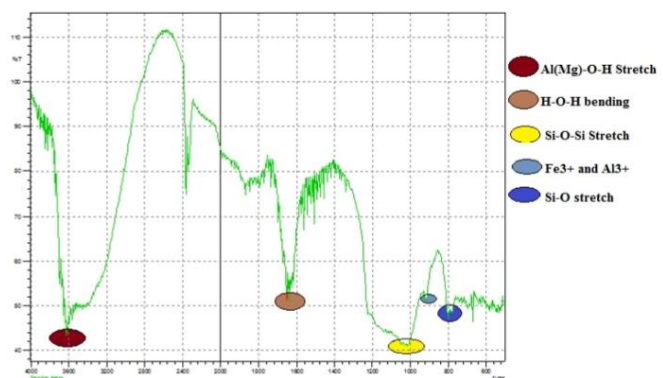


Figure 9. FTIR results of natural zeolite

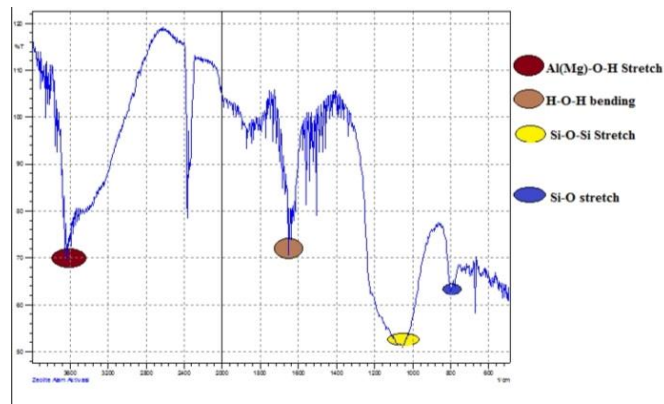


Figure 10. FTIR results of modified zeolite

Based on the FTIR analysis results, it is observed that no new functional groups are formed on the catalyst. Modification using acid causes an increase in bond strength, as indicated by the increase in transmittance percentage at certain wavelengths from the FTIR analysis results. However, this increase is not significantly visible due to the relatively low concentration of acid used.

4.3 The effect of reaction temperature on the yield of biodiesel production

The transesterification of Calophyllum inophyllum oil using modified zeolite and bentonite as catalysts were performed under following conditions : catalyst amount 10%, ratio of Calophyllum inophyllum oil to methanol 1:6, reaction temperature 50, 60, 65 and 70 °C and reaction time 5 hours.

The influence of reaction temperatures of 50, 60, 65, and 70°C on the yield of biodiesel produced using modified zeolite catalysts, modified bentonite, and a mixture of modified zeolite and bentonite in a 50:50 ratios is shown in Table 5.

Tabel 5. Biodiesel yield produced using modified catalysts

The type of catalyst and the ratio of catalyst amounts.	The yield of biodiesel based on reaction temperature.			
	50°C	60°C	65°C	70°C
Modified Zeolit (100:0)	78,36	88,19	83,19	81,15
Modified Bentonit (100:0)	67,73	78,84	72,09	70,58
Modified Zeolit and Bentonit (50:50)	70,83	82,36	75,49	73,11

Based on the data, it appears that increasing the transesterification reaction temperature from 50°C to 60°C leads to an increase in the yield of biodiesel. However, further increases in the transesterification reaction temperature above 60°C to 70°C result in a decrease in biodiesel yield.

At a temperature of 60°C, the highest yield of biodiesel was obtained for the three types of catalysts used. The highest biodiesel yield achieved was 88.19% with modified zeolite catalyst, 78.84% with modified bentonite catalyst, and 82.36%

with a mixture of modified zeolite and modified bentonite catalysts in a 1:1 ratio.

4.4 The influence of modified catalyst type on the yield of biodiesel production.

The experiment results indicate that the type of modified catalyst used in the transesterification process influences the yield of biodiesel obtained, as shown in Table 5. The use of modified zeolite catalysts yields a greater amount of biodiesel compared to modified bentonite catalysts and a mixture of modified zeolite and bentonite at a 50:50 ratio. This trend is observed across various transesterification reaction temperatures ranging from 50, 60, 65, to 70°C. This phenomenon occurs due to the differences in properties and characteristics among the three types of modified catalysts used in the transesterification process.

One distinguishing feature of zeolite, functioning as an adsorbent, is its expansive surface area and micro-sized pores. Bentonite, another adsorbent, possesses a surface area smaller than zeolite, with macro-sized pores. These qualities play a crucial role in the transesterification reaction, especially since the oil used often contains high levels of fatty acids due to its elevated water content. Zeolite's adsorbent nature significantly aids in water absorption during the transesterification process, leading to a higher biodiesel yield compared to bentonite. This aspect underscores bentonite's drawback, resulting in its comparatively lesser influence on biodiesel yield when compared to zeolite catalysts.

Based on the yield of the biodiesel products obtained, there is a noticeable relationship between the surface characteristics of the catalysts and their reactivity. The factors affecting the biodiesel yield include surface acidity, pore structure, surface area of the catalyst, and the effects of catalyst modification [12-18].

• Effect of Surface Acidity on Modified Catalysts

For modified zeolite catalysts, they generally have high surface acidity due to the presence of Bronsted and Lewis acid sites. These acid sites can enhance the transesterification reaction by providing active sites for the formation of intermediate products. The presence of strong acid like HCl used in the modification can promote the formation of reactive species from triglycerides and methanol, thereby increasing the rate of the transesterification reaction.

Modified bentonite catalysts, which are clay minerals, can have varying levels of acidity depending on the modifications performed. Modification with strong acid like HCl increases the acidity of the modified bentonite catalyst. This acidic nature can enhance the reaction by providing acidic sites that catalyze the transesterification reaction. However, the biodiesel yield with modified bentonite catalysts is lower than with modified zeolite catalysts because the acidity level of bentonite is lower than that of zeolite, affecting reactivity and biodiesel yield.

• Effect of Pore Structure on Modified Catalysts

Modified zeolite catalysts have a well-defined pore structure and large surface area. These properties significantly impact accessibility to active sites, which can enhance the transesterification reaction, thus improving biodiesel yield. Modified bentonite catalysts have irregular pore structures, and while acid activation increases their surface area, it is not as extensive as that of modified zeolite catalysts. The irregular pore structure of modified bentonite can affect the diffusion rate of reactants and products, making its performance in

transesterification less effective compared to modified zeolite catalysts.

• Effect of Surface Area on Modified Catalysts

Modified zeolite catalysts have a larger surface area, providing more active sites for the transesterification reaction. A larger surface area enhances the interaction between reactants and catalysts, leading to a higher biodiesel yield. Modified bentonite catalysts have a smaller surface area compared to modified zeolites. Although acid modification increases the surface area of bentonite, its effectiveness is lower than that of modified zeolites in providing active sites for reactant-catalyst interactions, resulting in a lower biodiesel yield.

• Effect of Catalyst Modification

Acid modification of zeolite can significantly alter its acidity and pore structure, which can affect catalytic performance. The increase in acid sites and pore distribution can enhance the catalyst's ability to drive the transesterification reaction rate, thus improving biodiesel yield. Modified bentonite catalysts experience similar changes as modified zeolite catalysts, but due to their lower surface area and less regular pore structure, their biodiesel yield is not as high as that of modified zeolite catalysts.

Based on the above explanation, the relationship between the surface characteristics of the catalysts and their reactivity is crucial in the production of biodiesel with modified solid catalysts.

4.5 The analysis results of biodiesel characteristics at the highest yield

Biodiesel produced from Calophyllum inophyllum oil using acid-modified zeolite and bentonite catalysts exhibits several specific properties influenced by the raw materials and catalyst technology used. The properties of the biodiesel products from this research have been tested according to ASTM parameters and Indonesian National Standard (SNI) to ensure they meet the requirements of current biodiesel technology.

The biodiesel produced under conditions yielding the highest output is analyzed for its characteristics according to ASTM standards, and the results are compared with the SNI requirements for biodiesel. The parameters include flash point, viscosity, density, cetane number, and FAME content analysis, as shown in Table 6.

Table 6. The characteristics of the biodiesel produced at the highest yield using modified zeolite catalyst at a reaction temperature of 60°C.

Parameter	Test results	SNI
Flash point, °C	121	Min 100
Viscosity, mm ² /s	5,633	2,3-6
Density, kg/m ³	887	850-887
Cetane number	53	Min 51
FAME	94.55	

Density testing is performed to ascertain its compliance with biodiesel standards and is juxtaposed against the SNI benchmark. The analysis reveals a density of 0.887 g/cm³ (887 kg/m³). The SNI specifies a density range for biodiesel of 850-887 kg/m³, confirming that the biodiesel derived from this study aligns with SNI regulations for biodiesel products.

The viscosity of the produced biodiesel is analyzed to ensure its compliance with the criteria for being declared as methyl ester according to the SNI standards. The viscosity of a fuel affects flow profile, atomization, and lubrication effectiveness. The viscosity is the most important property of biodiesels, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. The lower the viscosity of biodiesel, the easier it is to pump and atomize and achieve finer droplets [27]. The analysis results indicate that the viscosity of the biodiesel obtained at a measurement temperature of 40°C is 5.633 mm²/s, while the benchmark according to the SNI standards ranges from 2.3 to 6.0 mm²/s. Therefore, the biodiesel product meets the SNI standards.

The next test is the cetane number, which is essential because it indicates the diesel engine fuel's spontaneity to combust after being injected into the combustion chamber. Cetane number relates to the combustion quality of diesel fuel during compression ignition and also the ignition quality fuels [27]. The cetane number obtained for biodiesel from Calophyllum inophyllum is 53, while the SNI parameter for biodiesel cetane number is a minimum of 51. Hence, the biodiesel product meets the SNI requirements.

The flash point test on biodiesel is conducted to determine its ignition temperature when applied as fuel. A high flash point makes fuel storage easier as it is less prone to ignite at room temperature. The minimum value of flash point is required for safety and handling of the fuel. It is used to characterize the fire hazards of the liquids [27]. The test results indicate that the biodiesel derived from Calophyllum inophyllum oil under conditions yielding the highest output has a flash point of 121°C, therefore, this fuel is safe for handling and storage for some period of time. With high value of flash point, this biodiesel is considered as combustible. The test results show that the biodiesel product meets the SNI criteria, which stipulates a minimum flash point of 100°C.

Another test is to measure the fatty acid methyl ester (FAME) content in biodiesel. This test is conducted to determine the amount of fatty acids converted into methyl esters. Methyl ester analysis is carried out using a GC instrument [27]. The result of the methyl ester content analysis for biodiesel produced from calophyllum inophyllum oil is 94.55%.

Based on the testing results of the biodiesel product according to commercial biodiesel parameters as per SNI and ASTM requirements, it is evident that the biodiesel obtained meets the criteria for current technology, including quality and energy performance parameters, chemical composition (FAME), oxidative stability, physical characteristics, combustion properties, sustainability, and environmental factors.

Quality and energy performance are evaluated through energy content and viscosity. Biodiesel from Calophyllum inophyllum oil generally has a slightly lower calorific value compared to diesel fuel but is still adequate for use as fuel. The biodiesel product has a higher viscosity compared to diesel fuel. However, with the appropriate catalysts like acid-modified zeolite and bentonite, the viscosity of the biodiesel can be optimized to ensure good flow and efficient spraying in diesel engines.

Oxidative stability testing indicates that biodiesel from Calophyllum inophyllum oil tends to have better oxidative stability compared to biodiesel from some other vegetable oil sources, which is due to the natural properties of the oil. The modification of zeolite and bentonite catalysts with acid

reduces the formation of oxidizing compounds and improves the long-term stability of the biodiesel.

Physical characteristic testing includes the flash point. Biodiesel from Calophyllum inophyllum oil has a higher flash point compared to diesel fuel. Modifications to the catalyst can help lower the flash point by affecting the molecular structure of the ester in the biodiesel.

Combustion properties are tested through emission tests. Biodiesel from Calophyllum inophyllum oil using modified zeolite and bentonite catalysts produces cleaner emissions compared to diesel fuel, including reductions in carbon monoxide (CO), unburned hydrocarbons, and fine particulates. The use of acid-modified zeolite and bentonite catalysts impacts the combustion properties of biodiesel by enhancing combustion efficiency and reducing the formation of harmful by-products.

Given the properties and characteristics of the biodiesel products, it is apparent that biodiesel from Calophyllum inophyllum oil with zeolite and bentonite catalysts meets sustainability and environmental friendliness criteria.

The comparison of combustion performance and emissions of Calophyllum inophyllum oil biodiesel with diesel fuel in engine tests examines parameters such as thermal efficiency and combustion stability. In terms of thermal efficiency, the biodiesel product has a slightly lower calorific value compared to diesel fuel, but catalyst modifications can enhance combustion efficiency by optimizing the biodiesel properties. Acid-modified zeolite and bentonite catalysts help reduce viscosity and improve fuel atomization, which can enhance combustion efficiency.

Regarding combustion stability, this biodiesel product tends to exhibit more varied combustion characteristics depending on the composition of the Calophyllum inophyllum oil used. The use of acid-modified zeolite and bentonite catalysts can improve combustion stability by reducing issues related to incomplete combustion. Emission testing of Calophyllum inophyllum oil biodiesel shows lower levels of carbon dioxide, carbon monoxide, nitrogen oxides, unburned hydrocarbons, and particulates compared to diesel fuel. These results indicate that catalyst modifications affect combustion performance and emissions, making Calophyllum inophyllum oil biodiesel a more environmentally friendly alternative with competitive performance compared to diesel fuel.

Storage stability is a crucial factor to ensure that biodiesel remains effective and safe for use over a long period. Long-term storage stability evaluation of biodiesel products from Calophyllum inophyllum oil with modified zeolite and bentonite catalysts is still under testing. However, biodiesel products made from Calophyllum inophyllum oil with different catalysts generally involve critical aspects such as oxidative stability, hydrolysis stability, thermal stability, and resistance to contamination, physical, and chemical changes. Biodiesel from Calophyllum inophyllum oil shows good stability, but regular monitoring and testing are important to ensure its quality during storage. Modified catalysts can contribute to enhanced stability by reducing the formation of oxidizing compounds and improving the final quality of the biodiesel. The use of zeolite catalysts can help improve biodiesel stability by reducing unwanted by-products and enhancing the final quality of the biodiesel. Modified acid bentonite catalysts can reduce the formation of free fatty acids and improve stability against hydrolysis and oxidation.

5. CONCLUSION

The study indicates that *Calophyllum inophyllum* oil can effectively be transformed into biodiesel through esterification and transesterification processes using modified zeolite and bentonite catalysts. The biodiesel yield achieved with these modified catalysts is 88.19%, matching that of biodiesel produced with acid and base catalysts, which is 88.27%. The advantage of using these modified catalysts is their easy separation and ability to be reused in the biodiesel production process, making them eco-friendly. In contrast, traditional acid-base catalysts are difficult to separate and cannot be reused, resulting in industrial waste that requires management.

The use of modified catalysts offers potential for advancing biodiesel science and industry by reducing waste and lowering separation costs in the future. The resulting biodiesel meets the specifications outlined by the Indonesian National Standard (SNI), confirming its viability as a renewable fuel option.

Future research on the biodiesel production process from *Calophyllum inophyllum* oil using modified zeolite and bentonite catalysts holds significant potential for innovation and improvement. Innovation focus can be directed towards catalyst optimization, broader applications, and developing solutions for technical and economic challenges, which will play a key role in making the process more efficient and sustainable.

Catalyst optimization can be achieved through the development of hybrid catalysts by combining zeolite and bentonite with other catalytic materials (such as metals or metal oxides) to enhance catalytic activity and selectivity. Modifying the structure and composition of zeolite and bentonite to improve accessibility and reactivity with *Calophyllum inophyllum* oil, and using nanotechnology to create nanoparticles from zeolite and bentonite to increase active surface area and catalyst efficiency are also potential areas for optimization.

Improvements in the transesterification process can be achieved through integrated process technologies that combine transesterification reactions with biodiesel separation and purification, as well as optimizing operating conditions to enhance conversion and reaction efficiency.

For sustainability and material availability, alternative materials that can replace or complement zeolite and bentonite can be used, and recycling catalysts and managing waste from the modification process can help reduce environmental impact.

Broader application improvements can be pursued by diversifying feedstocks, adapting modified catalysts for various types of biodiesel feedstocks, or using a mix of *Calophyllum inophyllum* oil with other non-food oil feedstocks. Developing zeolite and bentonite catalyst modifications for industrial scale, integrating with new sustainable process technologies, and automating and controlling processes to enhance consistency and biodiesel production efficiency are also important.

To address technical challenges, solutions can focus on high stability of modified catalysts and long service life for industrial scale use. For economic challenges, efforts can be directed towards reducing the production costs of catalyst modifications. With the right approach, it is possible to significantly enhance biodiesel production efficiency and reduce environmental impact.

Recommendations for further research include exploring biodiesel production from other non-edible oils and testing catalysts derived from other environmentally friendly natural

materials to improve biodiesel yield, as well as conducting characterization of modified zeolite and bentonite catalysts using X-ray Photoelectron Spectroscopy (XPS). This advanced characterization technique is highly useful for understanding chemical surface changes in modified catalysts and can help in understanding how modifications affect oxidation states, composition, and surface reactivity. This is crucial for designing more efficient and durable catalysts. Through XPS analysis, researchers can monitor and optimize the catalyst modification process for better applications in industrial chemical reactions.

Another useful recommendation for future research is the design of a mini-reactor for biodiesel production from *Calophyllum inophyllum* oil. This involves designing a portable mini-reactor with a small but adequate capacity to meet local needs. It should include essential components such as a reaction tank, mixer, heater, filtration system, and separation tank. Safety and ease of use should be prioritized in the design, while mobility and durability are ensured through the use of high-quality materials and a compact design. With this design, it is expected that small-scale biodiesel production can be carried out efficiently and safely at various locations.

ACKNOWLEDGMENT

This work is supported by the Directorate of Research and Community Service, Directorate General of Higher Education, Ministry of Research and Technology, Republic of Indonesia, for funding this research through the Competency-Based Research (PBK) Grant in the fiscal year 2019 based on Contract No. 011/SP2H/AMD/LT/MULTI/L7/2019.

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Manuscript correction information for ACSM 28394 :

Biodiesel synthesis from calophyllum inophyllum utilizing modified zeolite and bentonite catalysts

Herman Hindarso^{1*}, Aning Ayucitra², Dian Retno Sari Dewi³, Nyoman Puspa Asri⁴

^{1,2} Department of Chemical Engineering, Widya Mandala Catholic University, Kalijudan 37, Surabaya, 60114, Indonesia

³ Department of Industrial Engineering, Widya Mandala Catholic University, Kalijudan 37, Surabaya, 60114, Indonesia

⁴ Department of Food Technology, Ciputra University, Citraland CBD Boulevard, Surabaya, 60219, Indonesia

Corresponding Author Email: herman@ukwms.ac.id

No.	Reviewer comments (Reviewer 1)	Revision results
1.	<u>Comprehensiveness and Modernity of Literature Review</u> The literature review on the use of modified zeolite and bentonite as biodiesel catalysts seems incomplete. The authors are advised to reference and incorporate more recent studies, especially from the last five years concerning innovations in solid material science and biodiesel catalysts. This will enhance the modernity and relevance of the research.	The latest research from the past 5 years has been added to Section 2: Literature Review (can be seen in the text highlighted in green).
2.	<u>Experimental Design and Methodology</u> The current description of the experimental design lacks detail in some critical parameters, such as the specific methods and conditions for catalyst modification. Detailed experimental conditions are crucial for the reproducibility of the results.	It has been revised with additional explanations and details in Section 3 (can be seen in the text highlighted in green).
3.	<u>Interpretation and Data Analysis of Results</u> Although the study provides biodiesel yield data using different catalysts, there is a lack of detailed scientific explanation behind the data. For example, analyses on how modified zeolite and bentonite affect the reaction mechanism and yields are missing. Add more discussion on the relationship between the catalyst's surface characteristics and its reactivity, possibly including the catalyst's surface acidity, pore structure, and their specific impacts on the reaction.	It has been revised, and an explanation of the influence of catalyst characteristics on reaction outcomes has been provided in Section 4.4 (can be seen in the text highlighted in green).
4.	<u>Innovation and Contribution</u> Comment: The paper has some innovative aspects in using modified zeolite and bentonite as	It has been revised in Section 1: Introduction (can be seen in the text highlighted in green).

	<p>catalysts, but the description of its unique contributions is not highlighted enough. Clearly point out the innovations in the field of solid material science, such as unique catalyst modification methods or new application mechanisms, and how these innovations advance biodiesel technology.</p>	
5.	<p><u>Sustainability and Environmental Impact</u> Although the paper emphasizes the environmental benefits of biodiesel, there is insufficient discussion on the environmental impacts of catalyst production and usage. Include results from a Life Cycle Analysis (LCA) of the catalysts, discussing the energy consumption and environmental emissions during their production and use, and how these processes can be optimized to reduce environmental impacts.</p>	It has been revised in Section 1: Introduction (can be seen in the text highlighted in green).
6.	<p><u>Depth and Prospective of Conclusions</u> The conclusion section is currently simplistic and lacks in-depth discussion on future research directions. Enhance the conclusions with discussions on potential future research directions, such as further optimization of the catalysts, possibilities for scale-up applications, and the technical and economic challenges involved.</p>	It has been revised in Section conclusion (can be seen in the text highlighted in green).
No.	Reviewer comments (Reviewer 2)	Revision results
1.	<p><u>Introduction</u> 1. The introduction should highlight the most recent advances that motivate this work to better frame its significance. 2. A brief critique of limitations of existing biodiesel production methods is needed to establish knowledge gaps.</p>	It has been revised in Section 1: Introduction (can be seen in the text highlighted in green).
2.	<p><u>Catalyst Design</u> 1. More details are required on the specific activation mechanisms in modifying the zeolite and bentonite catalysts. 2. Advanced characterization techniques like XPS could provide insights into changes in surface chemistry after modification. 3. The effect of varying acid concentration for catalyst modification should be analyzed.</p>	It has been revised in Section 1: Introduction and Section 4 (can be seen in the text highlighted in green).
3.	<p><u>Biodiesel Analysis</u> 1. The fuel properties of the produced biodiesel should be benchmarked against state-of-the-art biofuels to highlight advantages.</p>	It has been revised in section 5.5 results and discussion can be seen in the text highlighted in green).

	<p>2. A comparison of combustion performance and emissions with petroleum diesel is needed through engine testing.</p> <p>3. An evaluation of long-term storage stability can ascertain biodiesel quality over time</p>	
4.	<p><u>Process Optimization</u></p> <p>1. Statistical design of experiments could identify optimal parameters like catalyst loading, temperature, etc. for maximum yield.</p> <p>2. Techno-economic analysis and life cycle assessment can determine process viability and environmental impact.</p>	It has been added to Section 1: Introduction and Section 4: Methods (can be seen in the text highlighted in green).
5.	<p><u>Commercialization Potential</u></p> <p>1. Scalability of the proposed method should be analyzed considering practical limitations and requirements.</p> <p>2. Design of portable mini-reactors suited for on-site biodiesel generation could aid adoption.</p>	It has been added to Section 1.3: Literature review and Section conclusion (can be seen in the text highlighted in green).
6.	<p>Alternative Feedstocks</p> <p>Applicability of the method for other non-edible oils besides Calophyllum inophyllum should be explored.</p>	It has been added to Section 1.3: Literature review (can be seen in the text highlighted in green).
	Tambahan Revisi :	
	<p><u>In addition,</u></p> <ul style="list-style-type: none"> • Make sure that all pictures are clearly visible when zoomed to 120%; • make sure that all documents are cited, numbered and arranged in reference in order; • please provides affiliation following the format of "department (secondary institution), school (affiliated institution), city zip code, country" ; 	It has been revised based on the recommendations.

4. Paper accepted (18-09-2024)



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18 September, 2024

Herman Hindarso

Department of Chemical Engineering, Widya Mandala Catholic University,
Surabaya, 60114, Indonesia

Dear Herman Hindarso, Aning Ayucitra, Dian Retno Sari Dewi, Nyoman Puspa Asri,

MS: Biodiesel Synthesis from Calophyllum Inophyllum Utilizing Modified Zeolite and Bentonite Catalysts
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Biodiesel Synthesis from Calophyllum Inophyllum Utilizing Modified Zeolite and Bentonite Catalysts

Herman Hindarso^{1*}, Aning Ayucitra¹, Dian Retno Sari Dewi², Nyoman Puspa Asri³

¹ Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Surabaya 60114, Indonesia

² Department of Industrial Engineering, Widya Mandala Surabaya Catholic University, Surabaya 60114, Indonesia

³ Department of Food Technology, Ciputra University, Surabaya 60219, Indonesia

Corresponding Author Email: herman@ukwms.ac.id

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<https://doi.org/10.18280/acsm.480504>

ABSTRACT

Received: 10 May 2024

Revised: 4 September 2024

Accepted: 18 September 2024

Available online: 29 October 2024

Keywords:

Calophyllum inophyllum oil, transesterification, modified zeolite, modified bentonite, biodiesel

Biodiesel serves as a renewable, eco-friendly alternative fuel. Its production relies on converting triglyceride sources into methyl esters through transesterification. These triglycerides can be sourced from vegetable oils and animal fats. Previous studies often relied on acids and bases as catalysts. However, there's a lack of research exploring the use of modified zeolite and bentonite as catalysts, which hold the promise of higher yields compared to previous studies. In this study, biodiesel was derived from *Calophyllum inophyllum* via esterification and transesterification processes. Characterization of these catalysts was done using XRD and FTIR analyses. Transesterification to produce biodiesel occurred at temperatures ranging from 50 to 70°C over a reaction period of 5 hours. The largest yield of biodiesel was obtained at 60°C, with 88.19% using modified zeolite catalyst, 78.84% using modified bentonite catalyst, and 82.36% using a blend of modified zeolite and bentonite catalysts in a 1:1 ratio. Biodiesel resulting from the highest yield using modified zeolite catalyst underwent characteristic testing in accordance with SNI standards. The findings revealed a density of 887 kg/m³, viscosity of 5.633 mm²/s, cetane number of 53, flash point at 121°C, and methyl ester content of 94.55%.

1. INTRODUCTION

At present, the reserves of fossil fuels like crude oil, coal, and natural gas are dwindling due to escalating usage and their non-renewable nature [1]. Consequently, there is a pressing need for the development of alternative and renewable fuel sources [2]. Indonesia, as a nation, boasts a diverse range of natural resources, encompassing both renewable and non-renewable ones.

The demand for crude oil as the world's primary fuel source is substantial. However, this demand is not accompanied by an awareness that the combustion of processed crude oil products such as gasoline, diesel, and others has negative impacts on the environment and tends to harm the Earth in the long term [3]. The adverse effects of excessive fossil fuel usage include climate change due to global warming, often referred to as global warming [4-6].

Nowadays, the ongoing and swift consumption of crude oil as a fuel is leading to its diminishing reserves. Therefore, there is a demand for alternative energy sources and fuels that can evolve and hold promise for the future [4]. Biodiesel is a renewable alternative fuel for diesel engines derived from renewable sources such as vegetable oil, animal fats, and algae [7]. It exhibits combustion properties remarkably similar to diesel fuel, hence holds potential for substituting petroleum diesel [8-11].

Calophyllum inophyllum, a thick brown-colored vegetable

oil with a strong caramel-like scent [12], finds various uses among farmers in Kebumen and Cilacap, Central Java, Indonesia. It serves as a coating for roof tiles, aids in batik making, and is utilized in embalming [13]. In West Java, some fishermen rely on *Calophyllum inophyllum* as a fuel for their boats during maritime activities [14]. This oil is rich in unsaturated fatty acids, notably oleic acid, and contains unsaponifiable components like fatty alcohols, sterols, xanthenes, coumarin derivatives, phytols, isophytols, isophthalates, capillary acids, pseudobasilic acid (cyclohexadienone derivatives), and triterpenoid compounds, ranging from 0.5% to 2%, which possess medicinal properties [13].

Advantages of using *Calophyllum inophyllum* as a source of biofuel include its high oil content (up to 74%), its non-competition with food production and its availability is abundant in tropical countries like Indonesia [15]. *Calophyllum inophyllum* offers various benefits for biodiesel production and development: it naturally grows abundantly across Indonesia, easily regenerates, and bears fruit throughout the year, indicating its resilience to environmental conditions. It can be cultivated with ease either in single-crop fields or mixed forests and thrives in dry climates [16]. Nearly all parts of the *Calophyllum inophyllum* plant are valuable, yielding various economically significant products. Using *Calophyllum inophyllum* biofuel can also help reduce deforestation for firewood, given its high seed productivity

compared to other plants [13].

Biodiesel derived from *Calophyllum inophyllum* also offers advantages, including its comparatively high oil yield (40-73%) when compared to other plants like *Jatropha* and palm oil [17]. Some quality parameters already meet Indonesian standards, and *Calophyllum inophyllum* burns twice as long as kerosene. Additionally, it holds future potential as a blending component. Compared to fossil fuels, biodiesel has several benefits, such as renewability, higher energy efficiency, emissions reduction, and the possibility of using it as a complete diesel substitute with advanced processing technology [18]. It also offers better emission quality than diesel and can serve as a bio-kerosene alternative [19].

Recent developments in biodiesel production from *Calophyllum inophyllum* oil have advanced in several areas, including improved processing technology, the use of more efficient and eco-friendly catalysts, and better purification methods. Future progress is expected to focus on further reducing production costs through innovations and optimizations in the production process, as well as the introduction of new, more cost-effective and efficient catalysts. The importance of producing biodiesel from *Calophyllum inophyllum* oil lies in diversifying energy sources, fostering local economic growth, benefiting the environment, and providing a sustainable renewable energy option. Energy diversification is achieved by utilizing *Calophyllum inophyllum* oil as a feedstock for biodiesel, offering an alternative renewable energy source, decreasing reliance on fossil fuels, and strengthening energy security [15].

Local economic development is facilitated by the creation of economic opportunities, such as jobs for farmers and communities in tropical regions, through the planting and cultivation of nyamplung trees, which in turn boosts community income. Environmentally, biodiesel produced from *Calophyllum inophyllum* oil offers the advantage of reducing greenhouse gas emissions when compared to fossil fuels. Moreover, cultivating nyamplung trees can enhance soil quality and aid in carbon absorption. Nyamplung is a renewable and sustainable energy source, as it is a non-food plant that is easy to cultivate, grows rapidly, and requires minimal operational costs [17, 18].

The rationale for this study lies in the limited utilization of *Calophyllum inophyllum* oil, despite its considerable potential as a replacement for fossil fuels. Previous investigations commonly utilized acids and bases as catalysts, whereas there's limited research on employing modified zeolite and bentonite in *Calophyllum inophyllum* oil production. Despite their potential for higher yields compared to acids and bases, these modified catalysts are rarely explored in prior studies. An additional advantage of modified heterogeneous catalysts is the ease of separating the catalyst after the reaction, enabling its reuse and preventing any waste generation from the catalyst. This differs from the biodiesel production process using acid-base catalysts, which produces waste acids and bases during the separation of biodiesel products from the leftover catalyst. Hence, our research identifies a gap in the extant research in utilizing modified zeolite and bentonite as promising catalysts for achieving greater yields. In addition to these factors, the use of modified zeolite and bentonite as catalysts for producing biodiesel from *Calophyllum inophyllum* oil offers various innovative aspects that can enhance the efficiency and sustainability of the process. Here are some of the innovative aspects of this approach [15, 17-19]:

1. Use of Nature-Based Materials
 - Zeolite: Zeolite is a natural mineral with an excellent porous structure, allowing it to function as a catalyst with high absorption and selectivity capabilities. By modifying zeolite, we can enhance its catalytic activity in the transesterification of *Calophyllum inophyllum* oil.
 - Bentonite: Bentonite is a clay rich in montmorillonite, which can be modified to improve its catalytic properties. This modification often involves changes to the surface structure or the addition of active materials.
2. Catalyst Modification
 - Metal Addition: Modifying zeolite and bentonite with transition metals or other active metals can enhance their catalytic capabilities for the transesterification reaction. These metals can act as active centers for the chemical reaction.
 - Enhancing Acid/Base Properties: Chemical or physical modifications to zeolite and bentonite can improve the acid or base properties of the catalyst, which are crucial for speeding up the transesterification process.
3. Energy Efficiency
 - Low-Temperature Reaction Process: By using modified catalysts, the transesterification process of *Calophyllum inophyllum* oil can be carried out at lower temperatures compared to conventional catalysts, reducing energy consumption and operational costs.
 - Reusable Catalysts: Modified zeolite and bentonite generally exhibit good stability and can be reused across multiple reaction cycles without significant loss of catalytic activity.
4. Use of Renewable Resources
 - *Calophyllum inophyllum* oil: *Calophyllum inophyllum* oil is a renewable raw material, and utilizing modified zeolite and bentonite-based catalysts supports an environmentally friendly biodiesel production process.
5. Improvement in Biodiesel Quality
 - Purification and Product Quality: Modified catalysts can enhance the conversion of oil into biodiesel, resulting in higher quality biodiesel, including improved purity and physical characteristics that meet standards.
6. Waste Reduction
 - Minimized By-Products: The use of efficient catalysts can reduce the amount of by-products and waste, making the process cleaner and more environmentally friendly.
7. Availability and Cost
 - Affordable Catalysts: Zeolite and bentonite are relatively inexpensive materials that are abundantly available in Indonesia, so modifying them for use as catalysts in biodiesel production can reduce raw material and operational costs.
8. Adaptive Catalyst Design
 - Customizable Catalysts: Modifying zeolite and bentonite allows for adjustments to meet specific needs in the transesterification process, such as tailoring pore size or surface properties to enhance reactivity with *Calophyllum inophyllum* oil.

Overall, the innovation in using modified zeolite and bentonite as catalysts for producing biodiesel from *Calophyllum inophyllum* oil offers great potential to enhance process efficiency, reduce costs, and support sustainability in biodiesel production [17, 18]. The modification of zeolite and

bentonite for catalytic applications in biodiesel production involves several unique and innovative aspects that can provide significant benefits for the advancement of biodiesel production technology. Here is a description of the uniqueness of these modifications, their application mechanisms, and innovations.

Uniqueness of Zeolite and Bentonite Modifications

1. Porous Structure and Catalytic Properties
 - Zeolite: Zeolite features a crystalline structure with regular pores and specific pore sizes, allowing it to act as a catalyst with high absorption capacity and good reaction selectivity. Modifying zeolite can enhance its acid or base properties, increase pore size, or add active metals to accelerate transesterification reactions.
 - Bentonite: Bentonite is a clay with a laminar structure providing a large surface area for chemical interactions. Modifications typically involve changes in chemical composition or the addition of active materials to improve catalytic capacity [12-14].
2. Chemical and Physical Modifications
 - Zeolite: Chemical modifications, such as ion exchange and the addition of transition or other active metals, can enhance catalytic properties. Zeolites modified with active metals (e.g., Cu, Ni) can improve catalytic activity in transesterification reactions.
 - Bentonite: Modifications may include altering the structure or surface properties by adding activating agents or using techniques like filtering or precipitation to change acid/base properties and enhance catalytic activity [13, 14, 17].

Mechanisms of Catalyst Modification with Hydrochloric Acid

Specific Activation of Zeolite and Bentonite Catalysts Using Hydrochloric Acid (HCl) The modification of zeolite and bentonite catalysts with hydrochloric acid aims to improve the catalytic properties of these materials through several key mechanisms:

1. Removal of Impurity Cations
 - Mechanism: HCl interacts with alkali or alkaline earth metal cations trapped in the structure of zeolite or bentonite. These cations include sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}).
 - Reaction: HCl ionizes and releases H^+ ions, which replace the cations in the material's structure, resulting in the release of these cations as dissolved chlorides (e.g., NaCl, KCl).
 - Outcome: This process enhances the acidity of active sites in zeolite or bentonite and improves their catalytic activity.
2. Dealumination
 - Mechanism: Dealumination is the removal of aluminum (Al) from the crystalline framework of zeolite or bentonite. Under certain conditions, H^+ ions from HCl can attack and extract Al^{3+} from the framework, which is then carried away as AlCl_3 or related compounds.
 - Reaction: The process can be described by the reaction: $\text{Al-O-Si} + 3\text{H}^+ \rightarrow \text{H-O-Si} + \text{Al}^{3+}$, where the released Al^{3+} forms complexes with Cl^- ions from HCl.
 - Outcome: Removal of aluminum increases the number of Bronsted acid sites on the material's surface, enhancing acid properties and catalytic ability,

particularly for reactions requiring high acidity.

3. Increased Surface Area
 - Mechanism: HCl can remove amorphous material or unstructured components covering the pore surfaces of zeolite or bentonite. This process opens up more access to active sites within the material's pores.
 - Reaction: HCl dissolves metal oxides or other unstructured components that might obstruct the pores.
 - Outcome: The specific surface area of the material increases, enhancing its ability to act as a catalyst.
4. Modification of Crystal Structure
 - Mechanism: Under certain conditions, acid treatment can cause changes in the crystal structure of zeolite or bentonite, such as in pore size or distribution.
 - Reaction: This can occur through delamination or recrystallization due to the high acidity of HCl.
 - Outcome: These changes can produce materials with an optimal structure for specific catalytic applications, such as cracking or isomerization.
5. Removal of Organic Impurities
 - Mechanism: HCl can also help remove organic impurities present in zeolite or bentonite, which might affect catalytic efficiency.
 - Reaction: HCl reacts with organic compounds, especially if they are basic, forming salts that dissolve in the acid solution.
 - Outcome: Removal of these impurities improves catalyst activity by preventing blockage of active sites.

Based on the above description, modifying zeolite and bentonite with hydrochloric acid significantly enhances acidity, surface area, and catalytic activity, making them more effective for various catalytic applications [12, 15, 17-19]. Variations in HCl concentration during modification significantly affect the physical and chemical properties of the resulting catalysts. Factors influenced by HCl concentration include acidity, structural stability, surface area, adsorption capacity, and overall catalytic properties. Low concentrations of HCl moderately increase acidity without damaging the structure, while higher concentrations significantly enhance acidity and surface area but risk damaging the material's structure. Therefore, optimizing HCl concentration is necessary to balance increased acidity with structural stability for specific catalytic applications. The optimal HCl concentration for modifying zeolite is typically between 0.1 M and 2 M, while for bentonite, it ranges from 0.5 M to 3 M. Adjustments should consider material type, modification goals, and treatment conditions (time and temperature) to balance catalytic activity enhancement with maintaining material structural stability. In this study, zeolite and bentonite were modified using a 0.5 M HCl solution, which represents the optimum concentration for modifying both zeolite and bentonite.

Modification Application Mechanisms

1. Modification Processes
 - Zeolite:
 - Ion Exchange: This process replaces sodium ions in zeolite with active metal ions such as K^+ , Ca^{2+} , or other transition metals to enhance catalytic activity.
 - Metal Impregnation: Involves adding active metals to zeolite, which can improve catalytic capability for specific reactions.
 - Bentonite:
 - Addition of Catalytic Agents: Adding active

materials such as metals or acids/bases to the surface of bentonite to improve catalytic activity.

- Activation or Treatment: Methods like heating or using chemicals to alter the surface properties of bentonite, enhancing its catalytic ability [16-18].
- 2. Application in Biodiesel Production
 - Transesterification: Modified zeolite and bentonite are used in the transesterification process to convert Calophyllum inophyllum oil into biodiesel. These catalysts help accelerate the reaction between triglycerides and methanol or ethanol, producing methyl or ethyl esters (biodiesel) and glycerol.
 - Batch and Continuous Processes: Modified catalysts can be applied in both batch and continuous processes. They can be adapted for different reactor types, such as flow reactors or batch reactors [17-19].

Innovations for Technological Advancement

1. Energy Efficiency and Cost
 - Low-Temperature Processes: Modified catalysts enable reactions to occur at lower temperatures, reducing energy consumption and operational costs.
 - Recovery and Reusability: Modified catalysts generally have good durability and can be reused across multiple reaction cycles, reducing the need for new materials and lowering production costs [17-19].
2. Improved Biodiesel Quality
 - Purification: Modified catalysts enhance the conversion of oil to biodiesel, resulting in high-quality biodiesel that meets stringent quality standards [13, 14].
3. Waste Reduction and Environmental Impact
 - Minimized By-Products: Efficient catalysts reduce the amount of by-products and waste, making the process cleaner and more environmentally friendly.
4. Adaptation for Various Feedstocks
 - Flexibility: Modifications to zeolite and bentonite allow adaptation to various types of feedstocks, not just Calophyllum inophyllum oil but also other vegetable oils, expanding the technology's application and flexibility [14, 15].
5. Integrated Catalyst Design
 - Multi-Functional Catalysts: Development of catalysts with multifunctional capabilities, such as those that can perform multiple reactions simultaneously (e.g., transesterification and free fatty acid removal), improves process efficiency and reduces additional processing steps [18, 19].

Overall, modifying zeolite and bentonite for catalytic applications in biodiesel production offers significant advantages in efficiency, cost, and environmental impact. This innovative approach has the potential to drive technological progress in the biodiesel industry and enhance the sustainability of renewable energy production.

Life Cycle Assessment (LCA) Results for Zeolite and Bentonite Catalysts Modified with Acid

The Life Cycle Assessment (LCA) for zeolite and bentonite catalysts modified with acid involves a thorough evaluation of environmental impact, energy consumption, and emissions throughout the entire life cycle of these catalysts. Below are the analysis and strategies to optimize the process to reduce environmental impact:

1. Energy Consumption
 - Production Stage

- Extraction and Processing of Raw Materials: The energy required to mine and process zeolite and bentonite includes activities such as drilling, grinding, and drying. These activities require significant energy consumption.

- Acid Modification: The acid modification process, including heating and chemical use, requires additional energy. Chemical reactions and separation processes also contribute to energy consumption.

○ Usage Stage

- Catalyst Activation: If catalysts need to be activated before use, for example through heating, this also adds to energy consumption. However, this stage is usually lower compared to production.

- Process Efficiency: Efficient catalysts allow biodiesel transesterification to occur at lower temperatures, reducing energy requirements in biodiesel production.

○ Optimization Strategies

- Energy Efficiency: Apply energy-efficient technologies in the modification and activation processes, such as using high-efficiency heaters or heat recovery systems.

- Renewable Energy Use: Consider using renewable energy sources, such as solar or geothermal energy, in the production and modification processes [15-17].

2. Environmental Impact

○ Production Stage

- Chemical Use: Acid modification involves chemicals that can potentially be hazardous. Proper handling and effective waste management methods are needed to minimize environmental impact.

- Environmental Degradation: Mining and processing raw materials can cause environmental damage such as habitat disruption and soil or water pollution.

○ Usage Stage

- Catalyst Efficiency: More efficient catalysts reduce the amount of raw materials needed and decrease by-product production, which positively impacts the environment.

- Recycling and Reuse: Catalysts that can be recycled or reused reduce waste and the environmental impact of biodiesel production.

○ Optimization Strategies

- Green Chemistry: Use less hazardous acids and chemicals in the modification process. Develop effective waste management solutions.

- Sustainable Mining Practices: Implement environmentally friendly mining practices to reduce the environmental impact of raw material extraction [13-15, 17].

3. Emissions

○ Production Stage

- Air Emissions: The acid modification process can produce emissions such as volatile organic compounds (VOCs) and hazardous gases. Effective emission control and ventilation systems are required.

- Water Pollution: The use of acids and other chemicals can generate liquid waste that needs treatment to prevent pollution.

○ Usage Stage

- Emissions During Use: Efficient catalysts produce fewer emissions during the biodiesel production process compared to conventional catalysts.

- Optimization Strategies
 - Emission Control: Implement effective emission control technologies to capture and treat gases and pollutants from the production process.
 - Waste Treatment: Apply efficient waste treatment systems to manage liquid and solid waste from the modification process [13, 15-18].
- 4. Overall Process Optimization
 - Environmentally Conscious Design
 - Sustainable Catalyst Design: Design catalysts with a focus on efficiency, durability, and recyclability. Choose materials and processes that minimize environmental impact.
 - Recyclability: Ensure that catalysts can be recycled or reused efficiently to reduce waste.
 - Ongoing Evaluation and Improvement
 - Periodic Assessment: Conduct Life Cycle Assessments (LCA) regularly to identify areas for improvement in the catalyst life cycle.
 - Technological Innovation: Invest in research and development to create cleaner and more efficient modification and production processes.
 - Stakeholder Engagement
 - Collaboration: Work with stakeholders such as suppliers, customers, and regulators to promote environmentally friendly practices and sustainability in catalyst production [17-20].

By implementing these strategies, the environmental impact of producing and using zeolite and bentonite catalysts modified with acids can be minimized, contributing to a more sustainable and environmentally friendly biodiesel production process.

2. LITERATURE REVIEW

Calophyllum inophyllum can be obtained through several stages of processing [9].

1. Peeling the seeds from their hard shells.
2. Slicing them thinly.
3. Sun-drying for two days.
4. Crushing and steaming for 2 hours.
5. Pressing with a manual hydraulic machine or extruder, resulting in dark-colored oil due to impurities from the skin and chemical compounds like alkaloids, phosphatides, carotenoids, chlorophyll, and others. Pressing 2.5 kg of dried seed material without skins yields 1 liter of Calophyllum inophyllum oil.
6. Removal of latex, which involves separating latex and impurities from the oil using a 1% phosphoric acid solution.
7. Filtration, which separates oil from impurities to obtain clear oil.

The characteristics of Calophyllum inophyllum before and after latex removal are shown in Table 1 [20].

The composition of fatty acids constituting Calophyllum inophyllum can be seen in Table 2 [21].

The free fatty acid content of Calophyllum inophyllum before latex removal is very high. This is due to the fact that Calophyllum inophyllum comes from seeds that have aged, where the oxidation process of the oil has already begun while they are still in seed form. Through the latex removal process, the free fatty acid content will decrease, as will the values of several other parameters [22].

Table 1. The physical and chemical properties of Calophyllum inophyllum oil

Parameter	Before Latex Removal	After Latex Removal
Mositure content (%)	0.25	0.41
Density 20°C (g/mL)	0.944	0.940
Viskosity (cP)	56.7	53.4
Acid number (mg KOH/g)	198.1	194.7
Iod number (mg/g)	86.42	85.04
Refraktif index	1.447	1.478
Appearance	Dark green, thick, and pungent odor	Thick reddish-yellow

Table 2. The fatty acid composition of Calophyllum inophyllum oil

Fatty Acid	Composition
Palmitoleat acid (C16:1)	0.5 - 1 %
Palmitat acid (C16)	15 - 17 %
Oleat acid (C18:1)	30 - 50 %
Linoleat acid (C18:0)	25 - 40 %
Stearat acid (C18:0)	8 - 16 %
Arachidat acid (C20)	0.5 - 1 %
Gadoleat acid (C19:1)	0.5 - 1 %

The decline in viscosity and density values occurs because of the elimination of latex and impurities from the oil solution. The drop in saponification number is due to the introduction of phosphoric acid, while the decrease in iodine number is linked to the reduction in the quantity of unsaturated fatty acids resulting from the latex removal process. The outcome of the latex removal process manifests in a distinct color change of the oil, transitioning from dark green to shades of yellow and red.

After the latex removal process, Calophyllum inophyllum undergoes further processing, such as neutralization with NaOH, to transform it into biokerosene, which serves as a substitute for kerosene oil and is highly beneficial for heating purposes in rural communities [23]. As a fuel, it is evident that Calophyllum inophyllum exhibits a longer burning duration compared to kerosene oil, as experiments show that 1 ml of Calophyllum inophyllum burns for 11.8 minutes, while 1 ml of kerosene oil burns for only 5.6 minutes. Furthermore, during water boiling tests, it was found that 0.9 mL of kerosene oil was required, whereas only 0.4 mL of Calophyllum inophyllum was needed. These results indicate that Calophyllum inophyllum can be utilized as a household fuel source, providing significant benefits for daily use by communities.

Calophyllum inophyllum falls into the category of oils containing a mixture of saturated and unsaturated fatty acids with lengthy carbon chains. Its main components consist of oleic acid at 37.57%, linoleic acid at 26.33%, and stearic acid at 19.96%. The remainder includes myristic acid, palmitic acid, linolenic acid, arachidic acid, and erucic acid in smaller proportions [24].

The availability of nyamplung (Jatropha) raw materials for biodiesel production is quite promising, especially in Indonesia, where the nyamplung tree is widely spread across Java, Sumatra, Kalimantan, Sulawesi, and Nusa Tenggara. The Indonesian government has shown interest in the development of biofuels as part of its national energy strategy.

The development of nyamplung as a biodiesel source can be supported through structured development, including enhanced cultivation, seed processing, and government policies, including incentives for farmers and industries to grow and process nyamplung. With these measures, nyamplung can become a sustainable raw material source for biodiesel production in Indonesia [24, 25].

Biodiesel can be produced from both vegetable and animal oils. Vegetable oil and biodiesel belong to the same large group of organic compounds, namely the fatty acid ester group. Vegetable oil is a triglyceride of fatty acids with glycerol or triglyceride, while biodiesel is a fatty acid monoester with methanol. This difference in molecular structure has important consequences in assessing them as candidates for diesel engine fuel [25].

1. Vegetable oil (triglycerides) has a much larger molecular weight than biodiesel (methyl esters). This property causes triglycerides to relatively easily undergo cracking into various smaller molecules when heated without contact with air.
2. Vegetable oil has a much higher viscosity than diesel or kerosene as well as biodiesel, making it difficult for fuel injection pumps in diesel engines to produce good atomization when vegetable oil is sprayed into the combustion chamber.
3. Vegetable oil molecules are relatively more branched than fatty acid methyl esters, resulting in a lower cetane number for vegetable oil compared to methyl esters.
4. The cetane number is a measure of the ease of ignition or combustion of a fuel in a diesel engine.

Esterification is the process of converting free fatty acids into esters. This reaction involves combining fatty oils with alcohol. A suitable catalyst for this process is a substance with strong acidic properties, such as sulfuric acid, organic sulfonic acid, or strong acid cation exchange resin, which are commonly used catalysts in industrial applications [26].

To ensure that the reaction proceeds to complete conversion at low temperatures, an excess of methanol reactant must be added (usually greater than 10 times the stoichiometric ratio), and any water produced in the reaction must be removed from the oil phase. Through the appropriate combinations of reaction conditions and methods for removing water, the complete conversion of fatty acids to their methyl esters can be achieved within a few hours. The esterification reaction can be seen in Figure 1 below [21].



Figure 1. Esterification reaction of Calophyllum inophyllum

Esterification is often used to create biodiesel from oils with high levels of free fatty acids (acid value of 5 mg-KOH/g). During this phase, free fatty acids are transformed into methyl esters. Following esterification, the next step is typically transesterification. However, prior to transferring the esterification products to the transesterification phase, it's essential to remove any water and the majority of the acid catalyst present [21].

Transesterification, commonly known as alcoholysis, is the process of converting triglycerides (vegetable oil) into alkyl esters by reacting with alcohol, resulting in glycerol as a by-product. Among monohydric alcohols considered as alkyl group suppliers, methanol is predominantly used due to its affordability and high reactivity (thus, referred to as

methanolysis). Therefore, biodiesel is essentially fatty acid methyl esters. The transesterification reaction of triglycerides into methyl esters is depicted in Figure 2.

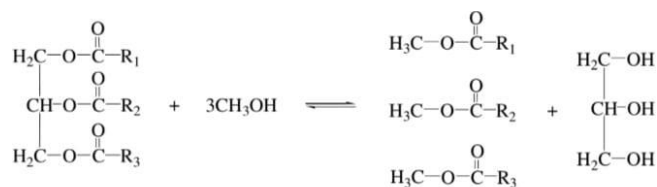


Figure 2. Transesterification reaction from triglycerides to methyl esters

Transesterification also involves the use of catalysts during its reaction phase. The presence of a catalyst maximizes the conversion attained, although the reaction proceeds slowly. Base catalysts are commonly employed in transesterification reactions because they accelerate the reaction. The objective of the transesterification reaction is to obtain fatty acid methyl esters. According to the principle of equilibrium reactions, there are various methods to shift the reaction equilibrium towards the products [27]:

1. Adding excess methanol to the reaction.
2. Separating glycerol immediately.
3. Lowering the reaction temperature (transesterification is an exothermic reaction).

Research into the production of biodiesel from *Calophyllum inophyllum* is increasingly undertaken by various researchers. Ilminafik and Sugara [28] conducted a study on biodiesel production from *Calophyllum inophyllum* using microwave heating, employing solid CaO catalyst at concentrations ranging from 2-6% of the oil weight. The objective of the research was to synthesize biodiesel from *Calophyllum inophyllum* through transesterification, with varying ratios of oil to methanol at 1:9 and 1:12, and microwave power levels at 100, 264, and 400 W. The study identified the optimal conditions for biodiesel yield to be 94% with a microwave heating power of 100 W, 4% catalyst concentration, and an oil to methanol molar ratio of 1:9 [28].

Atabani and da Silva César [29] conducted research on nyamplung seeds utilizing an esterification process with phosphoric acid to remove latex, yielding 85% *Calophyllum inophyllum*. This *Calophyllum inophyllum* was then converted into biodiesel through transesterification using ethanol and NaOH catalyst at 1% of the oil weight. Experimental conditions included a reaction temperature of 60°C and a reaction time of 60 minutes. The biodiesel obtained amounted to 80.89%, and its specifications met the SNI parameters. The subsequent study conducted by Demirbas et al. [21] utilized *Calophyllum inophyllum* and employed transesterification with methanol and 1.25% KOH catalyst, yielding biodiesel at 88.27% under reaction conditions of 60°C temperature and a reaction time of 121 minutes. The produced biodiesel met the specifications according to the SNI parameters [21].

Arumugam and Ponnusami [30] also conducted experiments on producing biodiesel from *Calophyllum inophyllum* using 1% solid KOH catalyst in a microwave reactor. The study aimed to explore the impact of microwave power, reaction time, and temperature on biodiesel yield. Transesterification was performed with varying microwave power levels of 100, 200, and 400 W, reaction times from 5 to 15 minutes, and temperatures from 50 to 70°C. The research

identified the most favorable conditions at 200 W power, 65°C reaction temperature, and 5 minutes reaction time, resulting in a biodiesel yield of 84.62%. Quality testing confirmed that the biodiesel met the SNI 04-7182-2006 standard. This investigation revealed that microwave irradiation could significantly accelerate the transesterification reaction, reducing the reaction time to 1/6 of the conventional method [30].

Subsequent research on biodiesel from *Calophyllum inophyllum* utilized a microwave reactor under reaction conditions of 60°C temperature and a duration of 60 minutes. The catalyst used was a liquid 1-butyl-3-methyl imidazolium hydrogensulphate (BMIMHSO₄) with an ion content of 15% of the oil weight. The study yielded biodiesel at 81.2%, and its specific characteristics met the SNI parameters [31].

The experiment conducted by Sema Aslan [32] for biodiesel production from rapeseed oil used a natural bentonite catalyst modified through calcination at 500°C for 2 hours, followed by impregnation with lithium acetate at 60°C for 24 hours, and then calcination at 500°C for 5 hours. The experiment results showed that the biodiesel yield was 98.80%. This result is better than that obtained with unmodified bentonite catalyst.

In another experiment, Marso et al. [33] used a modified graphene oxide (GO/metal) composite catalyst containing Al³⁺ and Fe³⁺ ions for the pre-esterification of *Calophyllum inophyllum* oil. The results achieved a conversion of stearic acid to methyl stearate of 92.72% and a reduction in free fatty acid (FFA) content in *Calophyllum inophyllum* oil of 95.37%. This process also resulted in a decrease in acid number of 65.75% using non-surfactant materials, and a reduction of 95.37% with the help of surfactants.

Another study on biodiesel production from nyamplung (*Calophyllum inophyllum*) oil was conducted by Trisunaryanti et al. [34]. This experiment used Ni and Pt catalysts with an active carbon support derived from coconut shell. The results with the Pt catalyst produced the highest liquid yield of 84.77 wt%, with the best hydrocarbon selectivity of 91 wt%, obtained at a hydrotreatment temperature of 550°C for 2 hours with a Pt catalyst to *Calophyllum inophyllum* oil ratio of 1:300. Using the Ni catalyst resulted in a lower liquid yield of 78.83 wt%, containing 86.2 wt% hydrocarbons under hydrotreatment conditions of 550°C for 2 hours and a Ni to oil ratio of 1:200. This study provided an alternative, cost-effective, and environmentally friendly process for producing high-quality biofuel from the abundant *Calophyllum inophyllum* oil, which could be explored for future development [35].

An interesting subsequent study for biodiesel production from *Calophyllum inophyllum* oil used a catalyst made from coconut sawdust impregnated with Ni. The catalyst was created by carbonizing coconut sawdust at 700°C for 2 hours under a nitrogen flow at a rate of 20 mL/min. It was then impregnated with nickel nitrate solution and calcined at 550°C. Using this catalyst for biodiesel production from *Calophyllum inophyllum* oil with a hydrotreatment process at 550°C for 2 hours resulted in a liquid yield of over 74% and a hydrocarbon content of 65% [36].

The next study on biodiesel production from nyamplung (*Calophyllum inophyllum*) oil used Ni and Pt catalysts with an active carbon support from coconut wood sawdust. The catalyst preparation was conducted both conventionally and using microwave heating. In the conventional method, the carbonization stage was performed at 700°C for 2 hours under inert nitrogen gas conditions with a flow rate of 20 mL/min,

followed by physical activation with carbon dioxide gas at a flow rate of 10 mL/min, a heating temperature of 500°C, and a time of 2 hours. In the microwave method, carbonization was done at 800 W for 10 minutes, followed by activation at 500°C for 1 hour under carbon dioxide flow conditions at a rate of 10 mL/min. Using monometallic Ni catalysts with microwave carbonization and activation for biofuel production resulted in a hydrocarbon yield of 15.85%, while monometallic Pt catalysts yielded less than 15.85% hydrocarbons. The use of bimetallic catalysts (2.5% Ni and 2.5% Pt) with microwave carbonization and activation yielded 33.1% hydrocarbons and a selectivity of 99.99% [36].

The various studies on biodiesel production from *Calophyllum inophyllum* mentioned above utilized both liquid and solid catalysts without any catalyst modification. The novelty of the research lies in the utilization of catalysts derived from natural materials that were subsequently modified. The modification of these catalysts aims to enhance the yield of biodiesel and ensure that its specifications meet the SNI test parameters.

In this study, the biodiesel production process from *Calophyllum inophyllum* was conducted using the transesterification process, which occurred in the liquid phase with heterogeneous catalysts zeolite and bentonite that were modified with acid and calcination. The resulting biodiesel was then analyzed for its characteristics according to SNI standards, including density, viscosity, cetane number, flash point, and methyl ester content.

3. METHODS

This study involves several phases: preparation of catalysts, extraction of *Calophyllum inophyllum* seeds using n-hexane solvent to obtain *Calophyllum inophyllum* and subsequent analysis of its characteristics, esterification stage to reduce the free fatty acid content in *Calophyllum inophyllum*, and transesterification stage to produce biodiesel. The yield of the resulting biodiesel is then calculated. The biodiesel with the highest product yield is further analyzed for its characteristics according to the American Society for Testing and Materials (ASTM) procedures and follows the requirements of the Indonesia National Standard (SNI) for biodiesel (SNI 04-7182-2006), including viscosity, density, cetane number, flash point, and methyl ester content. The types of modified catalysts (i.e., zeolite, bentonite, and a mixture of zeolite and bentonite) and the transesterification reaction temperature were chosen as factors in this study.

Below are the research steps:

1. Materials

The primary materials used in this study include *Calophyllum inophyllum* fruit obtained from the Ampel area of Surabaya and moisture of crushed seeds was removed under natural sunlight, natural zeolite and bentonite obtained from Pacitan, East Java, Indonesia. The reagents used include n-hexane, hydrochloric acid (purity 33%), and methanol Merck (purity 99.9%), sourced from PT. Kurniajaya, Surabaya.

2. Preparation of modified catalysts

The modified heterogeneous catalysts used were zeolite and bentonite. Prior to use, natural zeolite and bentonite was crushed using a JUNKE and KUNKEL micro hummer mill to obtain zeolite and bentonite with particle size of 170/240 mesh. Subsequently, the zeolite

and bentonite was treated with 30% of hydrogen peroxide solution to remove the organic impurities. Excess of hydrogen peroxide solution was removed by gently heating in a water bath and the solution was separated from the zeolite and bentonite. The purified zeolite and bentonite was repeatedly washed and dispersed in distilled water. After the water have been separated from zeolite and bentonite, the purified zeolite and bentonite was then dried in an oven at 110°C for 24 hours to remove moisture content from its structure. The dried zeolite and bentonite was finally crushed in a micro hummer mill to obtained powder zeolite with particle size of 170/240 mesh. Modification of zeolite and bentonite were prepared with HCl solution. A brief procedure of catalyst preparation is as follows: 100 g of natural zeolite powder was weighed and placed into a three-neck flask. Then, 400 mL of 0.5 M HCl solution was added until all the zeolite powder was submerged. The mixture was then heated to 100°C and stirred for 24 hours. Subsequently, zeolite and HCl solution was separated by filtration using a vacuum filter system. The zeolite catalyst was then oven-dried at 110°C for 24 hours and the resulting zeolite solid was calcined at 550°C for 4 hours. The same procedure was carried out for bentonite.

3. Calophyllum inophyllum extraction

The extraction process of dried Calophyllum inophyllum seeds was conducted to obtain Calophyllum inophyllum oil using n-hexane solvent with a ratio of 1:4 (weight:volume) by the Soxhlet method. The extracted oil was separated from the solvent mixture by distillation at 110°C for an hour to obtain Calophyllum inophyllum oil [31].

4. Analysis of free fatty acid content in Calophyllum inophyllum

A total of 10 g of Calophyllum inophyllum was weighed and mixed with 25 mL of neutral 96% alcohol. The mixture was heated in a water bath until boiling, then cooled to room temperature and 2 drops of phenolphthalein indicator were added. This solution was then titrated using 0.1 N NaOH solution until it turned pink, and then the content of free fatty acids in the Calophyllum inophyllum was calculated. This testing was also conducted on the oil resulting from the esterification process [31].

5. Esterification

The esterification process aims to decrease the free fatty acid content by reacting Calophyllum inophyllum with methanol at a molar ratio of 1:20 using a potent acid catalyst, specifically concentrated HCl. Calophyllum inophyllum is combined with 370 mL of methanol in a three-necked flask, and concentrated HCl, acting as the catalyst, is added at a quantity equivalent to 10% of the oil volume. The mixture undergoes a 2-hour reaction at 60°C. Upon completion of the reaction, the resulting methyl esters are separated from the mixture using a separating funnel, and the product is then analyzed to determine its free fatty acid level [37].

6. Transesterification

Transesterification of Calophyllum inophyllum oil into biodiesel was carried out in a 500 mL three-neck flask equipped with reflux condenser, temperature indicator, and controlled water bath heater. The transesterification reaction is carried out by adding modified catalysts, namely zeolite and bentonite. The molar ratio used

between Calophyllum inophyllum oil and methanol is 1:6, with the catalyst amounting to 10% of the oil's weight. In this study, 100 mL of Calophyllum inophyllum oil resulting from esterification is placed in a three-necked flask and mixed with 24.3 mL of methanol and 10% of the weight of modified zeolite or bentonite catalyst. The mixture is then stirred using a magnetic stirrer, and the reaction takes place for 5 hours at various temperatures, namely 50, 60, 65, and 70°C. After the reaction is completed, the mixture is filtered using a Buchner funnel under vacuum condition to separate the catalyst from the biodiesel and glycerol mixture. The biodiesel and glycerol are then separated using a separating funnel. The resulting biodiesel is subsequently dried in a vacuum rotary evaporator to remove its water content and the excess methanol. Biodiesel product was then repeatedly washed using warm distilled water (60°C). The fatty acid methyl ester or FAME layer (upper layer) was separated from water layer (bottom layer) using a separating funnel. The yield and characteristics of the resulting biodiesel are then analysed and calculated.

7. Characterization of biodiesel and catalyst

The biodiesel product obtained is subjected to characterization testing under conditions of maximum biodiesel yield, following SNI and ASTM parameters, including density, viscosity, flash point, cetane number, and methyl ester content. Density testing is performed using a pycnometer according to ASTM D1298, viscosity testing with a Brookfield Viscometer spindle no.21 at 100 rpm according to ASTM D445-10, 2010, flash point with a Pensky Marten Closed Tester according to ASTM D93, cetane number with a Cetane Number Tester GD-R3035 following ASTM D613 and D6887, while the fatty acid methyl ester content is analyzed using Gas Chromatography (GC Shimadzu 2014). The GC was equipped with a DB-wax Capillary column (30 m × 0.25 mm i.d. × 0.1 m film thickness, Agilent JW Scientific) and flame ionization detector (FID). Helium was employed as carrier gas at 40 cm/s. The injector temperature was 250°C at splitless condition. The FID was set at 300°C. The initial oven temperature was set at 50°C with equilibration time of 3 min. After isothermal period, oven temperature was increased to 250°C at heating rate of 10°C/min and held for 8 min. Peaks of methyl esters were identified by comparing them with the reference standard. The yield of biodiesel was determined by the following equation:

$$\text{Yield (\%)} = \frac{(\text{weight of biodiesel} \times \% \text{FAME in sample}) \times 100\%}{(\text{weight of Calophyllum inophyllum oil})} \quad (1)$$

These FAME tests are conducted at the Pertamina laboratory in Jagir, Surabaya. The limitations of this research are the characterization of modified zeolite and bentonite catalysts includes X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) tests conducted at the Energy Laboratory, Sepuluh Nopember Institute of Technology, Surabaya. Characterization analysis using X-ray Photoelectron Spectroscopy (XPS) was not employed. XRD testing utilizes a Philips X-pert Powder Analytical diffractometer with an X-ray diffractometer operating at 30 kV and 15 mA, with 2θ measurements ranging from 5° to 90°. While FTIR employs an Invenio-Bruker Corp. spectrometer.

4. RESULTS AND DISCUSSIONS

4.1 Calophyllum inophyllum oil analysis

The physical and chemical properties of Calophyllum inophyllum oil were determined using standard test methods. These include density (ASTM D1298, 2005), kinematic viscosity (ASTM D445-10, 2010) and free fatty acid content (ASTM D93, 2010).

The extracted Calophyllum inophyllum oil used as the raw material for biodiesel production exhibits characteristics as shown in Table 3.

Table 3. Calophyllum inophyllum characteristics

Parameter	Unit	Value
Density	g/cm ³	0.92
Kinematic viscosity	cP (on 25.6°C)	98
Free fatty acid	(%)	26.27

The Calophyllum inophyllum oil does not meet the criteria as a raw material for biodiesel production because its free fatty acid content exceeds 2%. Therefore, an esterification process is required for the Calophyllum inophyllum oil to meet the criteria as a raw material for biodiesel production, which is to reduce the free fatty acid content to the appropriate range for transesterification in biodiesel production. The requirement for oil to be used as a biodiesel feedstock is to have a maximum free fatty acid content of 2% [37].

Table 4 below presents the characteristics of Calophyllum inophyllum oil after undergoing the esterification process. From the results of the esterification stage conducted on the Calophyllum inophyllum oil, a decrease in the free fatty acid content to 1.71% was obtained. Therefore, the Calophyllum inophyllum oil resulting from the esterification process can be used as a raw material for biodiesel production to be further processed by transesterification.

Table 4. Calophyllum inophyllum oil after esterification

Parameter	Unit	Value
Density	g/cm ³	0.90
Kinematic viscosity	cP (on 25.6°C)	45
Free fatty acid	%	1.71

4.2 Modified catalysts characteristics

The modified catalysts were analyzed using X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) for characterization. XRD diffraction analysis was performed to identify the internal structure, bulk phase and crystallinity of the catalyst. XRD was employed to identify the Si/Al (Silica/Aluminum) compound content in both catalyst types. The XRD characterization results are depicted in the figure below.

Figures 3 and 4 depict the XRD analysis results for natural zeolite and after modification with acid, respectively.

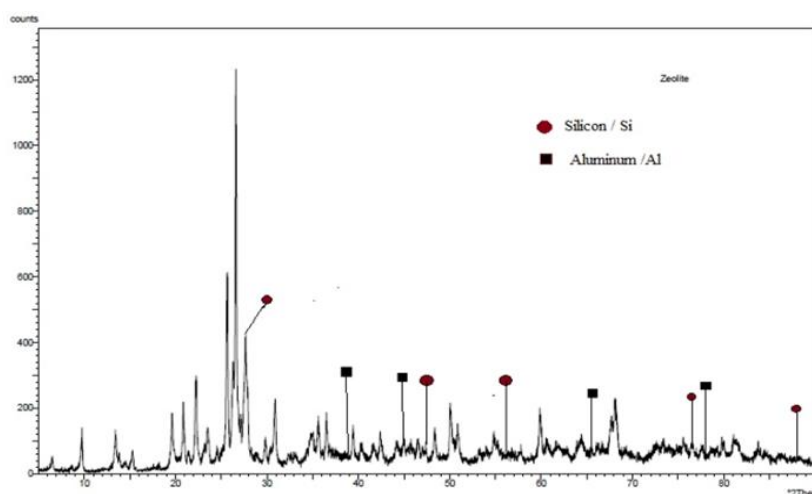


Figure 3. XRD results of natural zeolite

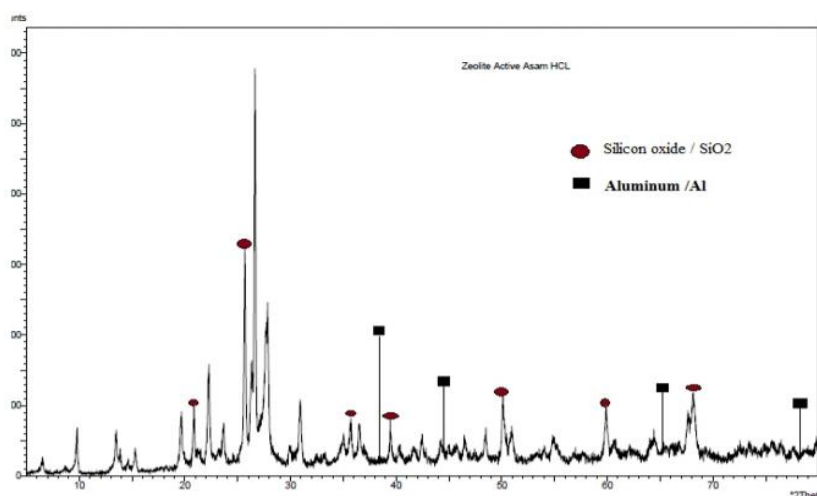


Figure 4. XRD results of modified zeolite

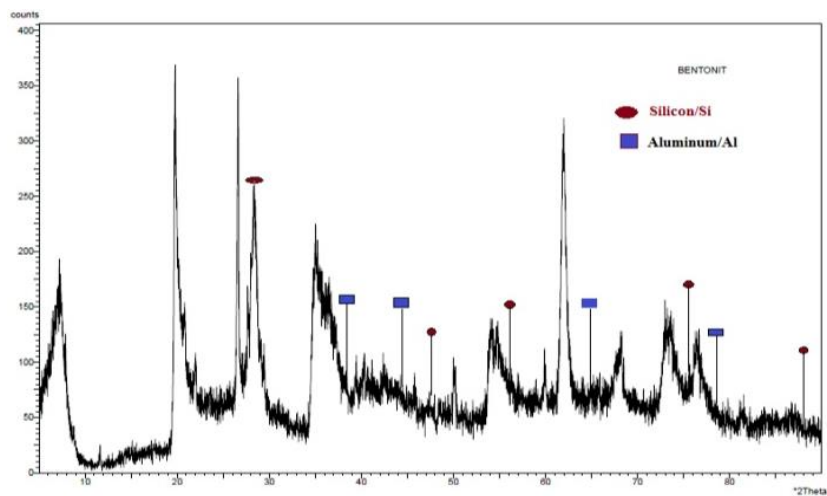


Figure 5. XRD results of natural bentonite

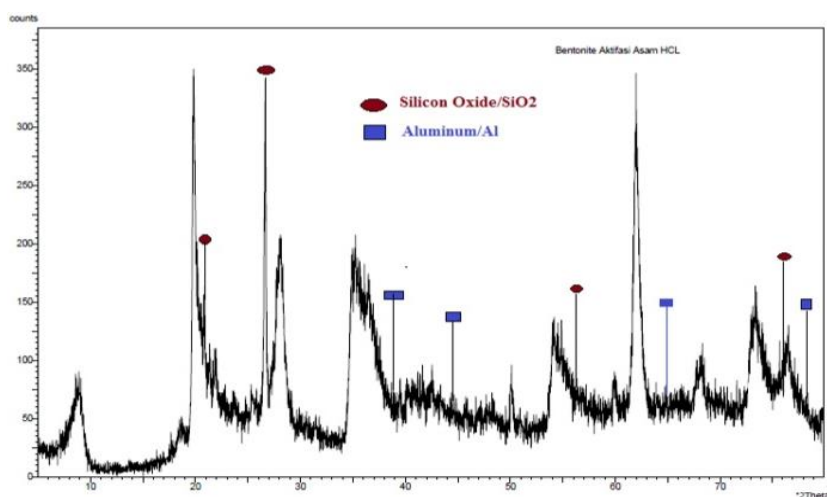


Figure 6. XRD results of modified bentonite

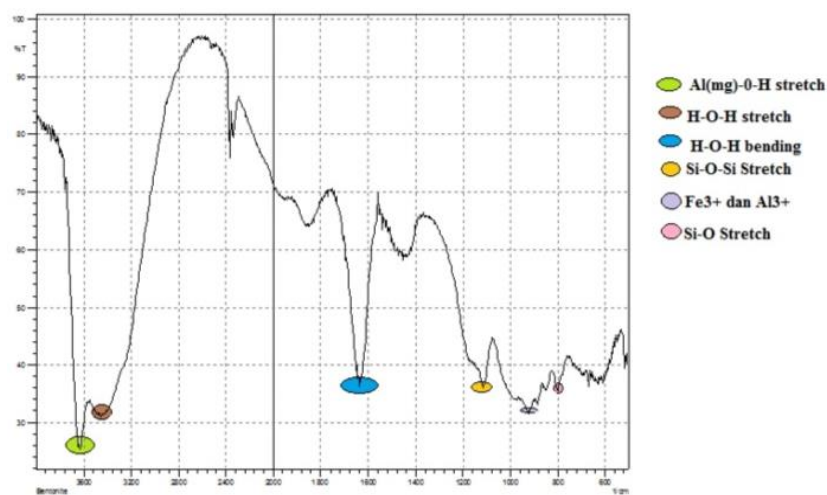


Figure 7. FTIR results of natural bentonite

Subsequently, Figures 5 and 6 show the XRD analysis results for natural bentonite and after modification with acid. The XRD characterization analysis results indicate a change in the characteristics of both catalysts before and after modification. This can be observed in Figures 3 and 4 for Zeolite. A comparison of these two figures shows a change in the Si content, with more SiO₂ compound formed, while the

Al compound decreases. This is consistent with the principle of catalyst activation with acid, which involves releasing Al atoms to optimize the aluminum content in the catalyst, thereby enhancing its catalytic properties and absorption. Silicon oxide and aluminium oxide is believed to play an important role during the transesterification of oil into fatty acid methyl esters since it has high catalytic activity.

A similar trend is evident in Figure 5 and Figure 6 regarding the bentonite catalyst, showing an augmentation in SiO_2 content following the modification process. However, the alterations resulting from the modification of both catalysts are not prominently observable due to the relatively low acid concentration utilized for the catalyst modification.

Figures 7 and 8 depict the FTIR analysis results for natural

bentonite and its modified form.

Next, Figures 9 and 10 show the FTIR analysis results for natural zeolite and its modified form. Catalyst characterization with FTIR aims to identify the functional groups present in both types of catalysts before and after the acid modification process.

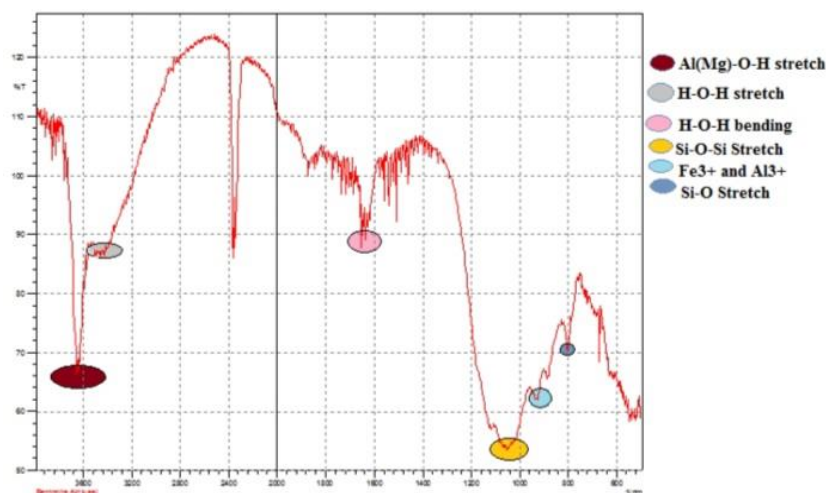


Figure 8. FTIR results of modified bentonite

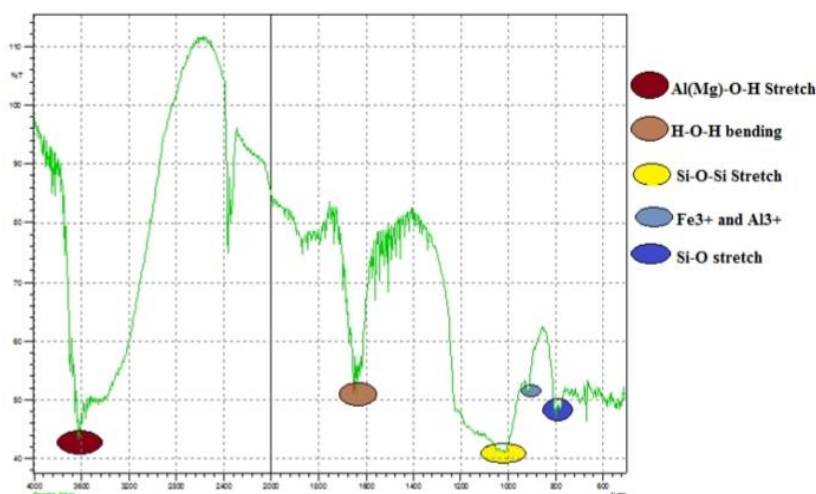


Figure 9. FTIR results of natural zeolit

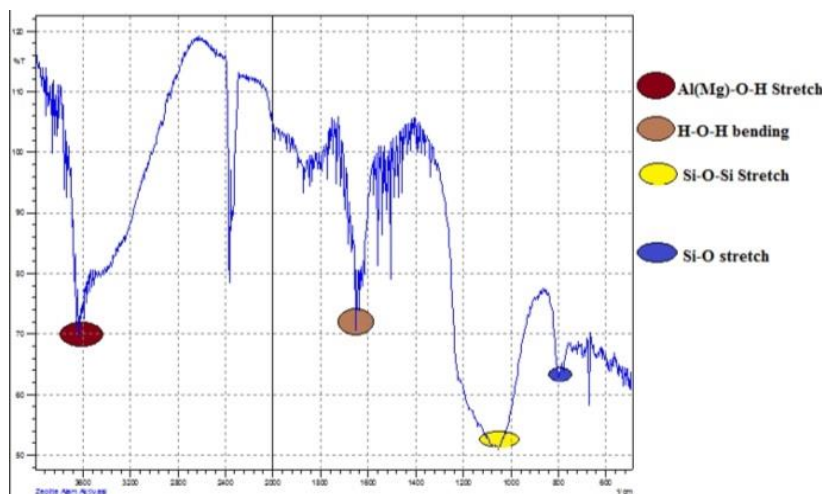


Figure 10. FTIR results of modified zeolite

Based on the FTIR analysis results, it is observed that no new functional groups are formed on the catalyst. Modification using acid causes an increase in bond strength, as indicated by the increase in transmittance percentage at certain wavelengths from the FTIR analysis results. However, this increase is not significantly visible due to the relatively low concentration of acid used.

4.3 The effect of reaction temperature on the yield of biodiesel production

The transesterification of *Calophyllum inophyllum* oil using modified zeolite and bentonite as catalysts were performed under following conditions: catalyst amount 10%, ratio of *Calophyllum inophyllum* oil to methanol 1:6, reaction temperature 50, 60, 65 and 70°C and reaction time 5 hours. The influence of reaction temperatures of 50, 60, 65, and 70°C on the yield of biodiesel produced using modified zeolite catalysts, modified bentonite, and a mixture of modified zeolite and bentonite in a 50:50 ratios is shown in Table 5.

Table 5. Biodiesel yield produced using modified catalysts

The Type of Catalyst and the Ratio of Catalyst Amounts	The Yield of Biodiesel Based on Reaction Temperature			
	50°C	60°C	65°C	70°C
Modified Zeolit (100:0)	78.36	88.19	83.19	81.15
Modified Bentonit (100:0)	67.73	78.84	72.09	70.58
Modified Zeolit and Bentonit (50:50)	70.83	82.36	75.49	73.11

Based on the data, it appears that increasing the transesterification reaction temperature from 50°C to 60°C leads to an increase in the yield of biodiesel. However, further increases in the transesterification reaction temperature above 60°C to 70°C result in a decrease in biodiesel yield.

At a temperature of 60°C, the highest yield of biodiesel was obtained for the three types of catalysts used. The highest biodiesel yield achieved was 88.19% with modified zeolite catalyst, 78.84% with modified bentonite catalyst, and 82.36% with a mixture of modified zeolite and modified bentonite catalysts in a 1:1 ratio.

4.4 The influence of modified catalyst type on the yield of biodiesel production

The experiment results indicate that the type of modified catalyst used in the transesterification process influences the yield of biodiesel obtained, as shown in Table 5. The use of modified zeolite catalysts yields a greater amount of biodiesel compared to modified bentonite catalysts and a mixture of modified zeolite and bentonite at a 50:50 ratio. This trend is observed across various transesterification reaction temperatures ranging from 50, 60, 65, to 70°C. This phenomenon occurs due to the differences in properties and characteristics among the three types of modified catalysts used in the transesterification process.

One distinguishing feature of zeolite, functioning as an adsorbent, is its expansive surface area and micro-sized pores. Bentonite, another adsorbent, possesses a surface area smaller than zeolite, with macro-sized pores. These qualities play a crucial role in the transesterification reaction, especially since the oil used often contains high levels of fatty acids due to its elevated water content. Zeolite's adsorbent nature significantly

aids in water absorption during the transesterification process, leading to a higher biodiesel yield compared to bentonite. This aspect underscores bentonite's drawback, resulting in its comparatively lesser influence on biodiesel yield when compared to zeolite catalysts.

Based on the yield of the biodiesel products obtained, there is a noticeable relationship between the surface characteristics of the catalysts and their reactivity. The factors affecting the biodiesel yield include surface acidity, pore structure, surface area of the catalyst, and the effects of catalyst modification [12-18].

4.4.1 Effect of surface acidity on modified catalysts

For modified zeolite catalysts, they generally have high surface acidity due to the presence of Bronsted and Lewis acid sites. These acid sites can enhance the transesterification reaction by providing active sites for the formation of intermediate products. The presence of strong acid like HCl used in the modification can promote the formation of reactive species from triglycerides and methanol, thereby increasing the rate of the transesterification reaction.

Modified bentonite catalysts, which are clay minerals, can have varying levels of acidity depending on the modifications performed. Modification with strong acid like HCl increases the acidity of the modified bentonite catalyst. This acidic nature can enhance the reaction by providing acidic sites that catalyze the transesterification reaction. However, the biodiesel yield with modified bentonite catalysts is lower than with modified zeolite catalysts because the acidity level of bentonite is lower than that of zeolite, affecting reactivity and biodiesel yield.

4.4.2 Effect of pore structure on modified catalysts

Modified zeolite catalysts have a well-defined pore structure and large surface area. These properties significantly impact accessibility to active sites, which can enhance the transesterification reaction, thus improving biodiesel yield. Modified bentonite catalysts have irregular pore structures, and while acid activation increases their surface area, it is not as extensive as that of modified zeolite catalysts. The irregular pore structure of modified bentonite can affect the diffusion rate of reactants and products, making its performance in transesterification less effective compared to modified zeolite catalysts.

4.4.3 Effect of surface area on modified catalysts

Modified zeolite catalysts have a larger surface area, providing more active sites for the transesterification reaction. A larger surface area enhances the interaction between reactants and catalysts, leading to a higher biodiesel yield. Modified bentonite catalysts have a smaller surface area compared to modified zeolites. Although acid modification increases the surface area of bentonite, its effectiveness is lower than that of modified zeolites in providing active sites for reactant-catalyst interactions, resulting in a lower biodiesel yield.

4.4.4 Effect of catalyst modification

Acid modification of zeolite can significantly alter its acidity and pore structure, which can affect catalytic performance. The increase in acid sites and pore distribution can enhance the catalyst's ability to drive the transesterification reaction rate, thus improving biodiesel yield. Modified bentonite catalysts experience similar changes as

modified zeolite catalysts, but due to their lower surface area and less regular pore structure, their biodiesel yield is not as high as that of modified zeolite catalysts.

Based on the above explanation, the relationship between the surface characteristics of the catalysts and their reactivity is crucial in the production of biodiesel with modified solid catalysts.

4.5 The analysis results of biodiesel characteristics at the highest yield

Biodiesel produced from *Calophyllum inophyllum* oil using acid-modified zeolite and bentonite catalysts exhibits several specific properties influenced by the raw materials and catalyst technology used. The properties of the biodiesel products from this research have been tested according to ASTM parameters and Indonesian National Standard (SNI) to ensure they meet the requirements of current biodiesel technology.

The biodiesel produced under conditions yielding the highest output is analyzed for its characteristics according to ASTM standards, and the results are compared with the SNI requirements for biodiesel. The parameters include flash point, viscosity, density, cetane number, and FAME content analysis, as shown in Table 6.

Table 6. The characteristics of the biodiesel produced at the highest yield using modified zeolite catalyst at a reaction temperature of 60°C

Parameter	Test Results	SNI
Flash point°C	121	Min 100
Viscosity, mm ² /s	5.633	2.3-6
Density, kg/m ³	887	850-887
Cetane number	53	Min 51
FAME	94.55	

Density testing is performed to ascertain its compliance with biodiesel standards and is juxtaposed against the SNI benchmark. The analysis reveals a density of 0.887 g/cm³ (887 kg/m³). The SNI specifies a density range for biodiesel of 850-887 kg/m³, confirming that the biodiesel derived from this study aligns with SNI regulations for biodiesel products.

The viscosity of the produced biodiesel is analyzed to ensure its compliance with the criteria for being declared as methyl ester according to the SNI standards. The viscosity of a fuel affects flow profile, atomization, and lubrication effectiveness. The viscosity is the most important property of biodiesels, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. The lower the viscosity of biodiesel, the easier it is to pump and atomize and achieve finer droplets [27]. The analysis results indicate that the viscosity of the biodiesel obtained at a measurement temperature of 40°C is 5.633 mm²/s, while the benchmark according to the SNI standards ranges from 2.3 to 6.0 mm²/s. Therefore, the biodiesel product meets the SNI standards.

The next test is the cetane number, which is essential because it indicates the diesel engine fuel's spontaneity to combust after being injected into the combustion chamber. Cetane number relates to the combustion quality of diesel fuel during compression ignition and also the ignition quality fuels [27]. The cetane number obtained for biodiesel from *Calophyllum inophyllum* is 53, while the SNI parameter for biodiesel cetane number is a minimum of 51. Hence, the biodiesel product meets the SNI requirements.

The flash point test on biodiesel is conducted to determine

its ignition temperature when applied as fuel. A high flash point makes fuel storage easier as it is less prone to ignite at room temperature. The minimum value of flash point is required for safety and handling of the fuel. It is used to characterize the fire hazards of the liquids [27]. The test results indicate that the biodiesel derived from *Calophyllum inophyllum* oil under conditions yielding the highest output has a flash point of 121°C, therefore, this fuel is safe for handling and storage for some period of time. With high value of flash point, this biodiesel is considered as combustible. The test results show that the biodiesel product meets the SNI criteria, which stipulates a minimum flash point of 100°C.

Another test is to measure the fatty acid methyl ester (FAME) content in biodiesel. This test is conducted to determine the amount of fatty acids converted into methyl esters. Methyl ester analysis is carried out using a GC instrument [27]. The result of the methyl ester content analysis for biodiesel produced from *Calophyllum inophyllum* oil is 94.55%.

Based on the testing results of the biodiesel product according to commercial biodiesel parameters as per SNI and ASTM requirements, it is evident that the biodiesel obtained meets the criteria for current technology, including quality and energy performance parameters, chemical composition (FAME), oxidative stability, physical characteristics, combustion properties, sustainability, and environmental factors.

Quality and energy performance are evaluated through energy content and viscosity. Biodiesel from *Calophyllum inophyllum* oil generally has a slightly lower calorific value compared to diesel fuel but is still adequate for use as fuel. The biodiesel product has a higher viscosity compared to diesel fuel. However, with the appropriate catalysts like acid-modified zeolite and bentonite, the viscosity of the biodiesel can be optimized to ensure good flow and efficient spraying in diesel engines.

Oxidative stability testing indicates that biodiesel from *Calophyllum inophyllum* oil tends to have better oxidative stability compared to biodiesel from some other vegetable oil sources, which is due to the natural properties of the oil. The modification of zeolite and bentonite catalysts with acid reduces the formation of oxidizing compounds and improves the long-term stability of the biodiesel.

Physical characteristic testing includes the flash point. Biodiesel from *Calophyllum inophyllum* oil has a higher flash point compared to diesel fuel. Modifications to the catalyst can help lower the flash point by affecting the molecular structure of the ester in the biodiesel.

Combustion properties are tested through emission tests. Biodiesel from *Calophyllum inophyllum* oil using modified zeolite and bentonite catalysts produces cleaner emissions compared to diesel fuel, including reductions in carbon monoxide (CO), unburned hydrocarbons, and fine particulates. The use of acid-modified zeolite and bentonite catalysts impacts the combustion properties of biodiesel by enhancing combustion efficiency and reducing the formation of harmful by-products.

Given the properties and characteristics of the biodiesel products, it is apparent that biodiesel from *Calophyllum inophyllum* oil with zeolite and bentonite catalysts meets sustainability and environmental friendliness criteria.

The comparison of combustion performance and emissions of *Calophyllum inophyllum* oil biodiesel with diesel fuel in engine tests examines parameters such as thermal efficiency

and combustion stability. In terms of thermal efficiency, the biodiesel product has a slightly lower calorific value compared to diesel fuel, but catalyst modifications can enhance combustion efficiency by optimizing the biodiesel properties. Acid-modified zeolite and bentonite catalysts help reduce viscosity and improve fuel atomization, which can enhance combustion efficiency.

Regarding combustion stability, this biodiesel product tends to exhibit more varied combustion characteristics depending on the composition of the *Calophyllum inophyllum* oil used. The use of acid-modified zeolite and bentonite catalysts can improve combustion stability by reducing issues related to incomplete combustion. Emission testing of *Calophyllum inophyllum* oil biodiesel shows lower levels of carbon dioxide, carbon monoxide, nitrogen oxides, unburned hydrocarbons, and particulates compared to diesel fuel. These results indicate that catalyst modifications affect combustion performance and emissions, making of *Calophyllum inophyllum* oil to biodiesel a more environmentally friendly alternative with competitive performance compared to diesel fuel.

Storage stability is a crucial factor to ensure that biodiesel remains effective and safe for use over a long period. Long-term storage stability evaluation of biodiesel products from *Calophyllum inophyllum* oil with modified zeolite and bentonite catalysts is still under testing. However, biodiesel products made from *Calophyllum inophyllum* oil with different catalysts generally involve critical aspects such as oxidative stability, hydrolysis stability, thermal stability, and resistance to contamination, physical, and chemical changes. Biodiesel from *Calophyllum inophyllum* oil shows good stability, but regular monitoring and testing are important to ensure its quality during storage. Modified catalysts can contribute to enhanced stability by reducing the formation of oxidizing compounds and improving the final quality of the biodiesel. The use of zeolite catalysts can help improve biodiesel stability by reducing unwanted by-products and enhancing the final quality of the biodiesel. Modified acid bentonite catalysts can reduce the formation of free fatty acids and improve stability against hydrolysis and oxidation.

5. CONCLUSION

The study indicates that *Calophyllum inophyllum* oil can effectively be transformed into biodiesel through esterification and transesterification processes using modified zeolite and bentonite catalysts. The biodiesel yield achieved with these modified catalysts is 88.19%, matching that of biodiesel produced with acid and base catalysts, which is 88.27%. The advantage of using these modified catalysts is their easy separation and ability to be reused in the biodiesel production process, making them eco-friendly. In contrast, traditional acid-base catalysts are difficult to separate and cannot be reused, resulting in industrial waste that requires management.

The use of modified catalysts offers potential for advancing biodiesel science and industry by reducing waste and lowering separation costs in the future. The resulting biodiesel meets the specifications outlined by the Indonesian National Standard (SNI), confirming its viability as a renewable fuel option.

Future research on the biodiesel production process from *Calophyllum inophyllum* oil using modified zeolite and bentonite catalysts holds significant potential for innovation and improvement. Innovation focus can be directed towards catalyst optimization, broader applications, and developing

solutions for technical and economic challenges, which will play a key role in making the process more efficient and sustainable.

Catalyst optimization can be achieved through the development of hybrid catalysts by combining zeolite and bentonite with other catalytic materials (such as metals or metal oxides) to enhance catalytic activity and selectivity. Modifying the structure and composition of zeolite and bentonite to improve accessibility and reactivity with *Calophyllum inophyllum* oil, and using nanotechnology to create nanoparticles from zeolite and bentonite to increase active surface area and catalyst efficiency are also potential areas for optimization.

Improvements in the transesterification process can be achieved through integrated process technologies that combine transesterification reactions with biodiesel separation and purification, as well as optimizing operating conditions to enhance conversion and reaction efficiency.

For sustainability and material availability, alternative materials that can replace or complement zeolite and bentonite can be used, and recycling catalysts and managing waste from the modification process can help reduce environmental impact.

Broader application improvements can be pursued by diversifying feedstocks, adapting modified catalysts for various types of biodiesel feedstocks, or using a mix of *Calophyllum inophyllum* oil with other non-food oil feedstocks. Developing zeolite and bentonite catalyst modifications for industrial scale, integrating with new sustainable process technologies, and automating and controlling processes to enhance consistency and biodiesel production efficiency are also important.

To address technical challenges, solutions can focus on high stability of modified catalysts and long service life for industrial scale use. For economic challenges, efforts can be directed towards reducing the production costs of catalyst modifications. With the right approach, it is possible to significantly enhance biodiesel production efficiency and reduce environmental impact.

Recommendations for further research include exploring biodiesel production from other non-edible oils and testing catalysts derived from other environmentally friendly natural materials to improve biodiesel yield, as well as conducting characterization of modified zeolite and bentonite catalysts using X-ray Photoelectron Spectroscopy (XPS). This advanced characterization technique is highly useful for understanding chemical surface changes in modified catalysts and can help in understanding how modifications affect oxidation states, composition, and surface reactivity. This is crucial for designing more efficient and durable catalysts. Through XPS analysis, researchers can monitor and optimize the catalyst modification process for better applications in industrial chemical reactions.

Another useful recommendation for future research is the design of a mini-reactor for biodiesel production from *Calophyllum inophyllum* oil. This involves designing a portable mini-reactor with a small but adequate capacity to meet local needs. It should include essential components such as a reaction tank, mixer, heater, filtration system, and separation tank. Safety and ease of use should be prioritized in the design, while mobility and durability are ensured through the use of high-quality materials and a compact design. With this design, it is expected that small-scale biodiesel production can be carried out efficiently and safely at various locations.

ACKNOWLEDGMENT

This work is supported by the Directorate of Research and Community Service, Directorate General of Higher Education, Ministry of Research and Technology, Republic of Indonesia, for funding this research through the Competency-Based Research (PBK) Grant in the fiscal year 2019 based on Contract No. 011/SP2H/AMD/LT/MULTI/L7/2019.

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