Synthesis of Ethylenediamine Modified Chitosan Beads for Biodiesel Production Catalyst: A Preliminary Study

Indah Permata Cantika *, Muhammad Ali Zulfikar, Handajaya Rusli

Department of Chemistry, Faculty of Sciences and Mathematics, Institut Teknologi Bandung, Bandung 40132, Indonesia

* Corresponding author: ipermatacantik@gmail.com

Article Info

Abstract

Biodiesel is an alternative fuel that can be easily produced through transesterification with the assistance of a catalyst. Palm oil is a widely utilized feedstock for biodiesel production due to its abundant availability. In this study, a catalyst was synthesized using chitosan (CS) modified with ethylenediamine (EDA) and cross-linked with epichlorohydrin (ECH) for a catalyst heterogeneous in transesterification reaction. The resulting product (CS/EDA/ECH) was characterized using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Its performance was evaluated for biodiesel production. The CS/ECH/EDA catalyst achieved optimal reaction conditions with 5% EDA concentration at room temperature, an oil: methanol ratio of 1:1 (v/v), a total volume of 10 mL of oil and methanol, and a catalyst mass of 0.75 grams. The methyl esters formed corresponded to the fatty acid content in palm kernel, namely methyl palmitate, methyl 9,10-octadecadienoate, methyl oleate, methyl 12,13-tetradecadienoate, and methyl stearate with the highest methyl ester conversion is methyl oleate. The CS/ECH/EDA catalyst exhibited consistent performance after three use cycles.

1. Introduction

Biodiesel results from transesterification between vegetable or animal oil and short-chain alcohol, facilitated by a catalyst to produce fatty acid alkyl esters and glycerol. At the end of the transesterification process, a mixture comprising two layers, glycerol and methyl esters, is obtained. According to Nasution *et al.* [1], biodiesel offers several advantages, including lower CO, NO, and sulfur emissions, making it more environmentally friendly. Additionally, the European Commission's Life Cycle Analysis (LCA) in 2013 demonstrated that biodiesel can reduce greenhouse gas effects by approximately 40-50%. Consequently, Kementerian Energi dan Sumber Daya Mineral (KESDM) Republik Indonesia [2] has been promoting the use of vegetable fuels (BBN), such as biodiesel (starting from B20 in 2016, B30 in 2020, B35 in 2023, and will increase to B40 in 2030 and B50 in 2050).

Palm oil is a reliable source of vegetable oil due to its abundant availability, and it finds application in various industries, including food, soap, and alternative fuel industries. According to Statista Research Department [3], Indonesia is the world's largest producer and exporter of palm oil, with a commodity production of approximately 46.2 million tons. The production of biodiesel using the transesterification principle requires the addition of a catalyst. According to Forzatti and Lietti [4], a catalyst is a substance that affects the rate of a chemical reaction but remains unchanged at the end.

Generally, catalysts in the transesterification process can be categorized into three types: enzyme, homogeneous, and heterogeneous. Enzyme catalysts are less favored due to the high cost of raw materials, limited interaction with short-chain alcohols, and susceptibility to denaturation. Homogeneous catalysts typically exhibit high activity and selectivity. However, their use presents drawbacks, such as difficulties in separation, regeneration, and water generation when using alkaline catalysts, which can trigger saponification reactions and decrease the biodiesel yield.

Heterogeneous catalysts are catalysts with a different phase than the reactants. Heterogeneous

catalysts are widely favored in the transesterification process due to their ease of regeneration and separation and their cost-effectiveness resulting from their ability to be reused. In principle, the use of catalysts has an important role in the formation of nucleophilic alkoxides from alcohol to attack the electrophilic carbonyl group in triglycerides, which causes the triglycerides to break up and form glycerol and methyl esters [5]. Therefore, the presence of a catalyst will increase the amount of biodiesel product. They offer advantages such as easy separation based on phase differences, renewability, and reusability. Commonly used catalysts include Na_2O/Al_2O_3 [6], SO_4^{2-}/ZnO [7], and Na_2O/Fe_3O_4 [8]. However, these catalysts have the disadvantage of being difficult to regenerate. One approach to overcoming this limitation is developing easily regenerative catalysts derived from natural materials.

Chitosan (CS) is a derivative of chitin obtained from shrimp shell waste. It possesses hydrophilic, biocompatible, non-toxic, and environmentally friendly properties. CS finds numerous applications, such as CO_2 separation from vehicle emissions to mitigate greenhouse gas effects [9], bio-adsorption for the removal of nitrogen-containing pollutants in wastewater [10], and catalyst in biodiesel production [11]. The amine groups in CS play a catalytic role in transesterification. However, CS has limited and non-free amine groups, leading to suboptimal catalytic performance.

Modification using a base such as ethylenediamine (EDA) has the potential to enhance the performance of CS. Epichlorohydrin (ECH), which can react with hydroxyl and amine groups, was used as a linker between CS and EDA. In this study, biodiesel was produced through a transesterification reaction with the addition of a synthesized CS/ECH/EDA catalyst to increase methyl esters. Catalyst performance was evaluated by parameters of EDA concentration, reaction temperature, oil: MeOH ratio, and the number of catalysts. The CS/ECH/EDA catalyst was also tested for its regeneration ability. The synthesis catalyst was characterized using FTIR to identify the functional groups produced by modified CS and SEM to observe changes in catalyst morphology. The performance of the catalyst was evaluated by comparing the number of methyl esters measured using GC-FID.

2. Experimental

This research was conducted in several stages, starting with the synthesis of modified CS and new CS bead catalysts, followed by the characterization of the catalysts. The synthesized catalyst was then applied to the biodiesel synthesis process, and the performance was evaluated using GC-FID.

2.1. Materials

The materials used in this study were chitosan from shrimp shells (Himedia, DD > 75%), epichlorohydrin (Sigma Aldrich, 99%), ethylenediamine (Sigma Aldrich, 99%), palm oil (40 g/100 mL saturated fat), methanol (Merck, 99.9%), acetic acid (Merck, 99.8%), and sodium hydroxide (Merck, MW 39.997 g/mol). All chemicals used

were of analytical grade, excluding palm oil, a commercially available household-use product.

2.2. Catalyst Preparation

Chitosan (CS) beads were prepared by dissolving a certain amount of chitosan in a 1% acetic acid solution. The mixture was then drop-casted into a 1 M NaOH solution while stirring. The formed beads were rinsed with distilled water and air-dried. These resulting beads were referred to as CS catalyst beads. For the modified CS catalyst beads, the wet CS beads were soaked in a 5% epichlorohydrin (ECH) solution for 5 hours at 60°C. The modified CS beads were rinsed and air-dried. Subsequently, the dried catalyst beads were further modified by immersing them in an ethylenediamine (EDA) solution with varying concentrations for 12 hours at 60°C. After immersion, the beads were rinsed with distilled water and air-dried. The dried beads were called CS/ECH/EDA catalyst beads.

2.3. Materials Characterization

Before and after contact, the synthesis catalyst beads, including CS, CS/ECH, and CS/ECH/EDA, were characterized using FT-IR Prestige-21 (Shimadzu, Japan) with the technology of KBr pellet over the wavenumber range 4000-450 cm⁻¹. A scanning electron microscope (JEOL JSM-6510 LA) was used to observe the surface morphology of materials. The synthesized biodiesel was analyzed using an Agilent 5977B GC/MSD instrument to identify the biodiesel compound content and an Agilent 7820A GC-FID instrument to determine the total area under the methyl ester peak.

2.4. Schema Process of Biodiesel Synthesis

In this research, the catalyst beads that have been produced are applied for biodiesel production through the transesterification reaction of palm oil with methanol with certain reaction parameters as in Schema 1.
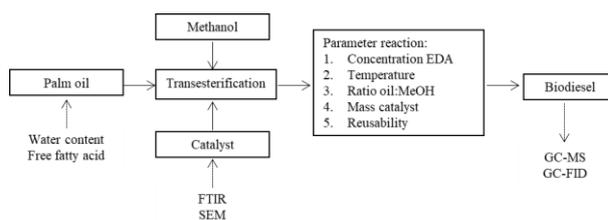
Schema 1. General process of biodiesel synthesis

2.5. Characterization of Palm Oil

Before reacting, the oil samples were characterized for water content and free fatty acid based on SNI 01- 5009.12-2001 regarding biodiesel. The quality of palm oil lies in its water content and free fatty acid. The higher water content and free fatty acid indicate low oil quality. Determination of water content could be determined through Eq. (1).

$$water\ content = \frac{W_1 - W_2}{W_0} \times 100\% \qquad \text{Eq. (1)}$$

Determination of free fatty acid could be determined through Eq. (2).

$$free\ fatty\ acid = \frac{ml\ KOH \times N\ KOH \times mr\ KOH}{w\ sample} \qquad \text{Eq. (2)}$$

2.6. Effect of Parameters on Transesterification Reaction

In each parameter of the transesterification reaction, the total area of the resulting methyl ester is calculated to see the effect of each parameter using Formula (1).

Total area methyl ester = area peak 1 + area peak 2 + ⋯ + area peak n   Formula (1)

2.6.1. EDA Concentration

The synthesized catalysts were applied as catalysts in biodiesel synthesis. A certain amount of palm oil was mixed with methanol at 1:0.25 (v/v) with a total volume of 10 mL. Then, 0.5 grams of CS/ECH/EDA catalyst with varying EDA concentrations of 1%, 3%, and 5% were added and stirred for 90 minutes at room temperature using a magnetic stirrer. The samples were then separated using a separating funnel and measured using GC-FID.

2.6.2. Reaction Temperature

A 0.5 gram CS/ECH/EDA catalyst with a 5% EDA concentration was mixed with a certain amount of palm oil and methanol at 1:0.25 (v/v) with a total volume of 10 mL. The mixture was stirred using a magnetic stirrer for 90 minutes at various temperatures, including room temperature, 40°C, 50°C, and 60°C. The samples were then separated using a separating funnel and measured using GC-FID.

2.6.3. Volume Ratio (Oil: MeOH)

A total of 0.5 grams of CS/ECH/EDA catalyst with a 5% EDA concentration was mixed with a certain amount of palm oil and methanol at various volume ratios oil: MeOH of (v/v) 1:0.25, 1:0.5, 1:1, 1:1.5, 1:1.25, with a total volume of 10 mL. The mixture was stirred using a magnetic stirrer for 90 minutes at room temperature. The samples were then separated using a separating funnel and measured using GC-FID.

2.6.4. Mass of Catalyst

The CS/ECH/EDA catalyst with a 5% EDA concentration was mixed with palm oil and methanol at a 1:1 (v/v) ratio with varying masses of 0.25, 0.5, 0.75, 1, and 1.25 grams in a total volume of 10 mL. The mixture was stirred using a magnetic stirrer for 90 minutes at room temperature. The samples were then separated using a separating funnel and measured using GC-FID.

2.7. Gas Chromatography Measurement Parameters

The synthesized biodiesel was analyzed using gas chromatography (GC) (GS-MS Agilent 5977B GC/MSD and GS-FID Agilent 7820A) with an Agilent 190915-433 HP-5 ms column (GC-MS) and Agilent 7820A HP-5 column (GC-FID) with dimensions of 30 μm × 250 μm × 0.25 μm. The oven parameters were set by starting at 140°C, a rate of 5°C/minute from 140°C to 300°C, and a hold time of 5 minutes. A sample volume of 1 μL was injected into the column for analysis. The biodiesel conversion was calculated based on the total area of the methyl ester compounds produced. In GS-MS, the separated compounds based on boiling points were identified by the Mass Spectroscopy (MS) detector by comparing each peak's fragmentation pattern with the MS database.

3. Results and Discussion

Palm oil was first characterized before reacting with methanol and a catalyst to obtain methyl ester through a catalytic transesterification reaction. The high water content and free fatty acids cause hydrolysis, which will change the oil into free fatty acids, causing rancidity [12] and causing the formation of soap, which will complicate the process of separating methyl ester from glycerol because of its emulsifying properties [13]. The maximum water content in the sample before being synthesized is <5% – sample weight. The maximum level of free fatty acids is 0.8 mg-KOH/gram sample. The experimental results found that the water content of the palm oil used was 0.130% and 0.3020 mg KOH/g for FFA. This indicates that the sample is ready to be synthesized.

The performances of the CS and modified CS catalysts were evaluated based on the total area of methyl esters produced. In the initial stage, GC-MS analysis was conducted to identify the main methyl ester compounds, which served as the basis for calculations. Methyl esters were produced by reacting palm oil with methanol in a 1:1 (v/v) ratio, using 0.75 grams of CS/ECH/EDA catalyst. Palm oil contains primary fatty acids such as palmitic, linoleic, oleic, and stearic [14]. The GC-MS results indicated the presence of methyl ester compounds resulting from the transesterification reaction of palm oil, as shown in Table 1, which can be used for further calculations.

Table 1. Comparison of retention time and biodiesel composition

Compound	Empirical formula	Retention time (min)		% methyl ester
		GC-MS	GC-FID	
Methyl palmitate	$C_{17}H_{34}O_2$	15.617	15.026	36.415
Methyl 9,10-octadecadienoate	$C_{19}H_{34}O_2$	18.789	18.054	9.781
Methyl oleate	$C_{19}H_{36}O_2$	18.906	18.191	39.845
Methyl 12,13-tetradecadienoate	$C_{15}H_{26}O_2$	19.078	18.278	4.029
Methyl stearate	$C_{19}H_{38}O_2$	19.354	18.634	9.928

Quantitative analysis was performed using GC-FID due to its comparable accuracy to GC-MS but at a lower cost. The performance comparison between GC-MS and GC-FID under the same conditions can be seen in Figure 1. The four main peaks used for analysis were well detected using GC-FID. The identified major methyl ester compounds and the retention time comparison between GC-MS and GC-FID are shown in Table 1.

As anticipated, an increase in the number of amine groups with basic properties enhances the ability of CS/ECH/EDA catalyst to catalyze the transesterification reaction. Adding amine groups (-NH) to the CS/ECH/EDA catalyst increases the number of active sites. The added amine groups promote the formation of alkoxides from methanol and contribute to the increased production of

methyl esters [15]. ECH enables EDA to bind throughout the CS structure, allowing for a maximum of five amine groups per CS molecule.
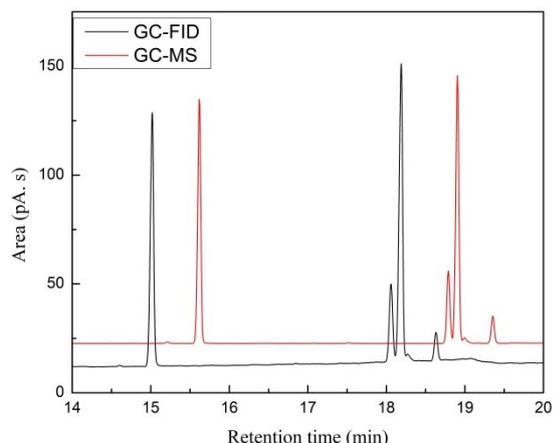

Figure 1. Comparison of retention time GC-MS and GC- FID

As shown in Figure 2, the concentration of 5% EDA exhibits the best catalytic performance. Lower concentrations of EDA result in lower catalytic activity. On the other hand, higher concentrations make the beads fragile, rendering them unsuitable for catalysis. Adding amine groups enhances the solubility of modified CS polymer in water, leading to the instability of the formed beads. In the transesterification reaction, temperature is also a determining factor in converting triglycerides to methyl esters. Conducting the synthesis transesterification reaction at temperatures below 65°C is preferable, as temperatures outside this range can lead to saponification reactions during biodiesel production, resulting in decreased density values and reduced biodiesel conversion rates [16].
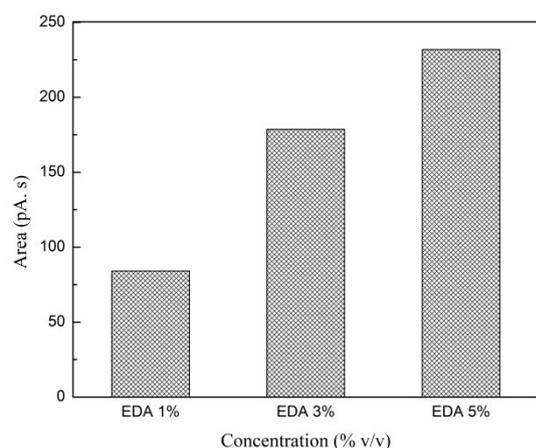

Figure 2. Effect of EDA concentration on the total area of the methyl ester area

Figure 3 illustrates that the CS/ECH/EDA catalyst performance is relatively unaffected by temperature variations [14, 15], thus requiring a higher reaction temperature to convert palm oil into biodiesel using an alkaline catalyst [16]. Therefore, a CaO-based catalyst was used, achieving optimal results at 65°C for the same reaction. This indicates the advantage of the CS/ECH/EDA catalyst, which can be applied at room temperature while

exhibiting superior transesterification performance. Conducting the reaction at room temperature offers economic and safety benefits and facilitates handling the resulting products.
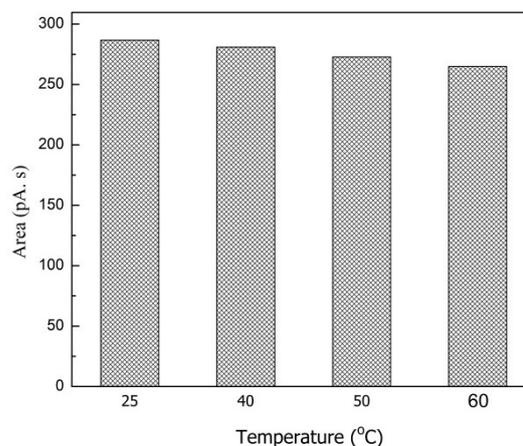

Figure 3. Effect of reaction temperature on the total area of the methyl ester area

The molar ratio of oil to methanol is an important parameter that influences the level of biodiesel conversion. The effect of the oil-to-methanol ratio on transesterification has been previously discussed by Musa [17], who observed an increase in methyl ester production at an oil-to-methanol molar ratio of 1:12 compared to a ratio of 1:6. Similarly, in the study by Unlu *et al.* [18], transesterification was conducted using alcohol and oleic acid with methanol as the alcohol source, and a cellulose-based membrane catalyst. It was found that increasing the oil-to-methanol ratio also increased the conversion of methyl ester, with a maximum oil-to-methanol molar ratio of 1:9. Therefore, increasing the oil-to-methanol ratio enhances the biodiesel conversion yield.
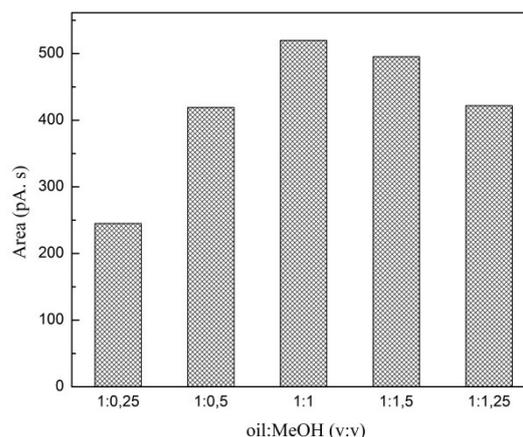

Figure 4. Effect of ratio oil: MeOH on the total area of the methyl ester area

In Figure 4, it can be observed that the reaction of a certain amount of oil as a source of triglycerides with the addition of a specific amount of methanol as a source of short-chain alcohol leads to the production of methyl esters as the main component of biodiesel. The optimal oil-to-methanol ratio for transesterification reactions was 1:1 (v/v). With a lower amount of methanol, the

transesterification reaction is not optimal, as methanol becomes the limiting reagent. On the other hand, with a higher amount of methanol, the limiting reagent becomes palm oil. Theoretically, this reaction requires a molar ratio of oil to methanol 1:3.

It has been reported that the amount of catalyst used in transesterification processes, whether homogeneous or heterogeneous, affects the yield of methyl esters [19]. The effect of catalyst addition was investigated within the 0.25-1.25 grams range. Figure 5 demonstrates the optimum condition when using 0.75 grams of catalyst. In principle, adding homogeneous and heterogeneous catalysts in transesterification reactions promotes the formation of nucleophilic alkoxides from alcohol to attack the electrophilic carbonyl group in triglycerides [5].
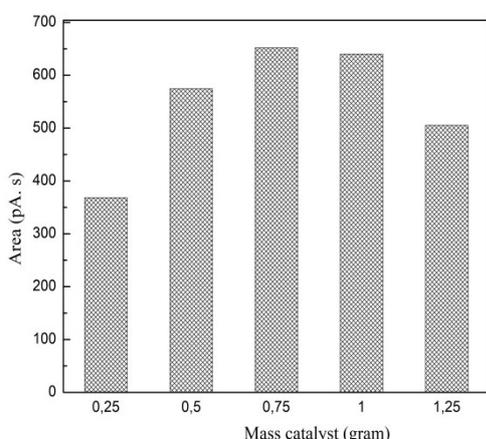

Figure 5. Effect of mass catalyst on the total area of the methyl ester area

The previously described mechanism is more likely to occur as the amount of catalyst used increases, thus increasing the number of products. However, when the catalyst amount exceeds 0.75 grams, a decrease in transesterification performance is observed. This can be attributed to the rapid reaction of all reactants with the catalyst, resulting in unreacted by-products that cover the catalyst surface. In practical applications, the mass range of 0.75 to 1.00 grams can be considered an option, as the difference in performance is only around 1.71%.

Ideally, heterogeneous catalysts have the advantage of being reusable. The performance of the CS/ECH catalyst in transesterification has been tested for up to 5 uses, as shown in Figure 6. The catalyst's performance remains relatively consistent until the 3rd use. In contrast, on the 4th use, it retains approximately 77% of its initial performance and remains relatively stable on the 5th use. This may be attributed to blocking of active sites by oil and biodiesel. Despite the decrease in performance, this catalyst is still superior to homogeneous catalysts as it can produce 4.5 times more product even up to the 5th use. When compared to other transesterification catalysts, such as acid-modified chitosan catalyst [20], which experienced a decrease in catalyst performance by 10% on the 2nd use and 43.84% on the 5th use, it can be concluded that the CS/ECH/EDA catalyst has excellent reusability capabilities.
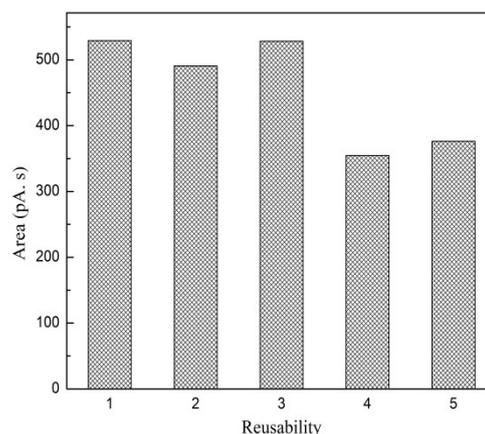

Figure 6. Effect reusability on the total area of the methyl ester area

This study also compared the performance of CS beads, CS/ECH beads, and CS/ECH/EDA beads for transesterifying palm oil into biodiesel under optimum conditions. Figure 7 shows that the CS/ECH/EDA beads catalyst has the highest total area of methyl esters. The increase in the total area of methyl esters on CS/ECH/EDA beads is eight times greater than CS beads and 7.5 times greater than CS/ECH beads. This demonstrates that adding EDA as an amine source is the most crucial factor in catalyst synthesis. The resulting product exhibited spherical granules with a distinct yellowish color for the CS/ECH/EDA catalyst, compared to CS and CS/ECH. Additionally, the CS/ECH/EDA catalyst appeared larger, ranging around 0.1 cm, in contrast to CS and CS/ECH. These physical changes indicate the successful modification of chitosan.
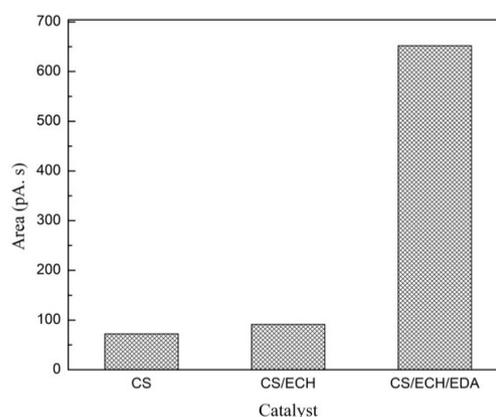

**Figure 7.** Comparison of catalyst to the total area of the methyl ester area

The modification process primarily targeted the hydroxyl (-OH) groups of chitosan, opening epoxy groups in epichlorohydrin (ECH) through the attack of chitosan's hydroxyl groups. The presence of halide groups in ECH facilitated its modification with ethylenediamine (EDA), as the halide groups, mainly -OH, act as good leaving groups. The reaction between CS/ECH/EDA was evidenced in Figure 8, as confirmed by FTIR characterization.
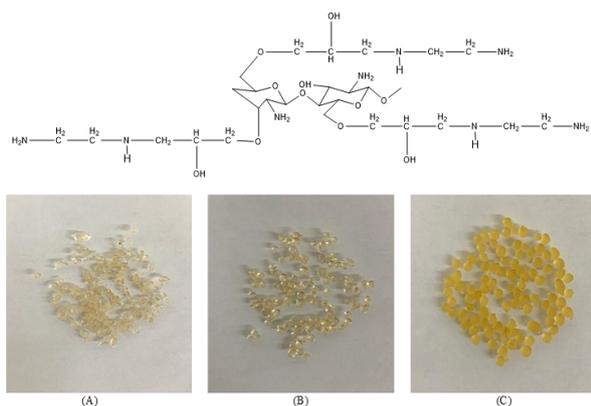
Figure 8. Structure of CS/ECH/EDA catalyst and visuals of (a) CS, (b) CS/ECH, (c) CS/ECH/EDA catalyst beads

The FTIR spectra of CS, CS/ECH, and CS/ECH/EDA displayed characteristic absorbance peaks, including the –OH stretching at 3415 cm⁻¹ and the C–H stretching at 2898 cm⁻¹ [21]. The addition of EDA to the CS/ECH modification resulted in an increased presence of amine groups attached to chitosan. This increase was demonstrated by the emergence of peaks around 1655 cm⁻¹ (primary N–H vibration) and 1566 cm⁻¹ (secondary N–H vibration). Similar results were obtained in the study conducted by Zhou *et al.* [22]. CS microspheres modified with ECH were used as Hg(II) adsorbents in water, showing comparable FTIR spectra to the CS/ECH/EDA catalyst synthesis.

In Figure 9, with the modification of the chitosan structure, the shape of the catalyst is more spherical. This is because the CS structure after modification is increasingly rigid due to ECH and EDA, which are bound to the catalyst.
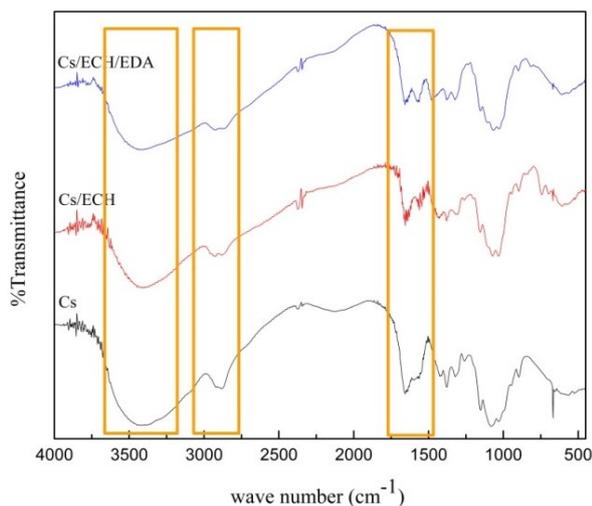

Figure 9. FTIR spectra of the synthesized catalyst

The CS/ECH and CS/ECH/EDA beads relatively do not experience shrinkage (Figure 10) as experienced by CS beads due to the drying process. This is due to the presence of cross-links formed between CS polymers with the help of ECH. This has the potential to increase the durability of the catalyst for multiple cycles of use, as shown by the results of the catalyst's repeated usage.
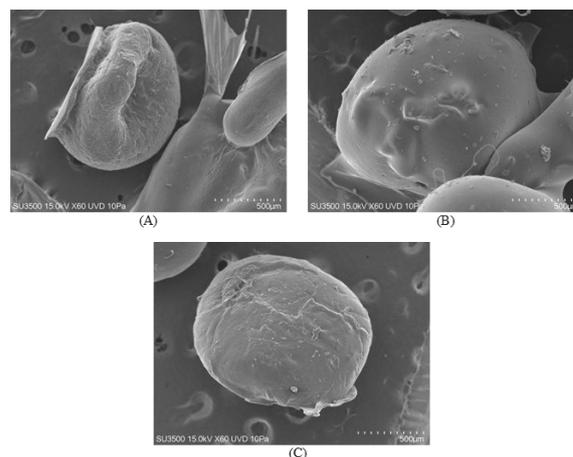

Figure 10. SEM images of catalyst beads (A) CS, (B) CS/ECH, (C) CS/ECH/EDA

Figure 11 also demonstrates increased peaks in the 2852–2915 cm⁻¹ range, indicating other compounds on the catalyst surface. Compared to the peaks of biodiesel and palm oil, it can be speculated that they correspond to residual biodiesel and palm oil adsorbed on the catalyst surface.
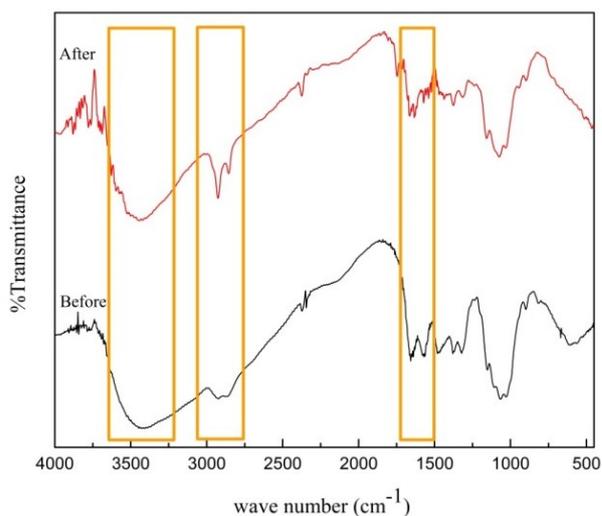
Figure 11. FTIR spectra of CS/ECH/EDA catalyst before and after contact

In Figure 12, there is no difference in morphology between the catalyst before and after contact. The only noticeable distinction is that the catalyst, after contact, exhibits a smoother surface compared to its pre-contact state. This is because there is still residual oil from the biodiesel synthesis reaction on the surface of the catalyst. Therefore, it can be concluded that the CS/ECH/EDA granular catalyst did not change physically.
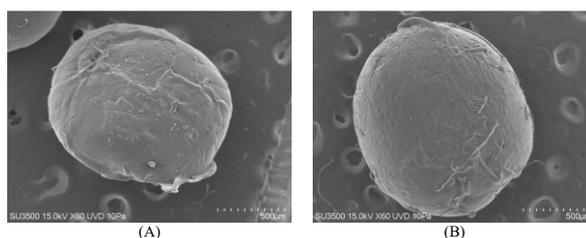
Figure 12. SEM images of CS/ECH/EDA catalysts (A) before and (B) after contact

Figure 13 shows a noticeable difference in absorbance in the 1500–1000 cm^{-1} region between the palm oil used and the synthesis biodiesel. The palm oil exhibits an absorbance peak at 1738 cm^{-1}, corresponding to the C=O vibration. This finding is consistent with the results reported by Samanta and Sahoo [23] in their IR spectrum shown in Figure 13. In the synthesized biodiesel, there is an additional absorbance peak at 1193 cm^{-1}, which corresponds to the O-CH$_3$ vibration, and at 1440 cm^{-1}, which corresponds to the CH$_3$ vibration. Both of these peaks are characteristic absorptions of biodiesel. These results are consistent with the findings reported by Marwan *et al.* [24], who also observed an absorbance peak at 1435 cm^{-1} corresponding to the CH$_3$ vibration (a characteristic of biodiesel).
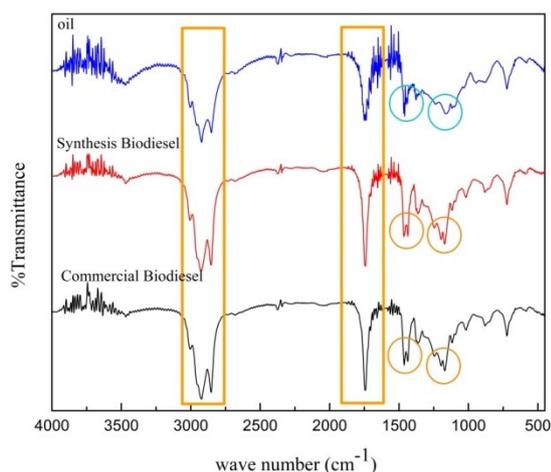

Figure 13. The IR spectra of oil, synthesized biodiesel, and commercial biodiesel

Table 2 shows a comparison of the performance of the present work with literature data on different catalysts for biodiesel production from different feedstock.

Table 2. Comparison of different catalysts for biodiesel production from different feedstock

Catalyst	Oil	Mass catalyst (-wt%)	Alcohol	molar ratio (oil: MeOH)	Temperature (°C)	Reaction time (min)	Ref.
Acidic chitosan membrane	Oleic acid	10%	Methanol	1:20	69	120	[20]
Zeolite/chitosan	Waste cooking oil (WCO)	–	Methanol	1:7	25	180	[25]
NaOH/ Chitosan-Fe$_3$O$_4$	Waste cooking oil (WCO)	0.5	Methanol	1:6	65	270	[26]
Guanidinylated chitosan	Soybean oil	20	Methanol	1:2.5	60	360	[11]
CC/ECH/EDA	Palm oil	7.5	Methanol	1:1	25	90	This work

4. Conclusion

The CS/ECH/EDA catalyst in the form of beads was successfully prepared and characterized using FTIR and SEM. The optimized conditions for the catalyst were determined to be a reaction with 5% EDA concentration, an oil: methanol ratio of 1:1 (v/v), 0.75 grams of catalyst mass, a reaction at 25°C, and a total substrate volume of 10 mL. Based on GC-FID analysis, the CS/ECH/EDA catalyst significantly increased the total area of methyl esters by eight times compared to the CS catalyst and 7.5 times compared to the CS/ECH catalyst. The synthesized biodiesel exhibited similar characteristics to commercial biodiesel. The composition of the produced biodiesel consisted of methyl palmitate, methyl 9,10-octadecadienoate, methyl oleate, methyl 12,13-tetradecadienoate, and methyl stearate, which are common fatty acid compositions found in palm oil. Remarkably, the CS/ECH/EDA catalyst demonstrated superior performance, resulting in a 4.5 times higher product yield than the transesterification reaction conducted without any catalyst, even after five cycles of usage.

Acknowledgment

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