

Aminated Porous Methacrylate-Based Polymer Monolith as an Anion Exchanger Microreactor for Sustainable Continuous Flow Transesterification of Palm Oil

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Abstract

The development of regenerable heterogeneous catalysts for sustainable biodiesel production remains a major challenge, particularly for continuous-flow systems. This study aimed to develop a functionalized methacrylate-based monolithic polymer as a catalytic microreactor for the continuous transesterification of palm oil. The novelty of this work lies in (i) the use of diethylamine (DEA) as an amination agent for poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) (PGMEGD) monoliths, (ii) the systematic optimization of the alkalization process to produce an anion-exchange resin, and (iii) the demonstration of catalyst regeneration through an effective sequential washing procedure. PGMEGD monoliths were synthesized *in situ* using a ternary porogenic system consisting of 1-propanol, 1,4-butanediol, and water, followed by functionalization with DEA at concentrations ranging from 5 to 25% and subsequent alkalization with NaOH. FTIR and SEM analyses confirmed successful chemical modification while preserving the interconnected three-dimensional porous structure of the monolith. The highest amine density of 3.43 mmol g⁻¹ was obtained at a DEA concentration of 20%, whereas an optimum OH⁻ exchange capacity of 3.28 mmol g⁻¹, corresponding to 96% of the amine density, was achieved after alkalization with 1.0 M NaOH. In the continuous transesterification of palm oil with methanol, the catalyst achieved an optimum biodiesel yield of 86.28% at a methanol-to-oil molar ratio of 9:1 and a flow rate of 0.05 mL min⁻¹. The catalyst maintained a biodiesel yield above 80% for four consecutive cycles, while regeneration using sequential citric acid-NaOH-ethanol washing restored more than 99% of its catalytic activity and exhibited a consistent recovery pattern over two regeneration cycles. These findings demonstrate that the PGMEGD-NH₂-OH monolithic resin is a promising catalytic microreactor for sustainable biodiesel production under continuous-flow conditions.

Keywords

Monolithic Polymer, Anion Exchanger Resins, Continuous Transesterification, Biodiesel, Palm Oil

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1. INTRODUCTION

Biodiesel, produced through the transesterification of triglycerides derived from vegetable oils or animal fats with short-chain alcohols such as methanol, has emerged as a promising renewable fuel because of its biodegradability and compatibility with conventional diesel engines (Aamir et al., 2022; Priya et al., 2021). Compared with petroleum-based diesel, biodiesel can reduce sulfur and particulate emissions by approximately 50-70%, thereby contributing to cleaner and more sustainable energy systems (Aljaafari et al., 2022; Deora et al., 2022). Among the various available feedstocks, palm oil is considered one of the most attractive resources in Southeast Asia because of its high oil productivity, year-round availability, and well-established industrial supply chain (Farobie and Harulistiyoso, 2022; United States Department of Agriculture,

2022).

The transesterification of palm oil is commonly catalyzed by heterogeneous base catalysts because they facilitate catalyst recovery and product purification. Various catalyst systems, including CaO-based materials (Fadarina et al., 2022; Minaria and Mohadi, 2016; Sitompul and Mohadi, 2017; Sulaiman et al., 2020; Wang et al., 2024), alkali-impregnated biomass (Zu et al., 2024) and modified zeolites (Sumari et al., 2024; Szkudlarek et al., 2024) have been developed to enhance catalytic activity and improve process efficiency. Nevertheless, these catalysts still suffer from several limitations. CaO-based catalysts are prone to calcium leaching into the methanol phase, which can result in catalyst deactivation and product contamination, whereas zeolite-based catalysts often experience diffusion limitations because of their predominantly microporous structures, which restrict the transport of large triglyceride

molecules (~800–900 Da). These limitations highlight the need for process-intensification strategies based on catalytic systems with interconnected pore networks and chemically stable active sites.

One promising approach is the use of porous monolithic microreactors, which possess an interconnected three-dimensional pore structure that can simultaneously serve as flow channels and catalytic support while minimizing diffusion resistance (Abiev, 2022; Chen et al., 2022; Zhao et al., 2024). Among various monolithic materials, poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) (PGMEGD), synthesized using a ternary porogenic system consisting of 1-propanol, 1,4-butanediol, and water, has attracted considerable attention because of its highly interconnected porous structure and reactive epoxy functionalities, which enable facile post-synthetic chemical modification (Amalia et al., 2021, 2022; Sabarudin et al., 2021). Owing to these characteristics, PGMEGD has been widely employed for enzyme immobilization, chromatographic separation, and chiral applications (Amalia et al., 2021, 2022; Sabarudin et al., 2021). In a previous study, L-arginine immobilized on PGMEGD was successfully applied as a heterogeneous catalyst for the batch transesterification of palm oil, achieving a FAME yield of 82.34% (Erwanto et al., 2026). However, conventional batch processes generally require longer reaction times and offer lower process efficiency than continuous-flow systems.

Despite the extensive use of PGMEGD in biocatalytic and separation applications, its utilization as an anion-exchange monolithic catalyst for continuous transesterification has not yet been reported. To the best of our knowledge, no study has investigated an amine-functionalized PGMEGD monolith as a regenerable catalytic microreactor for the continuous transesterification of palm oil. Therefore, this study aimed to (i) synthesize a PGMEGD-NH₂-OH monolith through diethylamine (DEA) amination followed by alkalization, (ii) optimize the DEA and NaOH concentrations to maximize the density of accessible basic sites, (iii) evaluate its catalytic performance in the continuous transesterification of palm oil, and (iv) investigate its regeneration and reusability. The resulting monolithic catalyst is expected to combine interconnected mass-transfer pathways, accessible basic active sites, and facile regeneration, thereby providing a promising platform for sustainable biodiesel production under continuous-flow conditions.

2. EXPERIMENTAL SECTION

2.1 Synthesis of Monolith PGMEGD

The PGMEGD monolith was prepared by adapting a previously reported method Erwanto et al. (2026) with slight modifications. The monolith was synthesized in situ inside a polytetrafluoroethylene (PTFE) tube (1 mm i.d., 3 mm o.d.; GL Science Co., Ltd., Japan) with a length of 10 cm, corresponding to a geometric reactor volume of approximately 78.5 μL . PGMEGD was synthesized through free-radical copolymerization of glycidyl methacrylate (GM, $\geq 97.0\%$, Merck, Germany) and ethylene glycol dimethacrylate (EGDMA, Merck, Germany),

where GM served as the functional monomer and EGDMA as the crosslinker. The polymerization formulation was prepared with a total monomer concentration (%T) of 40 and a crosslinking degree (%C) of 25. A porogen mixture of 1-propanol ($\geq 99.5\%$, Merck, Germany), 1,4-butanediol ($\geq 99\%$, Merck, Germany), and water was used at a volumetric ratio of 7:4:1 (v/v).

The polymerization solution was first sonicated for 5 min to ensure complete homogenization. Subsequently, 2,2'-azobisisobutyronitrile (AIBN, 12 wt.% in acetone, Merck, Germany) was added as the radical initiator at a concentration of 1% (w/v), followed by an additional 5 min of sonication. The resulting polymerization solution was then introduced into the PTFE tube, both ends were tightly sealed, and the tube was heated at 60 °C for 12 h to complete the polymerization. After polymerization, the PGMEGD monolith was flushed sequentially with ethanol and deionized water to remove residual monomers, porogenic solvents, and other unreacted species. The washed monolith was dried under vacuum to constant weight before further modification. The dry monolith mass was approximately 98 mg, determined gravimetrically from the difference between the weights of the PTFE tube before and after polymerization. Based on the geometric reactor volume and dry monolith mass, the apparent monolith bed density was approximately 1.25 g cm⁻³. Because the PGMEGD was formed as a continuous monolithic structure that filled the PTFE tube rather than as discrete particles, no interparticle void space was present within the reactor bed; fluid transport occurred through the interconnected pore network of the monolith.

2.2 Amination and Alkalization Monolith PGMEGD

The obtained PGMEGD monolith was then aminated using diethylamine (DEA, C₄H₁₁N, Sigma-Aldrich). DEA was selected as the amination reagent because previous studies comparing several tertiary and primary amines for epoxy-functionalized poly(glycidyl methacrylate)-based materials demonstrated that DEA provides the highest amination efficiency. Moreover, after conversion to the hydroxide form, DEA-functionalized materials exhibited superior catalytic performance for transesterification compared with those modified using tributylamine, tripropylamine, triethylamine, and ethanolamine (Maleki et al., 2022). Therefore, DEA was selected in this study to maximize the density of accessible basic sites while preserving the interconnected porous structure of the monolith. The PGMEGD monolith was aminated by continuously pumping DEA solutions with concentrations ranging from 5–25% through the column using a syringe pump (GL Science Co., Ltd., Japan) at a flow rate of 0.05 mL min⁻¹ for 3 h at 60 °C, yielding the PGMEGD-NH₂ monolith. After amination, the monolith was washed several times with ethanol (C₂H₅OH, $\geq 99.8\%$, Merck, Germany) to remove unreacted reagents and subsequently dried under vacuum at 60 °C. The amine density (AD) of the PGMEGD-NH₂ monolith was determined using Equation (1):

$$AD = \frac{(W_a - W_0)}{(M_{amine} - W_0)} \times 1000 \quad (1)$$

Where (AD) is the amine density (mmol g^{-1}), W_a is the mass of the PGMEGD-NH₂ monolith after amination (g) and W_0 is the initial mass of the PGMEGD monolith before amination (g), and M_{amine} is the molar mass of diethylamine (73.14 g mol^{-1}).

The PGMEGD-NH₂ monoliths prepared using different DEA concentrations were subsequently alkalized using 0.1 M NaOH solution (NaOH, $\geq 99.0\%$, Sigma-Aldrich) under continuous flow at 0.05 mL min^{-1} for 3 h at 60°C to convert the amine-functionalized monolith into the OH[−] form, producing PGMEGD-NH₂-OH as a monolithic anion-exchange resin with accessible basic active sites. The total basicity of each PGMEGD-NH₂-OH monolith was evaluated by back titration using 0.01 N benzoic acid solution ($\text{C}_7\text{H}_6\text{O}_2$, $\geq 99.5\%$, Merck, Germany), and the catalyst exhibiting the highest total basicity was subsequently selected for continuous transesterification experiments.

2.3 Transesterification Palm Oil Using PGMEGD-NH₂-OH

The catalytic activity of PGMEGD-NH₂-OH was investigated in the transesterification of palm oil (purchased from a local market, acid value of 0.25 KOH mg/g) with methanol (CH_3OH , $\geq 99.9\%$, Merck, Germany) using a monolithic flow reactor (Figure 1). The effect of the methanol-to-oil molar ratio (6:1–21:1) was evaluated at 50°C under a fixed flow rate of 0.05 mL min^{-1} using a 3 mL syringe pump (GL Science Co., Ltd., Japan). The influence of flow rate was subsequently examined by varying the flow rate from 0.03 to 0.15 mL min^{-1} while maintaining the optimum methanol-to-oil molar ratio obtained from the previous experiment. The reaction products were continuously collected, and the biodiesel yield was calculated to determine the optimum operating conditions according to Equation (2).

$$\text{Biodiesel mass yield (\%)} = \frac{M_b}{M_o} \times 100 \quad (2)$$

where M_b is the mass of the biodiesel product obtained (g) and M_o is the initial mass of palm oil fed into the reactor (g).

Under the optimum methanol-to-oil molar ratio and flow rate, the resulting biodiesel product was further analyzed by gas chromatography–mass spectrometry (GC-MS) to determine the fatty acid methyl ester (FAME) composition and confirm the conversion of triglycerides into methyl esters.

After the transesterification reaction, the catalyst was regenerated prior to reuse by sequential washing with 0.25 M citric acid solution, 1 M NaOH solution, and ethanol to remove adsorbed impurities and restore the catalytic active sites. The regenerated monolith was then dried before being reused in the subsequent reaction cycle.

3. RESULTS AND DISCUSSIONS

3.1 Physicochemical Properties

The PGMEGD monolith was successfully synthesized in situ using a relatively simple procedure adapted from a previously reported method (Erwanto et al., 2026). Unlike previous studies, the present work introduced a post-synthetic functionalization strategy involving amination with diethylamine (DEA) to generate amine-active sites within the monolithic structure, followed by alkalization with NaOH to convert the material into its OH[−] form, yielding a PGMEGD-NH₂-OH monolithic anion-exchange resin. This approach was designed to enhance the accessibility of basic active sites while preserving the interconnected porous architecture required for continuous-flow transesterification.

3.1.1 Amine Density (AD)

The effect of DEA concentration on the amine density (AD) of the PGMEGD-NH₂ monoliths is summarized in Table 1. Increasing the DEA concentration from 5% to 20% progressively increased the AD from 1.22 to 3.43 mmol g^{-1} , indicating that a greater availability of DEA molecules promoted the epoxy ring-opening reaction and enhanced the incorporation of amine functionalities onto the PGMEGD monolith. The selection of DEA was based on previous studies demonstrating that, among several amination reagents employed for epoxy-functionalized glycidyl methacrylate-based polymers, DEA exhibited the highest amination efficiency and subsequently produced the highest biodiesel yield after conversion to the hydroxide form (Maleki et al., 2022). Its relatively small molecular size also facilitates diffusion into the interconnected pore network while maintaining pore accessibility. A similar concentration-dependent increase in functional group incorporation has also been reported for the immobilization of L-arginine onto glycidyl methacrylate-based polymers (Erwanto et al., 2026). However, further increasing the DEA concentration to 25% resulted in a slight decrease in AD to 3.05 mmol g^{-1} . This decrease is likely attributable to steric hindrance and diffusion limitations arising from the excessive accumulation of grafted amine groups, which reduce the accessibility of the remaining epoxy groups located within the internal pore structure. Similar behavior has been reported for the functionalization of methacrylate-based polymers, where excessive amine concentrations decrease grafting efficiency because of restricted mass transport and limited accessibility to reactive sites (Erwanto et al., 2026; Maleki et al., 2022). Therefore, the PGMEGD-NH₂ monolith prepared using 20% DEA, which exhibited the highest amine density (3.43 mmol g^{-1}), was selected for subsequent alkalization and further characterization.

3.1.2 Characterization of Fourier Transform Infrared Spectroscopy (FTIR)

The success of the chemical modification was confirmed by Fourier-transform infrared (FTIR) spectroscopy (IR Spirit-T/ATR, Shimadzu), as shown in Figure 2. All materials, including PGMEGD, PGMEGD-NH₂, and PGMEGD-NH₂-OH,

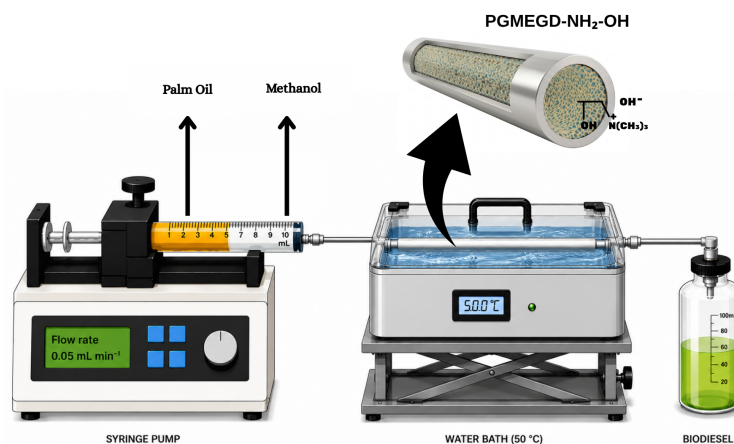


Figure 1. Schematic Representation of the Continuous-Flow Transesterification System Using the PGMEGD-NH₂-OH Monolithic Catalyst

Table 1. Effect of DEA Concentration On Amine Density (AD)

Polymer	DEA (%)	AD (mmol g ⁻¹)
PGMEGD-NH ₂	5	1.22
PGMEGD-NH ₂	10	1.78
PGMEGD-NH ₂	15	2.98
PGMEGD-NH ₂	20	3.43
PGMEGD-NH ₂	25	3.05

exhibited the characteristic ester carbonyl absorption band at approximately 1720 cm⁻¹, indicating that the methacrylate polymer backbone remained intact after both amination and alkalization. For the pristine PGMEGD monolith, the characteristic epoxy bands were observed at approximately 910 and 840 cm⁻¹, corresponding to the epoxy functionalities originating from glycidyl methacrylate units.

Following amination with DEA, the intensity of the epoxy bands decreased markedly, indicating the occurrence of epoxy ring-opening reactions between the epoxy groups of PGMEGD and the amine groups of DEA. Simultaneously, a broader absorption band appeared in the 3200-3500 cm⁻¹ region, which can be attributed to the stretching vibrations of N-H and O-H groups generated during the amination process. These spectral changes are consistent with previous reports on the amine functionalization of glycidyl methacrylate-based polymers, where the reduction of epoxy-related bands was considered a key indicator of successful chemical modification (Erwanto et al., 2026; Maleki et al., 2022).

After alkalization, the FTIR spectrum of PGMEGD-NH₂-OH showed no significant changes in the characteristic bands of

the polymer framework, suggesting that the conversion of the amine-functionalized monolith into its OH⁻ form occurred without altering the structural integrity of the polymer network. The preservation of the characteristic ester and amine-related bands further indicates that the alkalization process mainly involved ion-exchange interactions rather than additional covalent modifications. Overall, the FTIR results confirm the successful post-synthetic functionalization of PGMEGD into a monolithic anion-exchange resin while maintaining the chemical stability of the polymer matrix.

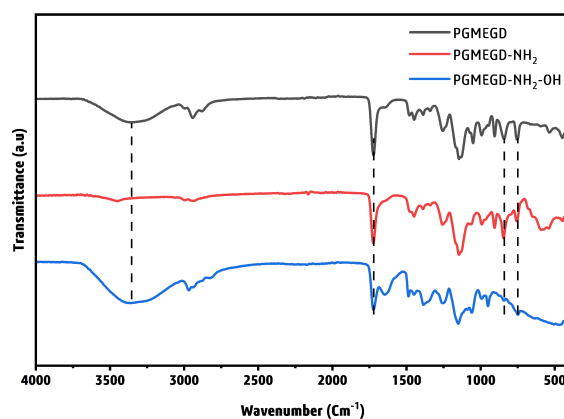


Figure 2. ATR-FTIR Spectra of PGMEGD (gray), PGMEGD-NH₂ (red), and PGMEGD-NH₂-OH (blue) Monoliths

3.1.3 Surface Morphology (SEM)

The surface morphology of the monolith was observed using a FEI Quanta 650 FEG Field Emission Scanning Electron Microscope (FESEM), and the quantitative globule-size distribution was determined from the SEM images, as shown in Figure 3.

A total of 100 globules were measured for each sample to obtain the corresponding average diameter and standard deviation. Pristine PGMEGD exhibited a porous monolithic structure composed of interconnected polymer globules forming a continuous three-dimensional network. The average globule diameter was 130.85 ± 11.09 nm, indicating a relatively narrow size distribution. Such globular morphology is a common characteristic of methacrylate-based polymer monoliths synthesized using porogenic systems containing 1,4-butanediol, 1-propanol, and water (Amalia et al., 2021; Erwanto et al., 2026). After amination with DEA, the average globule diameter increased to 180.82 ± 15.90 nm, accompanied by a broader size distribution. This increase may be associated with changes in the polymer surface during the epoxy ring-opening reaction with DEA. Nevertheless, the interconnected globular morphology was preserved without evidence of macroscopic structural collapse. Following alkalization, the average globule diameter was 182.67 ± 13.98 nm, which was comparable to that of PGMEGD-NH₂, indicating that the alkalization process did not substantially alter the globular morphology. Overall, the quantitative SEM analysis confirms that amination and alkalization modified the globule dimensions while preserving the interconnected three-dimensional monolithic structure, which is important for maintaining continuous pathways for reactant transport.

3.1.4 Surface Area and Porosity Analysis (BET)

Surface area and porosity analyses were performed using the Brunauer–Emmett–Teller (BET) method on a Quantachrome NovaTouch LX4 surface area analyzer at 77 K using N₂ as the adsorbate gas. Prior to measurement, the samples were degassed at 60 °C for 12 h. The textural properties of PGMEGD, PGMEGD-NH₂, and PGMEGD-NH₂-OH are summarized in Table 2, while the nitrogen adsorption-desorption isotherms and BJH pore-size distribution curves are presented in Figure 4(a) and Figure 4(b), respectively.

The pristine PGMEGD monolith exhibited a high BET surface area of $650.00 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $2.07 \text{ cm}^3 \text{ g}^{-1}$, indicating the formation of a well-developed interconnected porous network. This can be attributed to the ternary porogenic system (1-propanol/1,4-butanediol/water, 7:4:1, v/v), in which 1-propanol enhances polymer solvation, water promotes phase separation, and 1,4-butanediol moderates solvent strength, resulting in controlled pore formation and improved pore connectivity. Consequently, the obtained BET surface area was considerably higher than that reported for PGMEGD synthesized using a single-porogen system (Costa et al., 2020).

Following amination with 20% DEA, the BET surface area

decreased from 650.00 to $348.24 \text{ m}^2 \text{ g}^{-1}$ (46.4%), while the total pore volume decreased from 2.07 to $1.28 \text{ cm}^3 \text{ g}^{-1}$ (38.2%). This reduction is primarily attributed to the successful grafting of DEA molecules onto the epoxy groups lining the pore walls, which decreases the nitrogen-accessible surface area by partially occupying the pore space and restricting nitrogen access to the internal pore surfaces during BET measurements. This interpretation is supported by the substantial increase in amine density (3.43 mmol g^{-1}) together with the denser surface morphology observed in the SEM images. Although minor polymer chain rearrangement or localized swelling following chemical functionalization cannot be completely excluded, these effects are unlikely to be the dominant cause of the observed reduction in BET surface area. The post-polymerization modification strategy employed in this study was intentionally selected to preserve the rigidity of the poly(GMA-co-EGDMA) framework and minimize swelling or shrinkage, as previously reported for methacrylate-based monoliths (Ueki et al., 2004). Furthermore, the SEM images (Figure 3) revealed that the interconnected porous morphology was retained after amination, while the FTIR (Figure 2) spectra showed no significant changes in the characteristic absorption bands of the polymer backbone after chemical modification. These observations indicate that the monolithic framework remained structurally intact, suggesting that the reduction in BET surface area mainly reflects reduced pore accessibility caused by the introduced functional groups rather than degradation or collapse of the porous structure.

After alkalization, the BET surface area further decreased to $278.08 \text{ m}^2 \text{ g}^{-1}$, whereas the total pore volume decreased to $1.06 \text{ cm}^3 \text{ g}^{-1}$, corresponding to reductions of 20.2% and 17.2%, respectively. Since the alkalization step mainly converts the amine-functionalized monolith into the hydroxide form through ion exchange rather than inducing additional polymerization or crosslinking, the additional decrease in textural properties is most likely associated with reduced pore accessibility resulting from the presence of hydroxide-form functional groups within the pore channels. This interpretation is further supported by the FTIR spectra, which showed no significant changes in the characteristic absorption bands of the polymer backbone after alkalization, indicating that the polymer framework remained structurally intact.

The nitrogen adsorption-desorption isotherms shown in Figure 4(a) indicate that all samples retained their porous adsorption characteristics after chemical modification, although the total amount of adsorbed nitrogen gradually decreased following amination and alkalization. The corresponding BJH pore-size distribution curves (Figure 4(b)) further confirmed that the porous structure was preserved throughout the modification process. All samples exhibited pore diameters predominantly within the mesoporous region (2–50 nm) according to the IUPAC classification, with the dominant pore diameters located at approximately 13–15 nm. Although the differential pore volume decreased after functionalization, no appreciable shift toward microporous dimensions was observed, indicating that the interconnected mesoporous network remained intact.

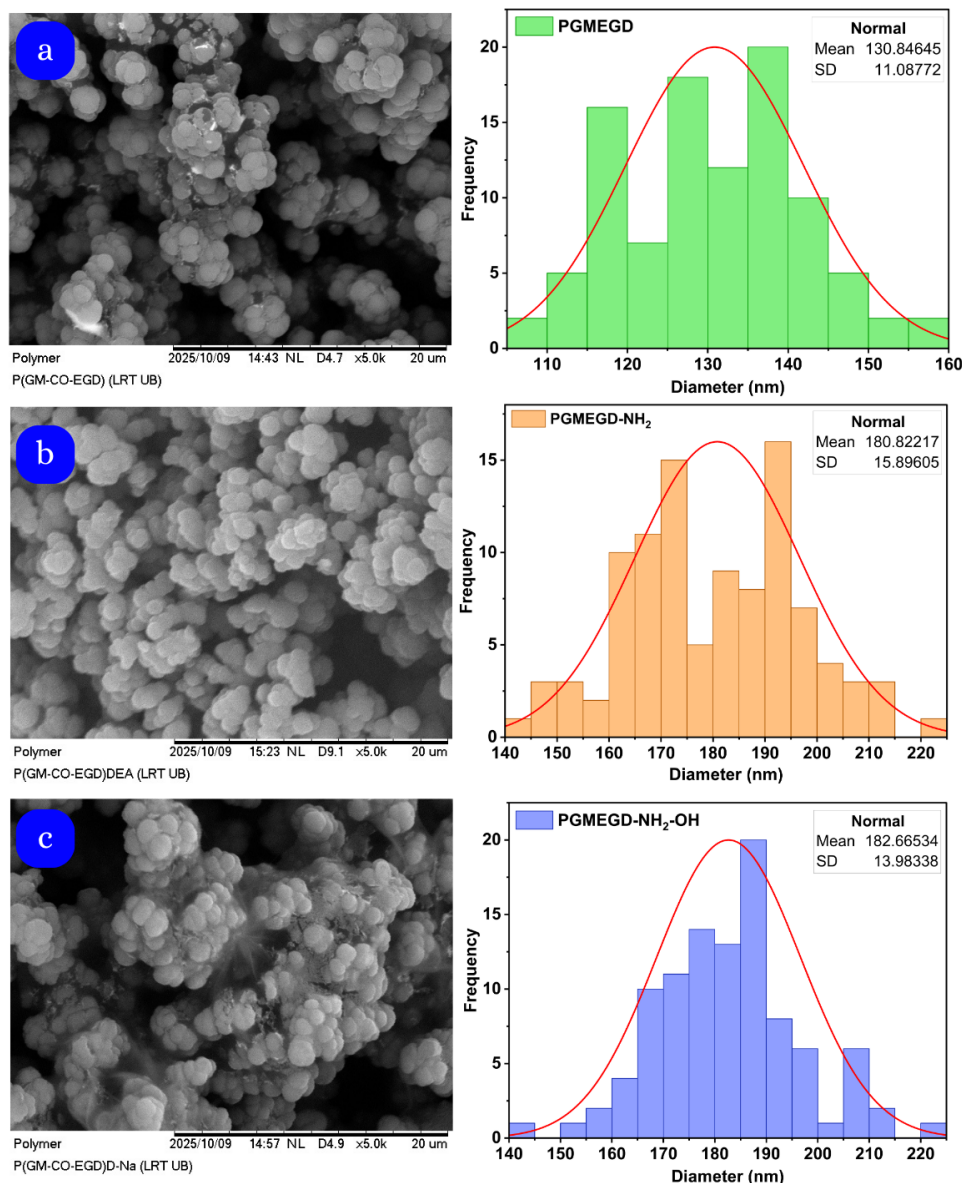


Figure 3. FESEM Micrographs and Globule-Size Distributions of (a) PGMEGD, (b) PGMEGD-NH₂, and (c) PGMEGD-NH₂-OH

Therefore, the reduction in BET surface area is more reasonably attributed to the decreased accessibility of the internal pore surface following chemical functionalization rather than collapse of the interconnected porous framework.

The preservation of the mesoporous structure is particularly advantageous for continuous-flow transesterification because pores within this size range facilitate the diffusion of bulky triglyceride molecules to the accessible basic active sites. Consequently, despite the gradual decrease in BET surface area and pore volume following chemical modification, the PGMEGD-NH₂-OH monolith retained sufficient porosity to ensure efficient mass transfer and excellent catalytic performance during

continuous biodiesel production.

3.1.5 Thermal Stability (TGA)

The thermal stability of the materials was evaluated by thermogravimetric analysis (TGA) using a Shimadzu DTG-60 in the temperature range of 25-1100 °C, as shown in Figure 5. PGMEGD exhibited higher thermal stability than the functionalized materials. The initial weight-loss stage observed for all samples occurred below 100 °C and was attributed to the removal of physically adsorbed water and residual volatile compounds trapped within the porous structure. PGMEGD remained relatively stable up to approximately 250 °C before

Table 2. BET and BJH Textural Properties of PGMEGD, PGMEGD-NH₂, and PGMEGD-NH₂-OH

Material	BET Surface Area (m ² g ⁻¹)	Total Pore Volume (cm ³ .g ⁻¹)	Dominant BJH Pore Diameter (nm)	IUPAC Pore Classification
PGMEGD	650.00	2.07	13.2	Mesoporous
PGMEGD-NH ₂	348.24	1.28	14.1	Mesoporous
PGMEGD-NH ₂ -OH	278.08	1.06	14.8	Mesoporous

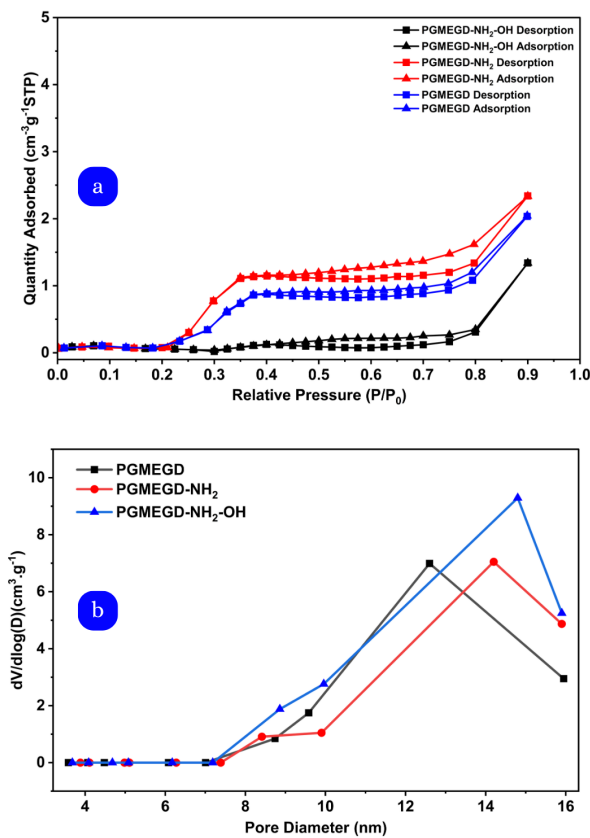


Figure 4. (a) N₂ Adsorption-Desorption Isotherms and (b) Barrett-Joyner-Halenda (BJH) Pore-Size Distributions of PGMEGD, PGMEGD-NH₂, and PGMEGD-NH₂-OH Monoliths

undergoing the main decomposition of the polymer framework. This behavior is consistent with the thermal characteristics previously reported for poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate)-based monoliths (Erwanto et al., 2026). In contrast, PGMEGD-NH₂ and PGMEGD-NH₂-OH exhibited earlier and more pronounced weight loss at lower temperatures, which can be attributed to the presence of amine functionalities and OH⁻ exchange sites introduced during the post-synthetic modification steps. Similar reductions in thermal stability following amination have been reported for various amine-functionalized polymeric materials (Maleki et al., 2022; Nasef et al., 2016). Nevertheless, all materials exhibited

sufficient thermal stability for the continuous transesterification process employed in this study, which was conducted at 50 °C. Therefore, the monolithic structure is expected to remain stable under the reaction conditions.

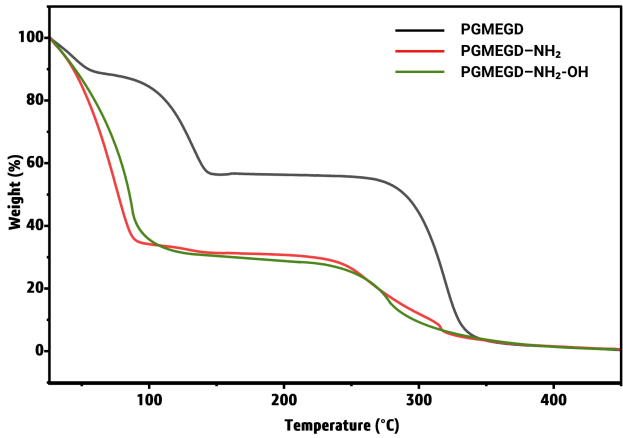


Figure 5. Thermogravimetric Analysis (TGA) Curves of PGMEGD (black), PGMEGD-NH₂ (red), and PGMEGD-NH₂-OH (green) Monoliths

3.1.6 Basicity Capacity

The total basicity of PGMEGD-NH₂-OH was quantified by a back-titration method using 0.01 N benzoic acid. Briefly, 0.1 g of PGMEGD-NH₂-OH monolith was added to 50 mL of 0.01 N benzoic acid solution in benzene and stirred for 24 h at room temperature to ensure complete neutralization of the basic groups. The excess benzoic acid was subsequently titrated with 0.01 N NaOH solution in ethanol using phenolphthalein as the indicator, with the endpoint determined by the disappearance of the indicator color. The total basicity (mmol g⁻¹) was calculated from the difference in titrant volume between the blank solution (without sample) and the sample. As summarized in Table 3, increasing the NaOH concentration from 0.1 to 1.0 M resulted in a significant increase in OH⁻ capacity from 1.85 to 3.25 mmol g⁻¹. This result indicates that higher NaOH concentrations promoted more effective ion exchange and conversion of the amine functionalities into their hydroxide form. Further increasing the NaOH concentration to 2.0 M produced only a slight increase in OH⁻ capacity to 3.28 mmol g⁻¹, suggesting that most of the accessible active

Table 3. Effect of NaOH Concentration on PGMEGD-NH₂-OH Capacity

NaOH (M)	OH ⁻ mmol g ⁻¹)
0.1	1.85
0.5	2.92
1.0	3.25
2.0	3.28
4.0	3.02

sites had already been converted at 1.0 M NaOH. In contrast, increasing the NaOH concentration to 4.0 M led to a decrease in OH⁻ capacity to 3.02 mmol g⁻¹. This decline may be associated with changes in the pore structure under highly alkaline conditions or with ion accumulation that reduces the accessibility of the active sites (He et al., 2022). Based on these results, the NaOH concentration of 1.0 M was chosen as the optimal condition for the alkalization process because it has resulted in a near-maximum OH⁻ capacity with a more efficient use of bases compared to higher concentration.

3.2 Effect of Reaction Parameters on Continuous Transesterification

The catalytic performance of the PGMEGD-NH₂-OH monolith was evaluated in a continuous transesterification system for the conversion of palm oil into fatty acid methyl esters (FAME). The two main parameters investigated were the ratio of methanol molar to oil as well as the feed flow rate, as both directly affect the reaction equilibrium and contact dynamics between the reactants and the catalyst active sites.

3.2.1 Effect of Methanol-to-Oil Molar Ratio

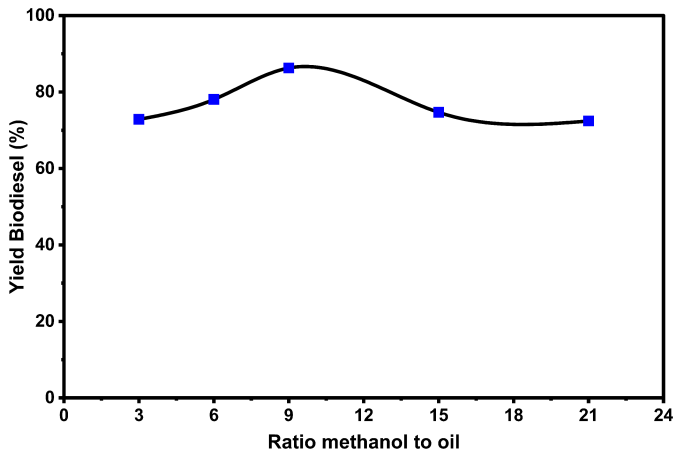


Figure 6. Effect of the Methanol-to-Palm oil Molar Ratio on Fatty Acid Methyl Ester (FAME) Yield Over the PGMEGD-NH₂-OH Monolithic Catalyst

Figure 6 illustrates the effect of the methanol-to-oil molar

ratio on FAME yield over the PGMEGD-NH₂-OH monolithic catalyst at 50 °C and a fixed flow rate of 0.05 mL min⁻¹. Increasing the methanol-to-oil molar ratio from 3:1 to 9:1 significantly enhanced the biodiesel yield from 62.85% to 86.28%. This improvement can be attributed to the greater availability of methanol, which shifts the transesterification equilibrium toward FAME formation in accordance with Le Chatelier’s principle. Similar behavior has been widely reported for heterogeneous-catalyzed transesterification systems (Lin and Tseng, 2024). However, a further increase in the methanol-to-oil molar ratio to 12:1 resulted in a decrease in biodiesel yield to 74.68%. Excessive methanol may dilute the concentration of triglycerides in the reaction mixture, thereby reducing the frequency of effective interactions between triglyceride molecules and the catalytic active sites. In addition, the increased methanol content can alter the hydrodynamic behavior within the monolithic reactor and reduce the residence time of triglycerides near the active sites, leading to lower conversion. Similar trends have been reported in previous studies, where excessive methanol was found to adversely affect biodiesel production in heterogeneous catalytic systems (Lin and Tseng, 2024). Therefore, a methanol-to-oil molar ratio of 9:1 was selected as the optimum condition for subsequent experiments.

3.2.2 Effect of Flow Rate

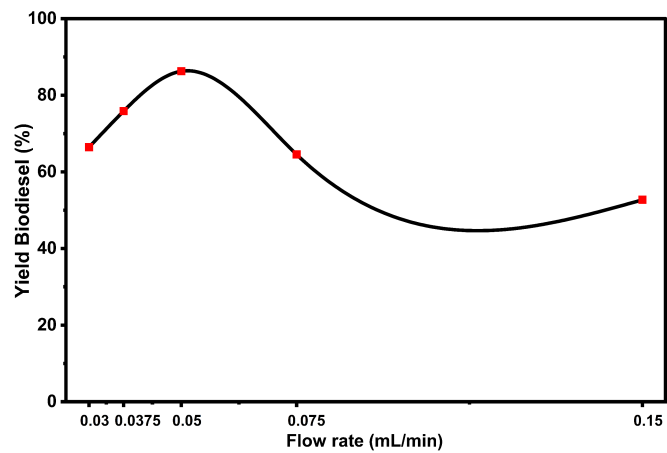


Figure 7. Effect of Flow Rate on Fatty Acid Methyl Ester (FAME) Yield Over the PGMEGD-NH₂-OH Monolithic Catalyst

The effect of feed flow rate on biodiesel yield is presented in Figure 7 using the optimum methanol-to-oil molar ratio of 9:1. In a continuous-flow reactor system employing a monolithic catalyst, the flow rate determines the residence time of the reactants inside the column and therefore becomes a critical parameter affecting the conversion level. Biodiesel yield increased from 78.59% to 86.28% when the flow rate was increased from 0.03 mL min⁻¹ to 0.05 mL min⁻¹. At a low flow rate of 0.03 mL min⁻¹, a relatively thick liquid boundary layer

is formed around the surface of the monolithic catalyst. This layer increases mass-transfer resistance, thereby hindering the diffusion of reactants toward the catalyst active sites. Increasing the flow rate to 0.05 mL min^{-1} reduces the thickness of the boundary layer, resulting in more efficient mass transfer and higher conversion. In contrast, a further increase in flow rate from 0.05 mL min^{-1} to 0.10 mL min^{-1} led to a decrease in biodiesel yield to 62.36%. This occurs because the residence time of the reactants inside the column becomes too short. As a result, the reactants do not have sufficient time to diffuse into the catalyst pores and interact with the active sites before leaving the reactor. This phenomenon has also been reported in previous studies on continuous transesterification systems using heterogeneous catalysts (Abdulla Yusuf et al., 2022). Therefore, a flow rate of 0.05 mL min^{-1} was selected as the optimal condition for subsequent evaluation.

3.2.3 Mechanism of the Transesterification Reaction

The proposed transesterification mechanism catalyzed by the PGMEGD- NH_2 -OH monolithic resin is illustrated in figure 8. The catalytic activity originates from hydroxide ions associated with the amine-functionalized sites introduced through DEA modification and subsequent alkalization. In the first step (1), these hydroxide ions act as Brønsted basic sites and abstract a proton from methanol, generating methoxide ions (CH_3O^-), which serve as the active nucleophilic species in the transesterification reaction. Simultaneously, water is formed as a by-product of the proton transfer process. In the second step (2), the generated methoxide ion attacks the electrophilic carbon atom of the carbonyl group in the triglyceride molecule, resulting in the formation of a tetrahedral intermediate. This nucleophilic attack increases the susceptibility of the ester bond toward cleavage and facilitates the conversion of triglycerides into methyl esters. In the third step (3), the tetrahedral intermediate undergoes rearrangement and decomposition, releasing one molecule of fatty acid methyl ester (FAME) and forming a diglyceride intermediate. The same reaction sequence subsequently occurs on the remaining ester groups of the diglyceride and monoglyceride intermediates until glycerol and three molecules of FAME are ultimately produced. The proposed mechanism is consistent with the successful introduction of amine functionalities confirmed by FTIR analysis and the catalytic activity observed during the transesterification reaction. Furthermore, the interconnected porous structure of the PG-MEGD monolith facilitates efficient mass transfer of methanol and triglyceride molecules to the active sites, thereby enhancing reactant accessibility and catalytic performance. The covalent attachment of the functional groups to the polymer matrix also minimizes catalyst leaching and contributes to catalyst stability during continuous operation.

To further evaluate the performance of the proposed PG-MEGD- NH_2 -OH monolithic catalyst, its catalytic performance was compared with recently reported heterogeneous catalysts employed in continuous biodiesel production. The reported continuous-flow systems employ various catalyst types, feed-

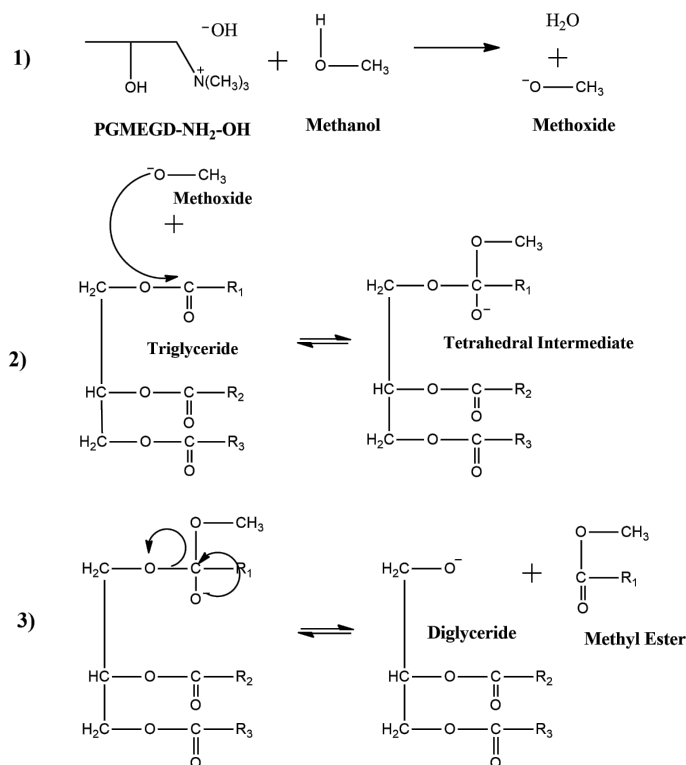


Figure 8. Proposed Reaction Mechanism for Triglyceride Transesterification with Methanol Over the PGMEGD- NH_2 -OH Monolithic Anion-Exchange Resin

stocks, reactor configurations, and operating conditions, making direct comparison challenging. Nevertheless, such a comparison provides a useful benchmark for assessing the performance of the present catalyst. The comparison is summarized in Table 4.

As shown in Table 4, biodiesel yields ranging from 71.10% to 99.32% have been reported for continuous heterogeneous catalytic systems employing different feedstocks, catalyst types, and reactor configurations. The differences in biodiesel yield should be interpreted in conjunction with the corresponding operating conditions, as direct comparison is complicated by variations in reaction temperature, methanol-to-oil molar ratio, catalyst amount, flow rate, feedstock composition, and reactor configuration. In the present study, the PGMEGD- NH_2 -OH monolithic catalyst achieved an FAME yield of 86.28% at a relatively mild temperature of 50°C , with a methanol-to-oil molar ratio of 9:1 and a flow rate of 0.05 mL min^{-1} . Although the yield was lower than those reported for some of the compared systems, the present monolithic configuration offers an important operational advantage because the catalyst is integrated directly into the flow reactor, eliminating the need for post-reaction catalyst separation. In addition, the PGMEGD- NH_2 -OH monolith exhibited good regeneration capability, with the catalytic activity and total basicity largely restored after regeneration, enabling repeated operation over

Table 4. Comparison of Recently Reported Heterogeneous Catalysts for Continuous Biodiesel Production Using Different Feedstocks and Reactor Configurations

Catalyst	Feedstock	Reactor	T (°C)	M:O	Flow Rate (mL min ⁻¹)	BY (%)	Ref
ZrO ₂ -TiO ₂ @MGO 4.75 g	UCO	MR	60	3:1	0.167	99.32	(Hadi et al., 2023)
CaO 0.03 g	PO	PMCR	65	24:1	8.9	99	(Chueluecha et al., 2017)
Demineralized Water Plant Sedimentation 0.083 g	Soybean Oil	MR	60	1:1.8	1.08	87.06	(Aghel et al., 2016)
Candida rugosa lipase 4g	CPO	PBR	60	6:1	0.4	71.10	(Hermansyah, 2023)
PGMEGD-NH ₂ -OH 1.25 g	PO	MFR	50	9:1	0.05	86.28	This work

Notes: M:O = Methanol-to-Oil Molar Ratio; UCO = Used Cooking Oil; CPO = Crude Palm Oil; PO = Palm Oil; MR = Micro Reactor; PBR = Packed-Bed Reactor; MFR = Monolithic Flow Reactor; PMCR = Pulsed Microchannel Reactor.

Table 5. FAME Profiles That Exist After Transesterification Reactions

Compound Name	Content (wt%)	
	This Work	Previous Work (Erwanto et al., 2026)
Methyl Laurate	0.93	0.596
Methyl Myristate	2.097	2.434
Methyl Palmitate	50.749	52.729
Methyl Stearate	3.31	5.547
Methyl Arachidate	0.41	0.318
Methyl Palmitoleate	0.15	0.187
Methyl Oleate	26.69	28.131
Methyl Linoleate	8.53	9.562
Methyl Linolenate	0.33	0.314

Table 6. Total Basicity of the PGMEGD-NH₂-OH Monolith Determined by Benzoic Acid Back Titration Before and After Repeated Transesterification Cycles and Regeneration

Catalyst Condition	Sampling Point	Total Basicity (mmol g ⁻¹)	Basicity Retention (%)
Fresh Catalyst	Fresh	3.25	100.0
After Four Reaction Cycles (Before R ₁)	Cycle 4	2.48	76.3
After First Regeneration	R ₁	3.18	97.8
After Another Four Reaction Cycles (Before R ₂)	Cycle 8	2.44	75.1
After Second Regeneration	R ₂	3.16	97.2

multiple cycles. Therefore, the performance of the PGMEGD-NH₂-OH monolith should be considered not solely in terms of biodiesel yield, but also in terms of its mild operating temperature, continuous-flow configuration, regenerability, and simplified catalyst handling. These characteristics demonstrate the potential of the monolithic catalyst for continuous biodiesel production.

3.3 FAME Composition Analysis by GC-MS

The successful conversion of palm oil triglycerides into fatty acid methyl esters (FAMEs) was confirmed by gas chromatography-mass spectrometry (GC-MS) analysis. The FAME composition obtained from the continuous transesterification of palm oil over the PGMEGD-NH₂-OH monolithic catalyst under the optimum reaction conditions (methanol-to-oil molar ratio of 9:1, flow rate of 0.05 mL min⁻¹, and temperature of 50 °C) is summarized in Table 5.

The FAME profile was dominated by three major components: methyl palmitate (50.75%), methyl oleate (26.69%), and methyl linoleate (8.53%). This composition is characteristic of palm oil-based biodiesel, in which palmitic acid (C16:0) and oleic acid (C18:1) are typically the predominant fatty acids (Erwanto et al., 2026; Sumari et al., 2024). Based on the degree of saturation, saturated FAMEs (C12:0, C14:0, C16:0, C18:0, and C20:0) accounted for 57.50% of the total FAME content, whereas unsaturated FAMEs (C16:1, C18:1, C18:2, and C18:3) represented 42.50%. This relatively high proportion of unsaturated FAMEs is advantageous for low-temperature fuel properties, as it generally reduces the cloud point and pour point of biodiesel (Kibar et al., 2023). Comparison with previous studies (Erwanto et al., 2026) revealed a similar FAME distribution, with only minor differences in the relative abundance of individual components (e.g., methyl palmitate: 50.75% vs. 52.73%; methyl oleate: 26.69% vs. 28.13%). These differences may be attributed to variations in the fatty acid composition of palm oil from different sources, as well as differences in the reaction conditions employed.

Notably, the biodiesel produced in the present study was synthesized using a continuous-flow transesterification system employing the PGMEGD-NH₂-OH monolithic catalyst. The similarity of the FAME composition to those reported in previous studies indicates that the continuous-flow operation effectively converted palm oil triglycerides into the corresponding methyl esters without substantially altering the characteristic fatty acid distribution of the feedstock (Erwanto et al., 2026). The interconnected porous structure of the monolith facilitated continuous contact between the reactants and the immobilized catalytic sites, thereby promoting mass transfer and catalytic conversion throughout the reactor. In addition, the continuous-flow configuration eliminated the need for catalyst separation after the reaction and simplified continuous operation. Overall, the GC-MS results demonstrate that the PGMEGD-NH₂-OH monolithic catalyst can function effectively as an integrated catalytic reactor for continuous biodiesel production while producing a FAME composition

consistent with that typically reported for palm oil-derived biodiesel. Importantly, the GC-MS analysis of the biodiesel product did not detect any nitrogen-containing compounds among the identified components, providing an initial indication that no detectable nitrogen-containing species were present in the analyzed product. However, GC-MS analysis alone cannot quantitatively exclude the possibility of trace leaching of nitrogen-containing or other catalyst-derived species. Therefore, a dedicated leaching study using appropriate elemental analysis will be conducted in future work to further verify the heterogeneous nature and long-term stability of the PGMEGD-NH₂-OH catalyst.

3.4 Catalyst and Regeneration Stability

Catalytic stability was evaluated through repeated continuous transesterification experiments under the optimum reaction conditions (methanol-to-palm oil molar ratio of 9:1, flow rate of 0.05 mL min⁻¹, and temperature of 50 °C) without regeneration between reaction cycles.

Figure 9a shows that the FAME yield remained above 80% during the first four consecutive reaction cycles, indicating good initial catalytic stability. However, prolonged operation without regeneration resulted in a progressive decline in catalytic performance, with the FAME yield decreasing to 19.84% after the eighth cycle. This reduction suggests gradual catalyst deactivation during continuous operation.

To restore catalytic activity, the spent monolith was regenerated by sequential washing with 0.25 M citric acid, 1.0 M NaOH, and ethanol. As shown in Figure 9b, the regeneration procedure effectively restored the FAME yield to approximately 86%, which was comparable to the initial catalytic performance (86.28%). After regeneration, the catalyst maintained a FAME yield of approximately 80% over the subsequent four reaction cycles before another regeneration was required. The second regeneration exhibited a similar recovery pattern, demonstrating the reproducibility of the regeneration procedure and the good reusability of the PGMEGD-NH₂-OH monolith. To further investigate the stability of the active sites during repeated operation, the total basicity of the catalyst was determined by benzoic acid back titration before and after repeated reaction cycles and regeneration (Table 6).

The total basicity measurements provide additional evidence of changes in the accessible basic sites during repeated catalyst operation. After four consecutive reaction cycles, the total basicity decreased from 3.25 to 2.48 mmol g⁻¹, corresponding to 76.3% retention of the initial value. This decrease indicates that a fraction of the accessible basic sites became less available during continuous operation. Following the first regeneration, the total basicity recovered to 3.18 mmol g⁻¹ (97.8% retention), which was consistent with the recovery of FAME yield observed in Figure 9b. A similar decrease and subsequent recovery of total basicity were observed before and after the second regeneration, indicating that the regeneration procedure restored most of the accessible basic sites. These results support the reversible nature of the changes in the cata-

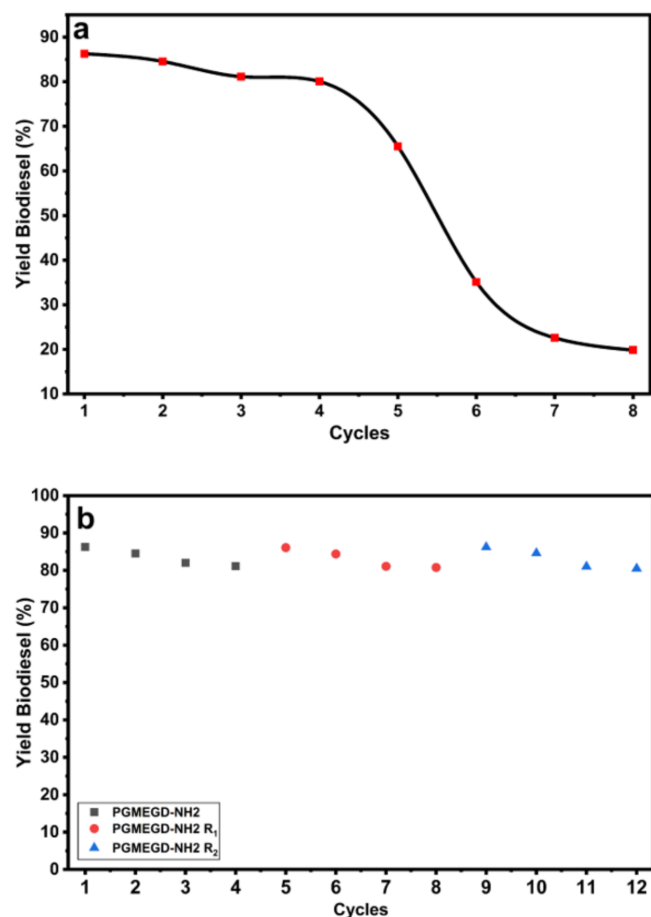


Figure 9. Catalytic Stability of the PGMEGD-NH₂-OH Monolithic Catalyst During Continuous Transesterification of Palm Oil: (a) Consecutive Reaction Cycles Without Regeneration and (b) Catalyst Regeneration After Every Four Reaction Cycles

lyst's basic character during repeated operation.

The decrease in catalytic activity was more pronounced than the decrease in total basicity, indicating that the loss of accessible basic sites alone may not fully account for the observed deactivation. The additional decrease in catalytic performance may be associated with reduced accessibility of the active sites during continuous operation, potentially due to the adsorption or accumulation of reaction-derived species within or on the surface of the monolith. However, because no direct post-reaction characterization of surface deposits was performed, the occurrence and chemical nature of such species cannot be conclusively established from the present data. Therefore, the observed changes are interpreted as evidence of reversible changes in catalyst accessibility rather than definitive proof of surface fouling.

FTIR analysis further supported the structural stability of the catalyst after repeated operation. As shown in Figure 10, the

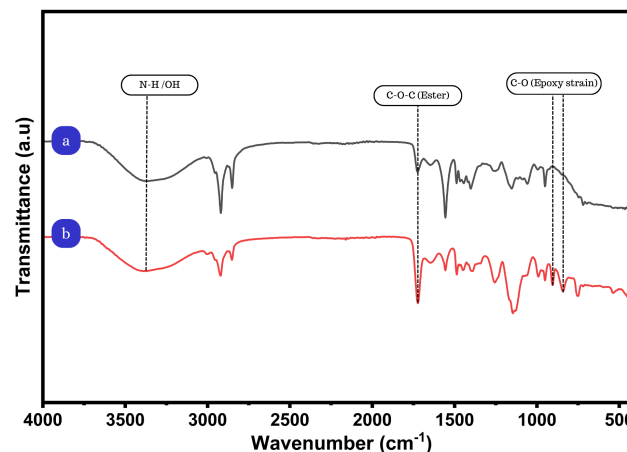


Figure 10. FTIR Spectra of the PGMEGD-NH₂-OH Catalyst After Four Reaction Cycles (a) Before and (b) After Regeneration

characteristic ester carbonyl band at approximately 1720 cm^{-1} and the broad O-H/N-H stretching band at $3200\text{--}3500\text{ cm}^{-1}$ remained essentially unchanged after repeated catalytic use and regeneration, indicating that the polymer framework and the grafted amine functionalities were preserved throughout the reaction. Similar observations have been reported for poly(GM-co-EGD)-based catalysts after repeated use (Erwanto et al., 2026), where no significant changes in the FTIR spectra were observed.

Compared with the previously reported L-arginine/poly-(GM-co-EGD) catalyst, which maintained catalytic activity for up to five reaction cycles without regeneration (Erwanto et al., 2026), the PGMEGD-NH₂-OH monolith exhibited a faster decline in activity under continuous operation. However, the present catalyst offers a significant advantage in terms of regenerability. The regeneration procedure restored approximately 98–99% of the initial total basicity and catalytic activity after each regeneration step, enabling stable catalyst reuse over repeated operating cycles.

Overall, the combined catalytic performance, total basicity, and FTIR results indicate that catalyst deactivation is predominantly associated with reversible surface deactivation and temporary blockage of accessible basic sites rather than irreversible degradation of the polymer framework. Although the present study did not determine the ion-exchange capacity using a standard IEC method, the recovery of total basicity after regeneration provides complementary experimental evidence that the accessible basic sites responsible for catalysis were effectively restored during repeated operation.

4. CONCLUSIONS

PGMEGD-based monolithic resins (PGMEGD-NH₂-OH) were successfully prepared through amination using diethylamine (DEA) at an optimum concentration of 20% (resulting

in an amine density of 3.43 mmol g^{-1}) followed by alkalization with 1.0 M NaOH (resulting in OH^- capacity of 3.31 mmol g^{-1} , equivalent to 96.5% of AD). The material has an interconnected three-dimensional pore structure as well as adequate thermal stability for operation at 50°C . As a catalytic microreactor for the continuous transesterification of palm oil with methanol, the catalyst achieved an optimum biodiesel yield of 86.28% at a methanol-to-oil molar ratio of 9:1 and a flow rate of 0.05 mL min^{-1} . The catalyst maintained biodiesel yield above 80% during the first four reaction cycles, and the regeneration procedure involving sequential washing with 0.25 M citric acid, 1 M NaOH , and ethanol successfully restored approximately 99% of the initial catalytic activity, enabling operation for up to 12 cycles through two regeneration steps. Further studies are required to evaluate long-term catalyst stability over a larger number of reaction cycles, optimize regeneration intervals, investigate the applicability of the catalyst to feedstocks with high free fatty acid contents, and perform techno-economic analyses to assess the feasibility of pilot-scale and industrial-scale implementation.

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