Journal of Engineering Research and Applied Science
Available at www.journaleras.com
Volume 14 (2), December 2025, pp 167-180
ISSN 2147-3471 © 2025

Reaction Kinetics and Mechanistic Shift in Non/Catalytic Esterification of PEGs: Microwave-Assisted vs. Conventional Esterification

Gülşen Karaca[1,3,*], Ömür Aras[1,2]

[1]Chemical Engineering, Bursa Technical University, Bursa Turkey
[2]Chemical Engineering, Kyrgyz-Turkish Manas University, Kyrgyzstan
[3]Sözal Chemical Industry and Trade Inc., R&D Center, Bursa, Turkey

Accepted 26 November 2025

Abstract

Esterification reactions play a crucial role in both industrial and biological systems, essential for the production of pharmaceuticals, polymers, and specialty chemicals. The esterification of polyethylene glycol (PEG) with chloroacetic acid (CAA) is important for surfactants, drug delivery systems, etc. This study investigates the esterification kinetics in a microwave-assisted, non-catalytic system, employing an alternative kinetic parameter estimation approach compared to conventional methods. Instead of separately analyzing temperature-dependent reaction rates, an optimization algorithm was used to simultaneously evaluate data from different temperatures. This novel method enhances the accuracy and reliability of kinetic parameters, while the absence of a catalyst significantly influenced the reaction mechanism, emphasizing the role of high-dielectric constant molecules. The esterification kinetics between CAA and PEGs were studied under both conventional and microwave-assisted conditions. Optimized kinetic data revealed that increasing PEG chain length resulted in decreased reaction rates, which was attributed to increased viscosity and steric hindrance effects. In the microwave method, lower rate constants were associated with the shorter thermal exposure of the reaction. Additionally, the collision frequency factor decreased with an increase in microwave power, due to the lower dielectric constants of PEG-based compounds. A significant change in reaction order was also observed under non-catalytic conditions; under microwave irradiation, PEG200 exhibited a reaction order of 1.5, while PEG400 showed second-order dependence. These findings offer new insights into the kinetic behavior of non-catalytic reactions and highlight the influence of molecular properties on reaction pathways. Ester formation was confirmed by FTIR and NMR analyses, providing evidence of successful esterification.

Keywords: *Esterification, Microwave, Kinetic Study, Optimization, Reaction Mechanism Shift*

1. Introductıon

Esters are versatile compounds with a wide range of applications across various industries, owing to their unique properties and pleasant aromas [1]. They are found ubiquitously as both natural and synthetic organics [2]. In addition to their significant impact as fuels, plasticizers, solvents, flavoring, and aroma compounds, esters are also utilized in the synthesis of pharmaceutical and agricultural chemical compounds, in the cosmetic industry, and in personal care product formulations [2,3].

Esters are frequently employed in the synthesis of softeners, emulsifiers, dispersants, detergents, and surfactants [4]. Due to their numerous applications across various industries, research into the synthesis of more efficient esters has garnered considerable interest.

Esterification reactions generally proceed very slowly in the absence of a catalyst and are thermodynamically reversible [5]. Therefore, a catalyst is typically required to accelerate the reaction [6]. To shift the equilibrium towards the forward direction, either a homogeneous or heterogeneous acid catalyst should be used, and the water produced during the reaction must also be removed [7]. Commonly used homogeneous acid catalysts in esterification reactions include sulfuric acid (H_2SO_4), hydroiodic acid (HI), hydrofluoric acid (HF), phosphoric acid (H3PO4), para-toluenesulfonic acid (p-TSA), formic acid (HCOOH) [8], and aluminum chloride ($AlCl_3$), while heterogeneous acid catalysts include ion exchange resins, zeolites, triorganic acids, sulfate oxides, aqueous zirconium oxide, and supported heteropoly acids [9]. Recently, the use of enzymes as catalysts in

*Corresponding author: krc.gulsen@gmail.com

esterification reactions has also gained attention [10,11].

The most common method for ester synthesis is catalytic, employing traditional heating techniques. However, traditional heating methods have some drawbacks, including long reaction times, uneven heating, high energy consumption, and low yields [12,13]. As an alternative to these methods, microwave-assisted heating, a novel energy source, is widely used [14]. Since microwave radiation can directly interact with materials at the molecular level, it provides uniform and rapid heating of reactants [15]. This rapid heating occurs due to ionic conduction or dipole rotation, which increases molecular dynamics. More intense molecular movements lead to more energetic collisions, thus enhancing the reaction rate [12]. As a result, high yields and purity products are obtained in short reaction times [14]. In the literature, studies involving the use of fatty acids and amino alcohols [16,17,18], diols [19], halogenated alcohols [20], alkyl diamines [21], acid chlorides [22], polyethylene glycols [203], alcohols [13,24,25], acids [26], and glycerol [27] as reactants in esterification reactions can be found. Additionally, studies have explored the use of acyl halides with diamines [28], polyols [29], and diols [30,31]. Furthermore, Dabiri and Honarvar (2020) studied the esterification of sunflower oil and glycerol [32], Chauhan et al. (2023) investigated the esterification of epoxy esters with imidazole [33], Shaban et al. (2022) examined the esterification of two different carboxylic acids [34], Sripada and Kastner (2023), and Huang et al. (2024) researched the esterification of an acid and alcohol [35], [36], and Lin et al. (2025) studied the esterification of gluten and starch [37], while Wang et al. (2022) investigated the esterification reaction of carboxylic acids and alcohols [38]. Fashi et al. (2024) conducted a study in which they performed microwave-assisted solid-state acetic acid esterification of corn starch and examined its structural and functional effects [39]. Using Zn-Mg-Al catalysts, Abas et al. (2020) employed microwave-assisted heating to achieve maximum conversion in the esterification of lauric acid with diethylene glycol [40]. In another study, artificial neural networks were used to predict the yield of biodiesel produced from palm oil fatty acid distillate using a TiO_2-ZnO mesoporous catalyst under microwave heating [41]. Tarigan et al. (2025) used calcined waste egg shells as a catalyst to produce biodiesel from high-fatty acid feedstocks under microwave irradiation [42]. Umrigar et al. (2022) synthesized biodiesel, known as mono alkyl esters of fatty acids, using oleic acid and various alcohols (methanol, ethanol, 2-propanol) under microwave-assisted conditions [43]. Sitepu et al. (2023) reported the microwave-assisted enzymatic esterification of various fatty acids (myristic and palmitic) with isopropyl alcohol, resulting in energy savings [44]. In their study, Akream et al. (2024) synthesized biodiesel from waste cooking oils under microwave-assisted conditions with a bi-functional ZnO-Ce/AC catalyst, achieving 99.6% yield [45]. Nayak et al. (2021) performed microwave-assisted esterification of kusum oil with silicotungstic acid, achieving 99.6% yield and found that microwave energy reduced the activation energy [46]. Lieu et al. (2016) applied a microwave-assisted esterification pre-treatment to reduce the free fatty acid content of seed oil with high free fatty acid content, achieving esterification with 94.43% yield [47]. Johari et al. (2024) studied the kinetic aspects of microwave-assisted transesterification of dairy waste scum oil in the presence of a catalyst, and compared it with a study using the same feedstock with traditional methods [48].

The chemical structure and chain length of reactants in a chemical reaction significantly influence both the molecular properties and the kinetics of the synthesis process. Although the literature includes several studies involving polyethylene glycol (PEG) derivatives with varying chain lengths, investigations focusing on short-chain PEGs remain limited. Furthermore, the effect of PEG chain length on the kinetics of esterification reactions has not been adequately clarified. In addition, a comprehensive comparative analysis of the kinetic behavior under conventional and microwave-assisted methods is lacking.

This study aims to determine the kinetic parameters of esterification reactions between PEGs of different molecular weights (PEG 200 and PEG 400) and chloroacetic acid under both conventional and microwave-assisted conditions (Figure 1). Before proceeding with the temperature-dependent experiments, preliminary trials performed under conventional conditions without a catalyst revealed that the reaction progressed rather slowly. Therefore, p-toluenesulfonic acid (p-TSA) was employed as a homogeneous catalyst in the conventional method. In the microwave-assisted method, however, the catalyst was not used, as it was observed to degrade under microwave irradiation. In both methods, the progress of the reaction was monitored using a titrimetric method, with methanol as the solvent, phenolphthalein as the indicator, and 0.5 N potassium hydroxide as the titrant. The experimental data obtained were analyzed using an optimization algorithm, and the kinetic parameters of the reactions were determined and compared. In this context, the hypothesis that an increase in PEG chain length reduces the reaction rate and that the microwave-assisted method exhibits a distinct kinetic profile was tested.

2. Experimental Section

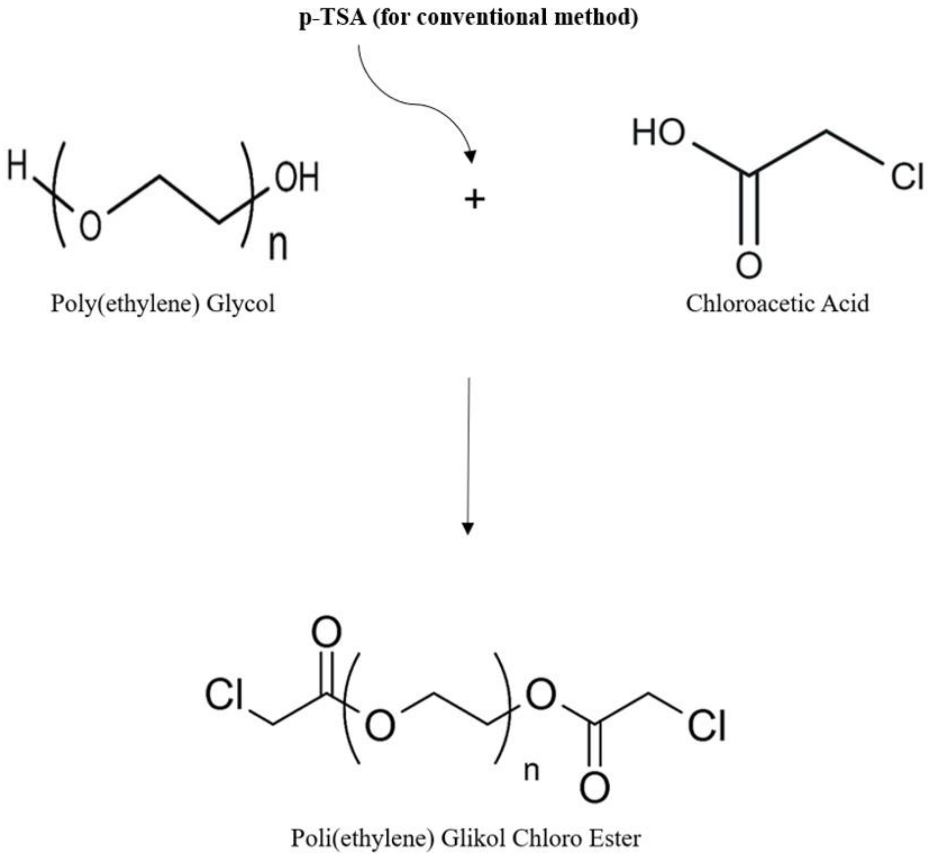
2.1. Chemical Reagents and Properties

Polyethylene glycol (200) (CAS No: 25322-68-3, Ataman Chem.), polyethylene glycol (400) (CAS No: 25322-68-3, Sözal Chem. Inc.), chloroacetic acid (CAS No: 79-11-8, ≥99%, Merck), methanol (CAS No: 67-56-1, ≥99.7%, Honeywell), potassium hydroxide (CAS No: 1310-58-3, ≥86%, Sigma-Aldrich), phenolphthalein (CAS No: 77-09-8, Merck), petroleum ether (CAS No: 64742-49-0, ≥86%, Kimyalab), and diethyl ether (CAS No: 60-29-7, ≥99.7%, Sigma-Aldrich) are the chemicals used in the experiments. All chemicals were used directly without any additional purification process.

Microwave reactions were carried out using a Milestone Ethos Easy microwave system (MA174-001) in a round-bottom flask with constant stirring speed (30%) and variable temperature using microwave power (max 450W).

The FTIR analysis of the synthesized polyethylene glycol chloro-esters (PEGnClEs) in this study was performed using a Perkin Elmer Spectrum Two model device located in the Chemistry Department at Bursa Technical University.

The ^{1}HNMR analysis of the synthesized polyethylene glycol chloro-esters (PEGnClEs) in this study was performed using a JEOL ECZ500R (11.75 Tesla) spectrometer located at the Central Research Laboratory (ARUM) of Eskişehir Osmangazi University.



n=2.4 : PEG200 , n=8.7 : PEG400

Figure 1. Molecular representation of the synthesis process for poly(ethylene glycol) chloroesters.

2.2. Experimental Procedure

In the conventional method, PEG$_n$ClEs were prepared through the esterification of 0.2 mol chloroacetic acid with 0.1 mol polyethylene glycol (PEG200 and PEG400) separately. As a catalyst, 0.01% p-Toluen Sulfonic Acid (p-TSA) was added to the reaction. The reactions were carried out at various temperatures under atmospheric pressure, and the water formed during the reaction was removed using a Dean-Stark apparatus (Figure 2a). The catalyst was removed from the final reaction mixture using petroleum ether [49,50]. In the microwave method, PEG$_n$ClEs was prepared through the microwave irradiation of 0.2 mol chloroacetic acid with 0.1 mol polyethylene glycol (PEG200 and PEG400) separately. No catalyst was used in the microwave experiments. The reactions were performed at various temperatures under atmospheric pressure, and the water formed during the reaction was removed using the same procedure as in the conventional method (Figure 2b) [51].

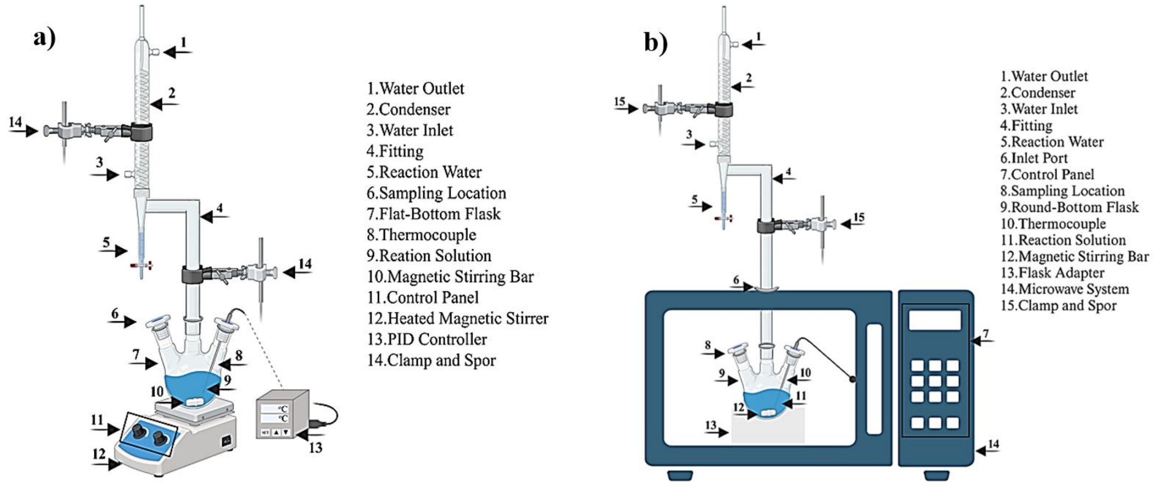


Figure 2. Schematic diagram of experiment setup a) conventional method b) microwave method.

2.3. Kinetic Study

The polyethylene glycol esterification reaction with chloroacetic acid carried out in this study is a bidirectional reaction. In this case, the esterification reaction occurs as a result of 1 mol of polyethylene glycol reacting with 2 mol of chloroacetic acid. The reactants consumed and the products formed in the reaction are encoded as shown in Eq. (1).

$$A + 2B \rightleftarrows C + 2D \quad (1)$$

Here, A represents polyethylene glycol, B represents chloroacetic acid, C represents polyethylene glycol chloroester, and D represents the water formed as a result of the reaction. The water formed during the reaction was collected and removed, ensuring that the reaction proceeded in one direction. Therefore, the rate equation for the esterification reaction of polyethylene glycol with chloroacetic acid can be expressed as shown in Eq. (2).

$$-r_A = k.[C_A]^a.[C_B]^b \quad (2)$$

Here, C_A represents the concentration of polyethylene glycol and C_B represents the concentration of chloroacetic acid at time t. k is the rate constant of the reaction, and a and b represent the reaction orders. In this reaction occurring in the liquid phase, the average densities are taken into account, and the following mole balance equation for liquid-phase reactions is obtained. To determine the stoichiometric coefficients in this equation, Eq. (2) and (3) provided below were used to derive Eq. (4) and (5).

$$\frac{dC_A}{dt} = r_A \quad (3)$$

$$-C_{A_0}.\frac{dX}{dt} = r_A = -k.[C_A]^a.[C_B]^b \quad (4)$$

$$\frac{dX}{dt} = \frac{-r_A}{C_{A_0}} = \frac{k.[C_{A0}(1-X)]^a.[C_{B0}(1-2X)]^b}{C_{A_0}} \quad (5)$$

Here, X represents the conversion of polyethylene glycol at time t, and C_{A0} and C_{B0} represent the initial concentrations of polyethylene glycol and chloroacetic acid, respectively. To determine the reaction rate constant parameters, samples were taken from the reaction at different time intervals, and titration was performed using a solution KOH prepared with methanol at a specific concentration. For titration, 0.5 g of the product was dissolved in 20 mL of methanol, and phenolphthalein indicator was added, followed by titration with KOH solution. The amount of KOH consumed (mL) was recorded, and the conversion at time t was calculated.

Additionally, for various reaction temperatures, the reaction orders (*a* and *b*) and the reaction rate constants *(k)* were determined according to the kinetic model that best fit the data from both the conventional and microwave methods. Subsequently, a regression was performed using the ideal gas constant *(R)* and reaction temperatures *(T)*, and the activation energies *(Ea)* and Arrhenius constants *(A)* were calculated based on the Arrhenius equation given in Eq. (6).

$$k = A.e^{\frac{-E_a}{RT}} \qquad (6)$$

The steps taken to determine the kinetic parameters are outlined in the flowchart in Figure (3). In this study, a comparison of the reaction kinetic parameters obtained for both methods, was conducted.

3. Results and Discussion

3.1. Optimization of Kinetic Model Parameters

In the microwave studies conducted with PEG200, reactions were carried out at temperatures of 110 °C, 138 °C, and 150 °C, and conversion values were obtained. In the conventional method, these studies were conducted at 90 °C, 110 °C, and 138 °C in the presence of a catalyst. The graph of conversions obtained by optimizing kinetic parameters using experimental data and model equations, along with the correlation coefficients, is shown in Figure (4).

In the microwave method with PEG400, studies were conducted at temperatures of 110 °C, 138 °C, and 150 °C, while in the conventional method, studies were carried out at 110 °C, 125 °C, and 138 °C with the presence of a catalyst, and conversions were obtained. The graph of conversions obtained by optimizing the kinetic parameters using experimental data and model equations, along with the correlation coefficients, is shown in Figure (5).

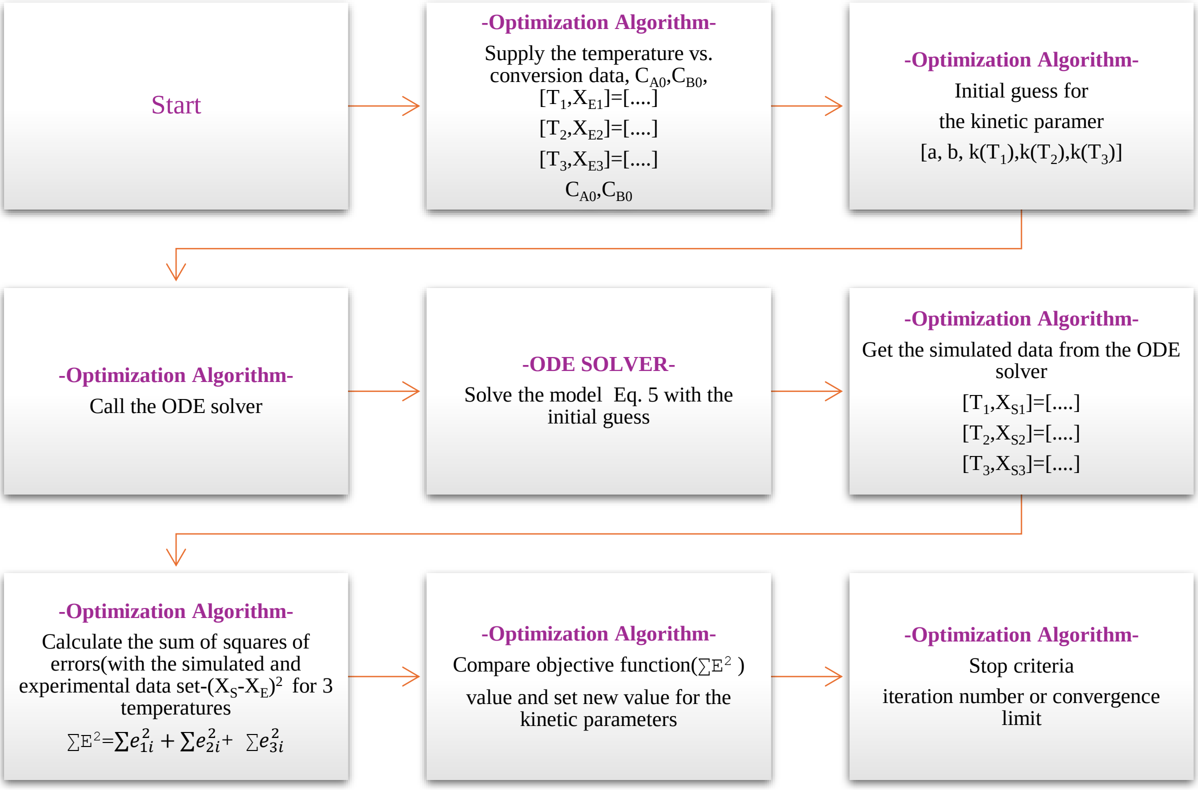


Figure 3. Kinetic parameter Optimization procedure flow diagram.

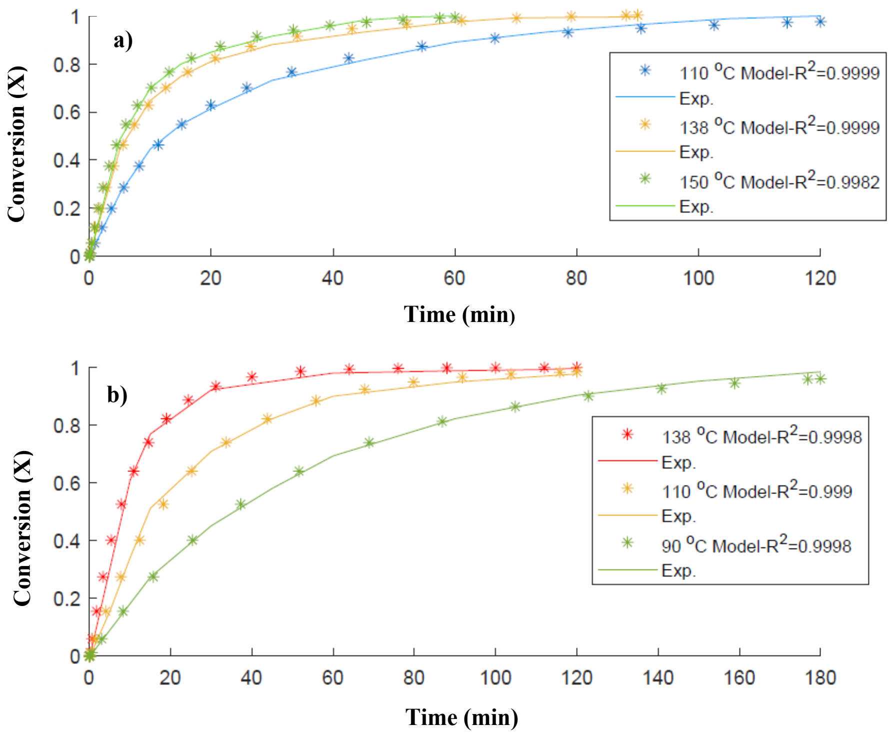


Figure 4. Experimental and simulation results of conversion (X) curves for reactions carried out at different temperatures using PEG200: a) microwave method, b) conventional method.

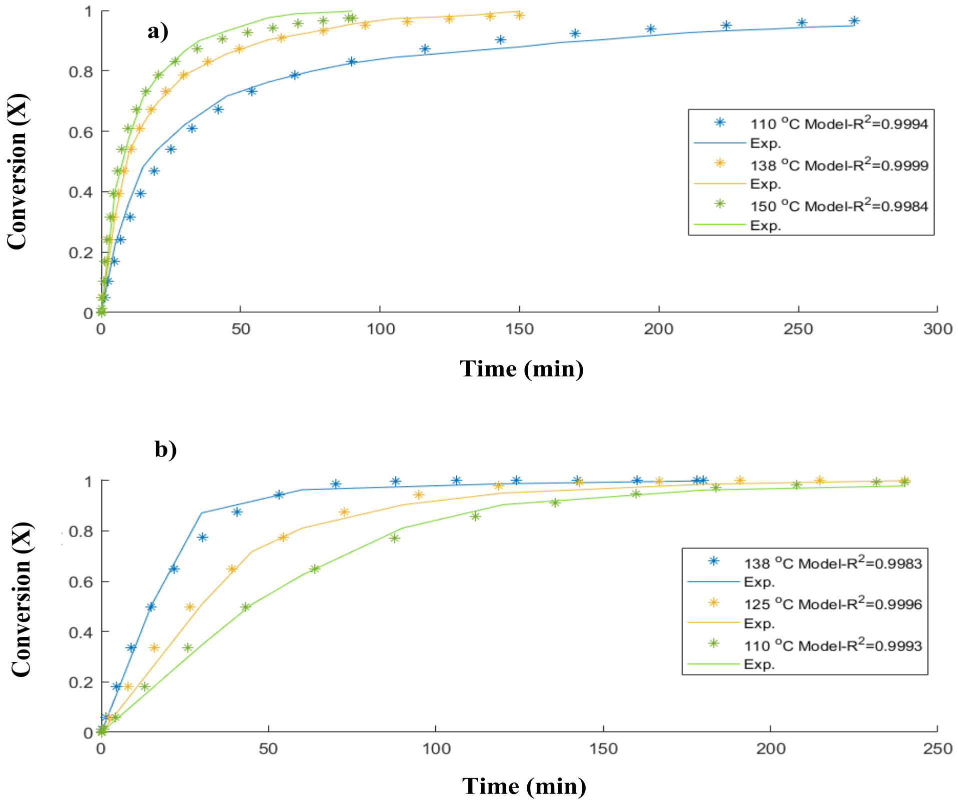


Figure 5. Experimental and simulation results of conversion (X) curves for reactions carried out at different temperatures using PEG400: a) microwave method, b) conventional method.

In both methods (Traditional and Microwave), high correlation coefficients and maximum fit were observed for PEG200 and PEG400, indicating that the model fits the experimental data very well. The increase in temperature led to a rapid increase in conversions, showing an exponential effect. This can be explained by the increase in molecular kinetic energy as the temperature rises, which results in a higher number of successful collisions and, consequently, an increase in reaction rate and conversion. The shorter reaction times for PEG200 are attributed to its lower molecular weight, shorter chain length, and viscosity, which allows for higher reactivity. As a result, the reactions with PEG200 were completed faster. In the catalytic experiments, PEG200 reached a conversion of 95% in 120 minutes, while for PEG400, this time extended to 180 minutes. When a catalyst was used, the conversion times for both PEG200 and PEG400 significantly decreased; a conversion of 92% and 87% was achieved in 30 minutes, respectively. It was also observed that the effect of the microwave method was nearly identical to the catalyst effect, and microwave experiments produced similar conversion times to the catalyst-assisted traditional methods. Notably, for PEG200, conversions above 98% were observed in 50 minutes at 138 °C, while for PEG400, these conversions were achieved in both methods in approximately 70 minutes. These findings suggest that both microwave and catalyst-assisted methods showed very similar effects, but the processes for PEG200 were completed faster.

Additionally, in order to more clearly observe the effect of the catalyst in the conventional method, experiments were conducted at the same temperature without the catalyst. The obtained results are presented in Figure 6.

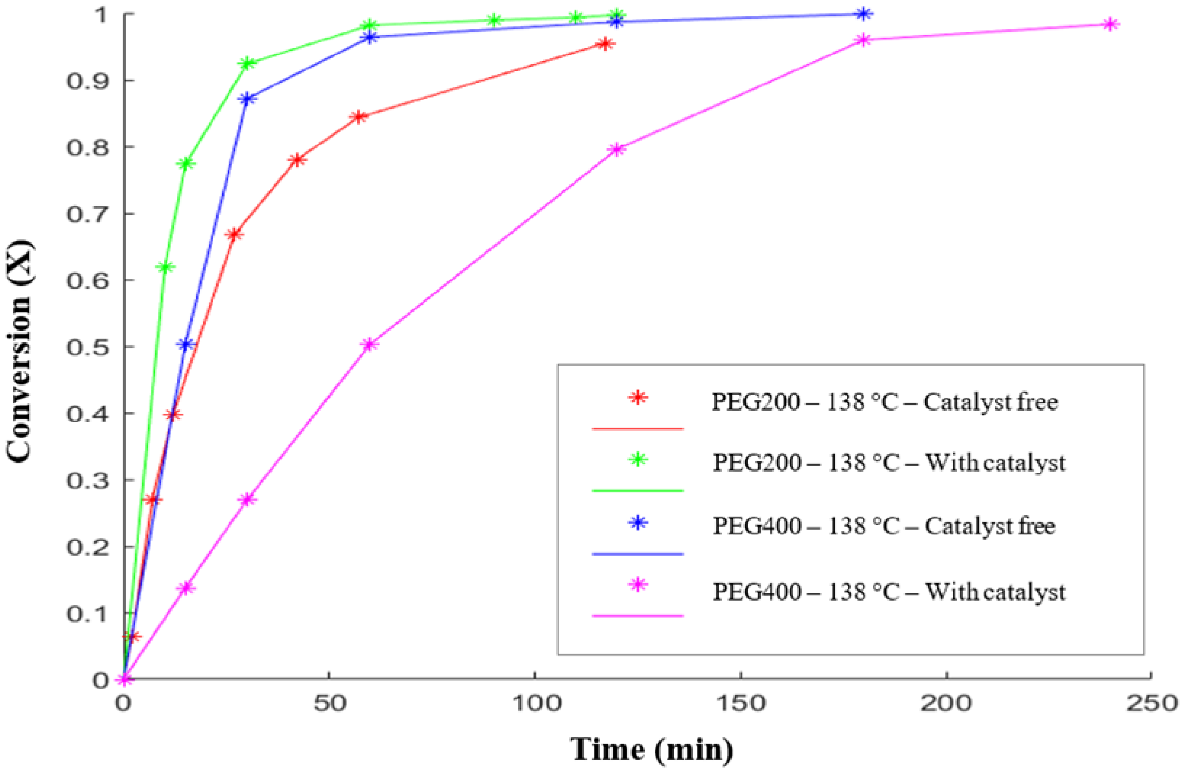


Figure 6. Catalyst effect on conversion (X) of reactions performed with PEG200 and PEG400 at 138°C using the conventional method.

The figure demonstrates a significant increase in reaction rate in the presence of the catalyst. In the absence of the catalyst, longer reaction times were required to reach the same level of conversion. This result indicates that the catalyst enhances the reaction kinetics by lowering the activation energy and thereby accelerates the reaction process.

In the microwave system, catalyst-assisted experiments were also conducted. However, the p-Toluenesulfonic acid (p-TSA) catalyst was found to be affected and degraded by microwave energy, so no catalyst was used in the microwave experiments. In the traditional method, it was observed that catalyst-free experiments were quite slow, but catalyst-free microwave experiments produced almost identical results to the catalyst-assisted traditional method experiments. By utilizing kinetic study data and the Arrhenius equation, the rate constants for the esterification reactions were calculated, and the values are provided in Table 1.

Table 1. Calculated reaction rate constants determined at different reaction temperatures.

Conventional		**Microwave**	
$PEG_{200}ClEs$ (with catalyst)		***$PEG_{200}ClEs$ (catalyst free)***	
T(K)	K	T(K)	k
411	0.0885	423	0.0249
383	0.0383	411	0.0202
363	0.0187	383	0.0098
$PEG_{400}ClEs$ (with catalyst)		***$PEG_{400}ClEs$ (catalyst free)***	
T(K)	K	T(K)	k
411	0.0492	423	0.0158
398	0.0275	411	0.0110
383	0.0169	383	0.0047

When examining the effect of temperature on the reaction rate constant, it was observed that the rate constant increased with rising temperature for each experiment. The fundamental reason for this increase is the collisions that occur due to the enhanced mobility of molecules at higher temperatures [54,55]. Based on the kinetic study data and the Arrhenius equation, the stoichiometric coefficients, Arrhenius constants, and activation energies for the conducted esterification reactions are provided in Table 2.

Table 2. Detailed kinetic data obtained from the reaction under various conditions, supported by optimization studies.

Conventional		**Microwave**	
$PEG_{200}ClEs$ (with catalyst)		***$PEG_{200}ClEs$ (catalyst free)***	
a	1.0775	**A**	0.1339
b	0.0054	**B**	1.5261
A	11279.02	**A**	221.0967
Ea/R	4830.6	**Ea/R**	3837.2
$PEG_{400}ClEs$ (with catalyst)		***$PEG_{400}ClEs$ (catalyst free)***	
a	0.8675	**a**	0.0046
b	0.0025	**b**	1.9949
A	95894.13	**A**	1626.686
Ea/R	5970.5	**Ea/R**	4888.4

When the data presented in Tables 1 and 2 are analyzed, it is evident that the conventional and MW methods provide significantly different results. In the conventional method, the reaction appears to follow approximately first-order kinetics for PEG200 and PEG400, while for CAA, it seems to follow zero-order kinetics (considering experimental errors and initial assumptions). In the MW method, where no catalyst is used, it is believed that the reaction mechanism changes completely. When PEG200 is used as a reactant, the reaction follows first-order kinetics with respect to CAA, and when PEG400 is used, the reaction follows second-order kinetics with respect to CAA.

In the MW method, the key parameter is thought to be the dielectric constant of CAA (ε_{CAA}: 33.4). This is because PEGs have a much lower dielectric constant (ε_{PEG200}:12.5, ε_{PEG400} : 17.5), and the chain length of the PEG is considered to be the major factor in the reaction mechanism. In the microwave method, the Arrhenius constant is approximately 50-60 times smaller than in the conventional method. This decrease can be related to the microwave absorption and collision theory. The activation energy for the reactions also decreases by about 25%, strengthening the reaction's dependence on concentration, which allows the reactions to be completed much faster compared to the conventional method.

As a result, in the conventional method with a catalyst, PEG200 achieves 98% conversion in 60 minutes, and PEG400 achieves 96% conversion, while without a catalyst, the conversions are 84% and 50%, respectively, over the same time. The MW method, on its own, can nearly match the catalytic effect, achieving similar conversion rates. These results are consistent with other findings reported in the literature [56-59].

3.2. Characterization of the Esterification Product by FTIR and ^{1}H-NMR

In order to support the structural verification of the synthesized products, Fourier Transform Infrared (FTIR) spectroscopy analyses were conducted, and the resulting spectra are presented in Figure 7. This analysis was performed to assess whether the esterification reaction proceeded successfully.

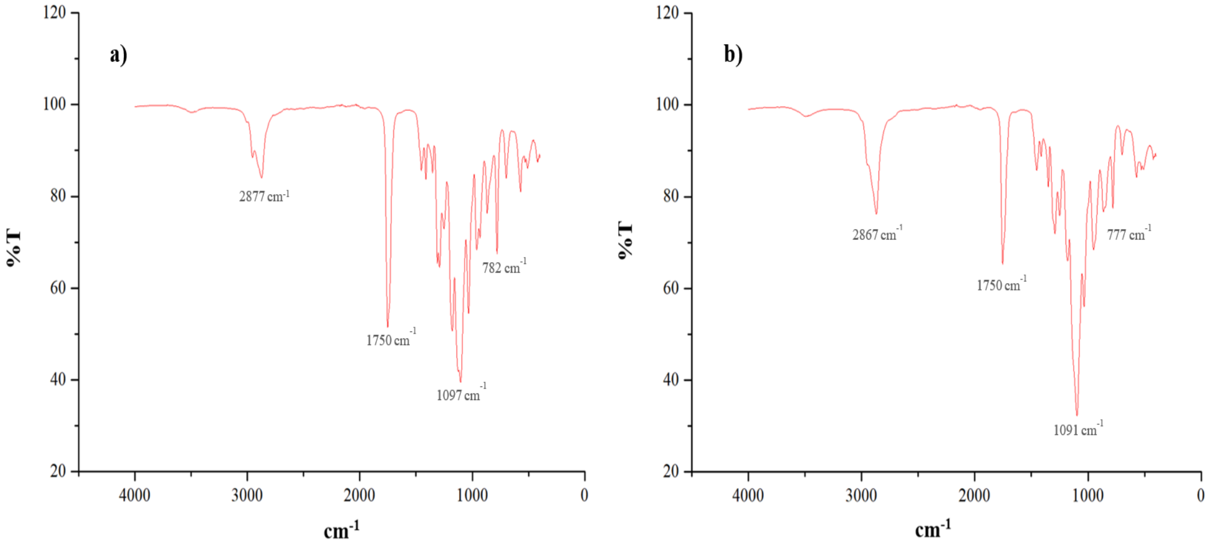


Figure 7. FT-IR spectra of synthesized polyethylene glycol chloro-esters a) PEG$_{200}$ClEs b) PEG$_{400}$ClEs

The FTIR spectra of the reactants are provided in the supplementary information. Figure S1 is the FTIR spectrum of chloroacetic acid. The peaks observed in the range of 3200–3570 cm^{-1} in Figure S2 and S3 are attributed to OH stretching vibrations [60–62]. Upon examining both spectra, it is observed that the broad peaks at 3442 cm^{-1} and 3411 cm^{-1} almost completely disappear in the PEG200ClEs and PEG400ClEs spectra. This indicates that water is absent in the final products. The peaks in the range of 2845–2977 cm^{-1} represent -CH$_2$ stretching vibrations [63,64]. The presence of peaks at the same positions in both the PEG spectra and the spectra of the synthesized products indicates that PEG molecules are still present in the final product.

The peaks in the 1700-1725 cm^{-1} range are attributed to the C=O stretching of carboxylic acids, while the peaks in the 1725-1750 cm^{-1} range are attributed to ester group C=O stretching vibrations [60]. The peak at 1750 cm^{-1} in the PEG$_{400}$ClEs and PEG$_{200}$ClEs spectra indicates the formation of the ester bond. The peaks in the 1050-1150 cm^{-1} range represent the stretching vibrations of C-O-C bonds [64]. The peaks at 1091 cm^{-1} in PEG$_{400}$ClEs and 1097 cm^{-1} in PEG$_{200}$ClEs show the presence of PEG molecules in the final product. The peaks in the 600-800 cm^{-1} range are attributed to C-Cl stretching vibrations [60,65]. The peaks at 777 cm^{-1} in PEG$_{400}$ClEs and 782 cm^{-1} in PEG$_{200}$ClEs indicate the presence of chlorine from chloroacetic acid in the final product. Overall, the FT-IR spectra provide strong evidence that the synthesis of the intended (PEG$_n$ClEs) was successfully achieved.

The ^{1}H-NMR spectra recorded in DMSO-d$_6$ confirmed the chemical structure of the synthesized polyethylene glycol chloroesters (PEG$_{200}$ClEs and PEG$_{400}$ClEs). The polyethylene glycol chloroesters have the same proton distribution. Only the number of repeating ethylene oxide units in each structure differs. The spectrum obtained for $PEG_{200}ClEs$ is presented in Figure 8.

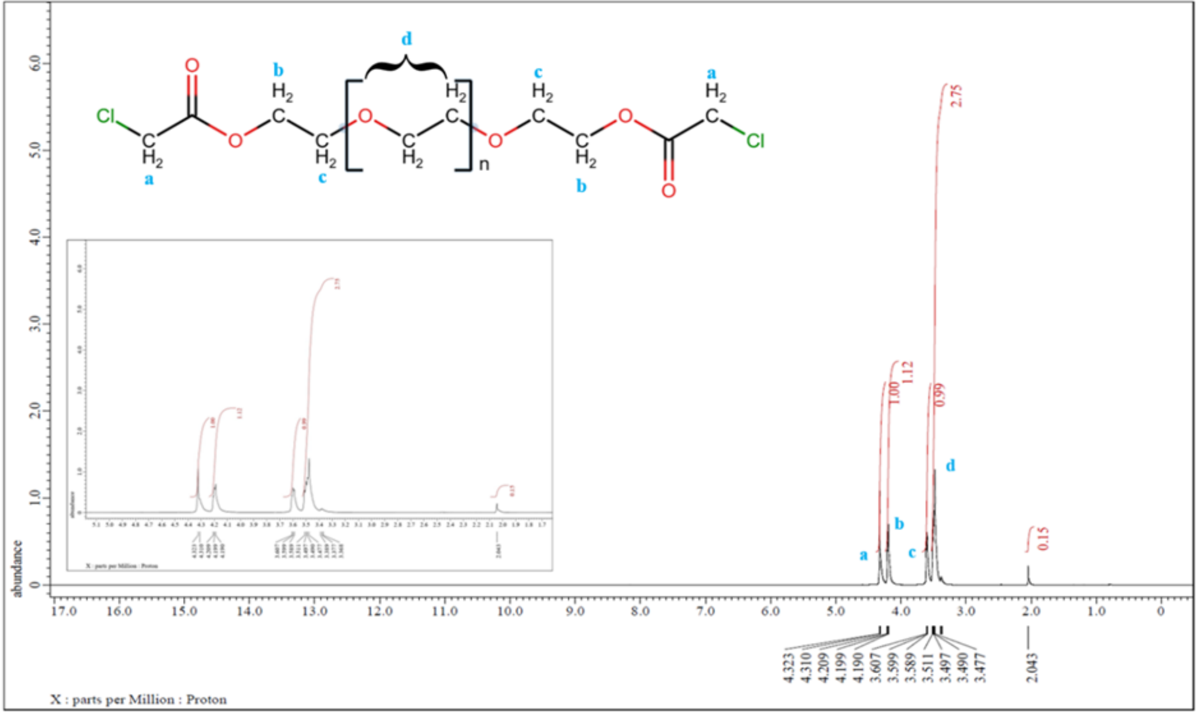


Figure 8. ^{1}H-NMR Spectrum of the synthesized $PEG_{200}ClEs$.

As a result of the characterization studies of the product, the information obtained from the FT-IR spectrum was confirmed by the NMR spectrum. Based on the results, it was concluded that the polyethylene chloro(di)ester structure was successfully synthesized as intended.

4. Conclusions

The results of this study underscore the advantages of employing an optimization-based approach for kinetic parameter estimation, particularly when dealing with multi-temperature datasets. The simultaneous analysis of reaction kinetics across different temperatures allowed for a more comprehensive and reliable parameter determination compared to conventional stepwise methods. Additionally, the absence of a catalyst led to a mechanistic shift in the reaction, where high-dielectric constant molecules played a more pronounced role. The esterification of PEG with chloroacetic acid represents an important reaction pathway for synthesizing functionalized polymeric materials with tailored physicochemical properties. By understanding the kinetic parameters governing this reaction, it is possible to optimize reaction conditions for enhanced product yield and efficiency. The ability to manipulate reaction orders through microwave-assisted methods further broadens the scope of esterification applications, particularly in solvent-free or low-energy synthesis approaches. The reaction order analysis further confirmed that the non-catalytic microwave-assisted process follows a distinctly different kinetic regime. In conventional catalyzed reactions, PEG followed a first-order reaction, whereas microwave-assisted non-catalytic conditions caused the reaction order to shift to 1.5 and 2 for PEG200 and PEG400, respectively. This suggests that the role of dielectric properties is more prominent in determining reaction kinetics, as the interaction of chloroacetic acid with PEG molecules is facilitated by its significantly higher dielectric constant. Moreover, the observed decline in collision frequency with increasing microwave power supports the hypothesis that PEG's lower dielectric constant reduces its interaction probability under these conditions. These findings contribute to a deeper understanding of reaction kinetics in non-catalytic environments and open new perspectives for future kinetic modeling and reaction engineering strategies.

Funding

This research was supported by the Scientific and Technological Research Council of Türkiye (TÜBİTAK) under project number 119C042.

Declarations

Conflict of interest The authors declare that they have no known competing fnancial interests or personal relationships that could have appeared to infuence the work reported in this paper.

References

[1] S., Ortega-Requena, C., Montiel, F., Máximo, M., Gómez, M. D., Murcia, J., Bastida, Esters in Industry: An Overview of the Reactors Used in Their Biocatalytic Synthesis, *Preprints*, (2023) 1-31. https://doi.org/10.20944/preprints202312.0518.v1.

[2] Z., Khan, F., Javed, Z., Shamair, A., Hafeez, T., Fazal, A., Aslam, W.B., Zimmerman, F., Rehman, Current developments in esterification reaction: A review on process and parameters, *Journal of Industrial and Engineering Chemistry*, 103 (2021) 80-101. https://doi.org/10.1016/j.jiec.2021.07.018.

[3] G.S., Piva B., Fischer, M., Peruzzolo, B.M.S., Puton, T., Weschenfelder, A., Junges, C., Steffens, R.L., Cansian, N., Paroul, Mathematical modeling of enzymatic esterification process between essential oil from Cymbopogon winterianus and cinnamic acid, *Industrial Crops and Products*, 222 (2024) 119919. https://doi.org/10.1016/j.indcrop.2024.119919.

[4] M., Mekala, V.R., Goli, Kinetics of esterification of methanol and acetic acid with mineral homogeneous acid catalyst, *Chinese Journal of Chemical Engineering*, 23 (2015) 100-105. http://dx.doi.org/10.1016/j.cjche.2013.08.002.

[5] A.A., Bhusari, B., Mazumdar, A.P., Rathod, R.D., Khonde, Kinetics of catalyzed esterification of acetic acid with n-butanol using carbonized agro-waste, *International Journal of Chemical Kinetics*, 52(1) (2020) 1-13. 10.1002/kin.21361

[6] V.S., Chandane, A.P., Rathod, K.L., Wasewar, P.G., Jadhav, Response Surface Methodology and Artificial Neural Networks for Optimization of Catalytic Esterification of Lactic Acid, *Chemical Engineering & Technology*, 43 (2020) 1-11. 10.1002/ceat.202000041.

[7] R., Farouq, Y., Selim, Functionalized Polyethylene Glycol as a Catalyst for Esterification of Salicylic Acid, *Journal of Polymers and the Environment*, 31 (2023) 2285-2293. https://doi.org/10.1007/s10924-022-02754-1.

[8] F.Z., Abdullah, A., Ma'amor, N.A., Daud, S.B.A., Hamid, Selective Synthesis Of PEG-Monoester Using Cesium Heteropoly Acid as Heterogeneous Catalyst, *Química Nova*, 40(5) (2017) 1-7. 10.21577/0100-4042.20170040.

[9] R., Sirsam, D., Hansora, G.A., Usmani, A Mini-Review on Solid Acid Catalysts for Esterification Reactions, *Journal of The Institution of Engineers (India): Series E*, 97(2) (2016) 167-181. 10.1007/s40034-016-0078-4.

[10] V., Singhania, M., Cortes-Clerget, J., Dussart-Gautheret, B., Akkachairin, J., Yu, N., Akporji, F., Gallou, B.H., Lipshutz, Lipase-catalyzed esterification in water enabled by nanomicelles. Applications to 1-pot multi-step sequences, *Chemical Science*, 13 (2022) 1440-1445. 10.1039/d1sc05660c.

[11] Y.J., Lee, H.W.,Kim, J., Lee, B.H.,Kim, I.H.,Kim, Synthesis of structured lipids using microalgae oil and capric acid via a two-step enzyme reaction. *Process Biochemistry*, 150 (2025) 213-250. https://doi.org/10.1016/j.procbio.2025.01.009.

[12] M., Zarei, M.T., Golmakani, A., Sardarian, Green synthesis of banana flavor using different catalysts: a comparative study of different methods, Green Chem. *Physical Review Letters*, 13:2 (2020) 83-92. 10.1080/17518253.2020.1737739.

[13] A., Cindioglu, A.S.I., Ibrahim, Ö., Sönmez, Microwave-assisted esterification of oleic acid using pyrrolidonium-based bronsted-acidic ionic liquids catalyst, *Fue,* 382 (Part B) (2025) 133791. https://doi.org/10.1016/j.fuel.2024.133791.

[14] X.C., Gu, Q.F., Zhang, Y.H., Pang, X.F., Shen, Microwave-assisted esterification and electro-enhanced solid-phase microextraction of omega-3 polyunsaturated fatty acids in eggs, *Food Chemistry*, 448 (2024) 139060. https://doi.org/10.1016/j.foodchem.2024.139060.

[15] R.M.,Kulkarni, J.K., Dhanyashree, E., Varma, S.P., Sirivibha, Microwave assisted glycerol esterification using CeO_2, ZrO_2, mixed metal oxide catalyst, *Materials Today: Proceedings*, 102 (2024) 416-427. https://doi.org/10.1016/j.matpr.2023.10.130.

[16] A.S., Bansode, D.D., Pukalei, N.L., Jadhav, U., Sayed, D.V., Pinjari, Sonochemical enzymatic esterification of oleic acid and tri-ethanolamine for a fabric softener in textile application, *Chemical Engineering & Processing: Process Intensification*, 137 (2019) 128-136. https://doi.org/10.1016/j.cep.2019.02.013.

[17] N., Esmaeiliani, M., Arami, F.M., Mazaheri, S.M., Bidoki, A comparison between microwave-assisted and thermally synthesized esterquat softeners used as textile softening agents, The Journal of The Textile Institute, 105:6 (2014) 569-574. 10.1080/00405000.2013.827392.

[18] A.R., Tehrani-Bagha, K., Holmberg, Cationic Ester-Containing Gemini Surfactants: Physical-Chemical Properties, *Langmuir*, 26(12) (2010) 9276-9282. 10.1021/la1001336.

[19] S.B., Hiware, V.G., Gaikar, Solvent-free esterification of stearic acid and ethylene glycol with heterogeneous catalysis in a stirred batch microwave reactor, *SN Applied Sciences*, 2 (2020) 712-721. https ://doi.org/10.1007/s4245 2-020-2486-9.

[20] P., Patial, A., Shaheen, I., Ahmad, Gemini Pyridinium Surfactants: Synthesis and Their Surface Active Properties, *Journal of Surfactants and*

*Detergen*ts, 17 (2014) 929-935. 10.1007/s11743-014-1563-8)

[21] S.M., Shaba, A.A., Taha, A.H., Elgad, S.T., Taha, V.M., Sabet, D.H., Kim, A.H.E., Moustafa, Insights on Gemini cationic surfactants influence AgNPs synthesis: Controlling catalytic and antimicrobial activity, *Journal of Molecular Liquids*, 397 (2024) 124071. https://doi.org/10.1016/j.molliq.2024.124071.

[22] D., Liu, X., Yang, T., Mao, X., Shang, L., Wang, Synthesis and characterization of gemini ester surfactant and its application in efficient fabric softening, *Journal of Molecular Liquids,* 299 (2020) 112236 . https://doi.org/10.1016/j.molliq.2019.112236.

[23] S., Dutta, M., Ghosh, D., Mitra, Performance evaluation studies of PEG esters as biolubricant base stocks derived from non-edible oil sources via enzymatic esterification, *Industrial Crops and Products*, 195 (2023) 116429. https://doi.org/10.1016/j.indcrop.2023.116429.

[24] W.V., Lobo, O.A.R.L., Paes, A.D.S., Sıosa, W., Pinheiro, C.A.S., Sousa, J.A., Bezerra, L., Novita, I.F., Cheng, L.K.C., Souza, F.A., Freitas, Application of sulfonated passion fruit seeds as a heterogeneous catalyst in the esterification of oleic and levulinic acids: Optimization of reaction parameters. *Industrial Crops and Products*, 241 (2025) 122355 . https://doi.org/10.1016/j.renene.2025.122355.

[25] R., Cai, G., Hu, Y., Chenyang, Z., Huang, X., Wang, B., Han, Amino-acid-functionalized methanesulfonate ionic liquids as effective and reusable catalysts for oleic acid esterification, *Sustainable Materials and Technologies*, 43 (2025) e01190. https://doi.org/10.1016/j.susmat.2024.e01190.

[26] C.H., Kuo, P., Nargotra, T.H., Lin, C.J., Shieh, Y.C., Liu, Ultrasonication-assisted lipase-catalyzed esterification of chlorogenic acid: A comparative study using fatty alcohol and acids in solvent and solvent-free conditions, *Ultrasonics Sonochemistry*, 113 (2025) 107218 . https://doi.org/10.1016/j.ultsonch.2024.107218.

[27] L.G., Tonutti, M.A., Maquirriain, C.A., Querini, M.L., Pisarello, B.O.D., Costa, Sulfonic SBA-15 silica with amphiphilic properties: Effect of incorporating hydrophobic groups on the esterification of glycerine with fatty acids, *Applied Catalysis A: General*, 692 (2025) 120115. https://doi.org/10.1016/j.apcata.2025.120115.

[28] Q., Zhang, Z., Gao, F., Xu, S., Tai, X., Liu, S., Mo, F., Niu, Surface Tension and Aggregation Properties of Novel Cationic Gemini Surfactants with Diethylammonium Headgroups and a Diamido Spacer, *Langmuir,* 28 (2012) 11979-11987. dx.doi.org/10.1021/la3011212.

[29] M., Akram, H., Lal, M, Osama, F., Ansari, S., Anwar, K., Din, A., Ahmad, Samreen, N., Azum, H.M., Marwani, A.M., Asiri, An Insight View on Synthetic Protocol, Surface Activity, and Biological Aspects of Novel Biocompatible Quaternary Ammonium Cationic Gemini Surfactants, *Journal of Surfactants and Detergents*, 24(1) (2020) 1-15. 10.1002/jsde.12450.

[30] N., Fatma, M., Panda, K., Din, M., Beg, Ester-bonded cationic gemini surfactants: Assessment of their cytotoxicity and antimicrobial activity, *Journal of Molecular Liquids*, 222 (2016) 390-394. http://dx.doi.org/10.1016/j.molliq.2016.07.044.

[31] Z., Gao, S., Tai, Q., Zhang, Y., Zhao, B., Lü, Y., Ge, L., Huang, X., Tang, Synthesis and Surface Activity of Biquaternary Ammonium Salt Gemini Surfactants with Ester Bond, *Wuhan University Journal of Natural Sciences*, 13(2) (2008) 227-231. 10.1007/s11859-008-0219-9.

[32] A., Dabiri, B., Honarvar, Investigation of Interfacial Tension Reduction, Wettability Alteration, and Oil Recovery Using a New Non-ionic Oil-Based Surfactant from Gemini Surfactants Family Coupled with Low- Salinity Water: Experimental Study on Oil-Wet Carbonate Rock, *Journal of Surfactants and Detergents*, 23(4) (2020) 821-829. https://doi.org/10.1002/jsde.12400.

[33] V., Chauhan, M., Kumar, I., Soni, P., Shandilya, S., Singh, Synthesis, physical properties and cytotoxic assessment of ester-terminated gemini imidazolium surfactants, *Journal of Molecular Liquids*, 387 (2023) 122645. https://doi.org/10.1016/j.molliq.2023.122645.

[34] S.M., Shaban, E.H.I., Ismael, A.M., Elsharif, A.H., Elged, N.M.E., Basiony, Preparation gemini non-ionic surfactants-based polyethylene oxide with variable hydrophobic tails for controlling the catalytic and antimicrobial activity of AgNPs. *Journal of Molecular Liquids*, 367 (2022) 120416. https://doi.org/10.1016/j.molliq.2022.120416.

[35] S., Sripada, J.R., Kastner, Continuous catalytic esterification using a solid acid activated carbon monolith: Comparison of granular and monolith forms with a commercial catalyst. *Chemical Engineering Journal*, 476 (2023) 146586. https://doi.org/10.1016/j.cej.2023.146586.

[36] J., Huang, Y., Li, R., Zhang, L., Wang, M., Bao, X., Yu, Ternary deep eutectic solvents for esterification of 2-methypropenoic acid with alcohols, *Organic & Biomolecular Chemistry*, 22(39) (2024) 7951-7955. https://doi.org/10.1039/d4ob01180e.

[37] Q., Lin, W., Zhao, W., Liang, J., Zeng, H., Gao, W., Li, Glutaric anhydride esterification promotes

wheat starch/glutein composite gel interaction: Formation, characterization, and oleogel applications, *Food Research International*, 201 (2025) 115562. https://doi.org/10.1016/j.foodres.2024.115562.

[38] J., Wang, H., Cui, J., Wang, Z., Li, M., Wang, W., Yi, Enhancing esterification of small molecular acids with alcohols by molten salt hydrates, *Applied Catalysis A: General*, 638 (2022) 118640. https://doi.org/10.1016/j.apcata.2022.118640.

[39] A., Fashi, A.F., Delavar, A., Zamani, N., Noshiranzadehi, H., Ebadipur, H., Ebadipur, H., F., Khanban, Green modification of corn starch through repeated freeze-thaw cycles (RFTC), microwave assisted solid state acetic acid esterification (MSAE), and by dual RFTC/MSAE treatment, *Food Hydrocolloids*, 146 (2024) 109303. https://doi.org/10.1016/j.foodhyd.2023.109303.

[40] N.A., Abasi, R., Yusof, M.K., Aroua, H.A., Aziz, Z., Idris, Production of palm-based glycol ester over solid acid catalysed esterification of lauric acid via microwave heating. *Chemical Engineering Journal*, 382 (2020) 122975. https://doi.org/10.1016/j.cej.2019.122975.

[41] S., Soltani, T.R., Shojaei, N., Khanian, T.S.Y., Chong, N., Asim, Y., Zhao, Artificial neural network method modeling of microwave-assisted esterification of PFAD over mesoporous TiO2–ZnO catalyst. *Renewable Energy,* 187 (2022) 760-773. https://doi.org/10.1016/j.renene.2022.01.123.

[42] J.B., Tarigan, A.F., Barus, N.T., Simamora, R.S., Tarigan, S., Perangin-angin, J., Ginting, E.K., Sitepu, Y.H., Taufiq-Yap, Microwave-intensified esterification of high-free fatty acid feedstock into biodiesel using waste chicken eggshells as a heterogeneous catalyst. *Case Studies in Chemical and Environmental Engineering*, 11 (2025) 101107. https://doi.org/10.1016/j.cscee.2025.101107.

[43] V.R., Umrigar, M., Chakraborty, P.A., Parikh, H.P., Kohli, Optimization of process parameters for oleic acid esterification using microwave reactor: Catalytic activity, product distribution and reactor energy model. *Energy Nexus*, 7 (2022) 100127. https://doi.org/10.1016/j.nexus.2022.100127.

[44] E.K., Sitepu, S., Hudiyono, Z.A.P., Sinaga, R., Pramudhita, D., Desmita, Y.F., Ginting, F., Sebayang, J.B., Tarigan, Microwave-Assisted Enzymatic Esterification Production of Emollient Esters, *ACS Omega*, 8 (2023) 39168-39173. https://doi.org/10.1021/acsomega.3c04336

[45] N.S., Akream, M.I., Hamd, S.A., Gheni, F.T., Al-Sudani, A.E., Mohammed, H.R., Mohammed, M.M., Ali, S.M.R., Ahmed, N., Türkoz Karakullukçu, A.K., Tahah, High-yield activated carbon based ZnO-Ce bifunctional catalyst for production of biodiesel from waste cooking oil. *Energy Conversion and Management*, 321 (2024) 119054. https://doi.org/10.1016/j.enconman.2024.119054.

[46] S.N., Nayak, M.G., Nayak, C.P., Bhasin, Parametric, kinetic, and thermodynamic studies of microwave-assisted esterification of Kusum oil. Fuel Communications, 8 (2021) 100018. https://doi.org/10.1016/j.jfueco.2021.10 0 018.

[47] T., Lieu, S., Yusup, M., Moniruzzaman, Kinetic study on microwave-assisted esterification of free fatty acids derived from Ceiba pentandra Seed Oil. *Bioresource Technology*, 211 (2016) 248-256. http://dx.doi.org/10.1016/j.biortech.2016.03.105.

[48] S.A.M., Johari, M.A.A., Farid, M., Ayoub, N.A., Rashidi, Y., Andou, Optimization and kinetic studies for biodiesel production from dairy waste scum oil via microwave assisted transesterification. *Environmental Technology & Innovation*, 34 (2024) 103580 . https://doi.org/10.1016/j.eti.2024.103580.

[49] S.M., Tawfik, A.A., Abd-Elaal, S.M., Shaban, A.A., Roshdy, Surface, thermodynamic and biological activities of some synthesized Gemini quaternary ammonium salts based on polyethylene glycol. *Journal of Industrial and Engineering Chemistry*, 30 (2015) 112-119. http://dx.doi.org/10.1016/j.jiec.2015.05.011.

[50] A.A., Abd-Elaal, S.M., Shaban, S.M., Tawfik, Three Gemini cationic surfactants based on polyethylene glycol as effective corrosion inhibitör for mild steel in acidic environment. *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 24 (2017) 54-65. http://dx.doi.org/10.1016/j.jaubas.2017.03.004.

[51] F., Tamaddon, S.E., Tadayonfar, Facile microwave-assisted preparation of an ester-based cationic gemini surfactant for the improved micellar synthesis of aminocyanopyridines. *Journal of Molecular Structure*, 1207 (2020) 127728. https://doi.org/10.1016/j.molstruc.2020.127728.

[52] X., Xu, Y., Sun, W., Wang, L., Ju, R., Shu, H., Gu, An overview of polyethylene glycol composite phase change materials: Preparation, physicochemical properties and application. *Journal of Energy Storage*, 104 (2024) 114581. https://doi.org/10.1016/j.est.2024.114581.

[53] L., Szentpály, S., Kaya, Introduction to Chemical Reactivity. *Chemical Reactivity*, (2022). pp.17-19. 10.1016/B978-0-32-390259-5.00006-8.

[54] S., Oza, P., Kodgire, S.S., Kachhwaha, Shockwave power reactor (SPR)-assisted esterification of blended non-edible oils: Optimization and kinetics studies. *Thermal Science and Engineering Progress*, 59 (2025)103337. https://doi.org/10.1016/j.tsep.2025.103337.

[55] P., Mwenge, A., Luboya, S., Muthubi, H., Rutto, T., Seodigeng, Biodiesel Production from Animal Fats

Using Blast Furnace Geopolymer Heterogeneous Catalyst: Optimisation and Kinetic Study. *Arabian Journal for Science and Engineering*, (2025) https://doi.org/10.1007/s13369-024-09895-6.

[56] N., Zarei, M.T., Golmakani, M., Keramat, M., Majdinasab, A., Karami, Process intensification for the autocatalytic esterification of citronellol using microwave radiation. *LWT*, 145 (2021) 111358. https://doi.org/10.1016/j.lwt.2021.111358.

[57] A., Mulay, V.K., Rathod, Microwave-assisted heterogeneous esterification of dibutyl maleate: Optimization using response surface methodology. *Chemical Data Collections*, 34 (2021) 100740. https://doi.org/10.1016/j.cdc.2021.100740.

[58] P., Mazo, L., Rios, D., Estenoz, M., Sponton, Self-esterification of partially maleated castor oil using conventional and microwave heating. *Chemical Engineering Journal*, 185-186 (2012) 347-351. 10.1016/j.cej.2012.01.099.

[59] J., Zheng, Z.M., Png, S.H., Ng, G.X., Tham, E., Ye, S.S., Goh, X.J., Loh, Z., Li, Vitrimers: Current research trends and their emerging applications. *Chemical Engineering Journal*, 51 (2021) 586-625. https://doi.org/10.1016/j.mattod.2021.07.003.

[60] A.B.D., Nandiyanto, R., Ragadhita, M., Fiandini, Interpretation of Fourier Transform Infrared Spectra (FTIR): A Practical Approach in the Polymer/Plastic Thermal Decomposition. Indonesian Journal of Science and Technology, 8(1) (2023) 113-126. 10.17509/ijost.v8i1.53297.

[61] F., Askari, M., Zandi, P., Shokrolahi, M.H., Tabatabaei, E., Hajirasoliha, Reduction in protein absorption on ophthalmic lenses by PEGDA bulk modification of silicone acrylate-based formulation. *Progress in Biomaterials*, 8(3) (2019) 169-183. 10.1007/s40204-019-00119-x.

[62] M., Sahu, V.R.M., Reddy, B., Kim, B., Patro, C., Park, W.K., Kim, P., Sharma, Fabrication of Cu2ZnSnS4 Light Absorber Using a Cost-Effective Mechanochemical Method for Photovoltaic Applications. *Materials*, 15(5) (2022) 1708-1724. https://doi.org/10.3390/ma15051708

[63] G.C., Carvalho, M.F.V., Moura, H.G.C.,Castro, J.H.S., Junior, H.E.B., Silva, K.M., Santos, Z.M.S., Rocha, Influence of the atmosphere on the decomposition of vegetable oils: study of the profiles of FTIR spectra and evolution of gaseous products. *Journal of Thermal Analysis And Calorimetry*, 140 (2020) 2247-2258. https://doi.org/10.1007/s10973-019-08960-9.

[64] N., Akram, M., Saeed, M., Usman, A., Mansha, F., Anjum, K.M., Zia, I., Mahmood, N., Mumtaz, W.G., Khan, Influence of Graphene Oxide Contents on Mechanical Behavior of Polyurethane Composites Fabricated with Different Diisocyanates. *Polymers*, 13 (2021) 444-460. https://doi.org/10.3390/polym13030444.

[65] H.A., Miller, J., Ruggeri, A., Marchionni, M., Bellini, M.V., Pagliaro, C., Bartoli, A., Pucci, E., Passaglia, F., Vizza, Improving the Energy Efficiency of Direct Formate Fuel Cells with a Pd/C-CeO2 Anode Catalyst and Anion Exchange Ionomer in the Catalyst Layer, *Energies*, 11, (2018) 369-381. 10.3390/en11020369.