

Article

Kinetic and Thermodynamic Analysis of Waste Cooking Oil Transesterification for Biodiesel Production in a Microreactor

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Abstract

Biodiesel production offers a promising route towards the achievement of net-zero emissions by 2050. However, current reliance on unsustainable feedstocks and inefficient processes hampers its commercial viability. This study investigates the transesterification of waste cooking oil (WCO) with methanol in a continuous microreactor (1 mm internal diameter) and systematically compares pseudo-homogeneous and biphasic second-order kinetic models for describing the reaction. The biphasic model provided the highest predictive accuracy by explicitly accounting for interfacial mass transfer and phase interactions, whereas the pseudo-homogeneous model offered a simpler formulation with comparable overall statistical performance when model complexity was considered. The activation energy estimated using the biphasic model was 15.61 kJ mol⁻¹, which is lower than values typically reported for homogeneous base-catalysed systems, which is consistent with the enhanced mass-transfer characteristics of the microreactor. Thermodynamic activation parameters were also determined, resulting in an activation enthalpy of 12.93 kJ mol⁻¹, an activation entropy of -272.3 J mol⁻¹ K⁻¹ and an activation free energy of 94.08 kJ mol⁻¹, indicating an energetic barrier to the formation of the activated complex and a more ordered transition state than the reactants. The results demonstrate that explicit treatment of phase interactions improves kinetic prediction while providing practical guidance for selecting kinetic models according to the intended engineering application. These findings support the use of intensified microreactor systems and physically representative kinetic models for the design and scale-up of sustainable biodiesel production processes.

Keywords: transesterification; microreactor; waste cooking oil; kinetic modelling; biphasic system



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1. Introduction

To achieve the goal of net-zero emissions by 2050, as outlined in the Paris Agreement, numerous solutions have been proposed, including the adoption of biodiesel as a sustainable energy source [1]. Biodiesel is often considered a carbon-neutral fuel because it is produced from renewable biomass and the CO₂ released during its combustion roughly equals the amount absorbed by the feedstock during its growth. However, this balance can be affected by factors such as land use change, agricultural inputs, and processing emissions. It is also compatible with existing diesel-powered engines, making it a viable alternative to conventional fossil fuels, especially in the transportation sector, which is a

major contributor to global greenhouse gas (GHG) emissions [2]. However, despite its potential, biodiesel faces two primary challenges that hinder its large-scale adoption: reliance on edible oil feedstocks, which impacts food security, and inefficiencies in production processes that result in high costs [3].

To overcome these barriers, several strategies have been proposed. One effective approach is the use of non-edible feedstocks, such as waste cooking oil (WCO), which not only alleviates competition with food supplies but also valorises a waste product that would otherwise be discarded [4]. Furthermore, advancements in process intensification—specifically, the use of microreactors—offer significant advantages, including enhanced heat and mass transfer, higher reaction rates, and the ability to operate continuously, thereby improving the overall efficiency of biodiesel production [5]. Conventional stirred reactors typically require longer reaction times to overcome mass-transfer resistances, as observed by Muranaka et al. [6], who found that the initial reaction rate was increased significantly, achieving an increase in the interfacial area of approximately seven times.

While the use of waste cooking oil (WCO) offers significant sustainability and cost advantages over edible oils, it also introduces several processing challenges that directly affect reaction kinetics and conversion efficiency. WCO typically contains elevated levels of free fatty acids (FFAs), which, in the presence of a base catalyst and water, can lead to unwanted saponification reactions that reduce methyl ester yields [7]. High FFA content often necessitates a pretreatment step to esterify the FFAs before transesterification. In addition, WCO tends to exhibit higher viscosity due to the presence of polymerised degradation products formed during cooking. This elevated viscosity hinders mass transfer between the immiscible WCO and methanol phases by lowering diffusion coefficients and decreasing mixing efficiency, thereby slowing the overall reaction rate [8]. Microreactors, as a form of process intensification, are particularly suitable for biodiesel production due to their high surface area-to-volume ratio, which minimises mass-transfer limitations and allows for rapid and efficient reactions [9]. Their ability to handle small volumes with precise control makes them ideal for complex reaction systems, such as the transesterification of WCO with methanol. When combined with WCO feedstock, microreactors can significantly enhance the sustainability and efficiency of the biodiesel production process. However, optimization of reactor design and operational parameters requires a detailed understanding of the reaction kinetics [8].

Kinetic modelling is crucial for the design of efficient biodiesel production processes, the optimization of reactor performance and the scaling-up of production processes. Numerous studies have investigated the kinetics of the transesterification reaction, with pseudo-homogeneous models being the most commonly employed. These models simplify the system by assuming the reaction is kinetically controlled, neglecting mass transfer effects. Whilst these models provide reasonable accuracy, they may not fully capture the complexities of WCO systems [10–12]. Alternative approaches, such as those based on the two-film theory for biphasic systems [13] or irreversible pseudo-homogeneous kinetics [14], have also been explored to account for specific reaction dynamics. Table 1 summarises various kinetic models for transesterification, highlighting their underlying assumptions and main findings.

Despite the progress in kinetic studies, several gaps remain in the current literature. Firstly, there is limited research focused on non-edible feedstocks like WCO, which are critical for ensuring the sustainability of biodiesel production. Furthermore, few studies have systematically compared the accuracy of multiple kinetic models to determine the most appropriate approach for specific systems. Finally, while some investigations explore the use of microreactors for biodiesel production, they often overlook the potential influence

of the microreactor's high surface area-to-volume ratio on reaction kinetics and mass-transfer phenomena.

Table 1. Summary of transesterification reaction-kinetic models reported in the literature.

Feedstock	Reactor	Catalyst	Kinetic Model	Main Findings	Reference
Palm oil	Batch and microreactor	KOH	Intrinsic rate kinetics with two-film theory mass transfer	Model showed good agreement with experimental data; the microreactor achieved the same conversion with a residence time 720 times shorter than the batch reactor; results successfully used for scale-up	[13]
Canola oil	Batch reactor	KOH	Pseudo-first-order and pseudo-homogeneous irreversible	Activation energy (E_a) of the pseudo-first order model was found to be 16.9% higher than that of the pseudo-homogeneous irreversible model	[14]
Castor oil	Batch reactor	Eversa transform (Enzyme)	Ping-pong bi-bi mechanism	Methanolysis and hydrolysis occurred simultaneously in enzyme-catalysed reactions, with methanolysis dominating; an adjusted model improved experimental fit	[15]
Vegetable oil	Interdigital micromixer reactor	KOH and NaOH	Biphasic with intrinsic kinetic rate laws	Model aligned with existing literature but required modifications to capture specific interfacial area effects	[16]
Palm and mustard oil	Batch reactor	KOH	Three-step, second order	Fatty acid composition had a greater impact on reaction kinetics than chain-length distribution	[17]
Palm oil	Microreactor	NaOH	Pseudo-homogeneous, reversible second order	Model predicted results within 7.6% deviation up to the onset of droplet coalescence	[18]
Sunflower oil (ethanol)	Microreactor	Sodium ethoxide	Biphasic, three-step	High model accuracy across different microreactor diameters and ethanol-to-oil ratios; model also proved useful for optimising a glycerol removal system	[19]

This paper aims to address these gaps by investigating the transesterification of WCO with methanol in microreactors, focusing on comparing the accuracy and applicability of pseudo-homogeneous and biphasic kinetic models. The pseudo-homogeneous model, often used as a standard, will be evaluated alongside the biphasic model, which explicitly considers the two-phase nature of the system and leverages the unique surface-area-to-volume-ratio characteristic of microreactors. By combining experimental results with kinetic modelling, this study seeks to enhance understanding of the overall conversion kinetics within the context of a lumped approximation and inform the design of efficient, sustainable, and scalable biodiesel production processes.

2. Materials and Methods

2.1. Materials

The raw material for transesterification was waste cooking oil, which was provided by Greenergy Biofuels Teesside Limited, UK; the chemical and physical properties are shown in Table 2. Methanol was purchased from Sigma-Aldrich, Gillingham, UK. The catalyst, KOH, was purchased from Scientific Laboratory Supplies, Nottingham, UK. The internal standards were obtained from Merck, UK.

Table 2. Chemical and physical properties of the waste cooking oil (WCO).

Chemical Property	Content
FFA content	1.33%
Water content	0.05%
Acid value	0.02 mg KOH/g
Saponification value	194 mg KOH/g
Density	912 kg m ⁻³

2.2. Transesterification Reaction in Microreactors

A methanol solution was prepared by dissolving the KOH into methanol for fixed methanol-to-oil ratios and catalyst concentrations of 6:1 and 3 wt%, respectively. The experimental rig was then set up as shown in Figure 1. A peristaltic pump (P-230, Harvard

Apparatus, Holliston, MA, USA) was used to transfer WCO into the microreactor system. The WCO was heated to 50–60 °C to lower the viscosity in order to avoid clogging the microreactor. The methanol solution was pumped into the system via a syringe pump (PHD ULTRA™ Syringe Pump Infuse Only Standard, Harvard Apparatus, Holliston, MA, USA), and the two phases were mixed in a microfluidic T-mixer with the methanol entering perpendicular to the WCO. The mixture then passed through the microreactor, which was submersed in a water bath at 60 °C. The reacted mixture was deposited in a vial, which was submersed in an ice bath to stop the reaction and ensure controlled residence time. The residence time was controlled by changing the tube length from 0.5 m to 5 m, yielding residence times of 0–3.5 min. This methodology is reflected by other studies that investigated the use of microreactors for biodiesel production [6].

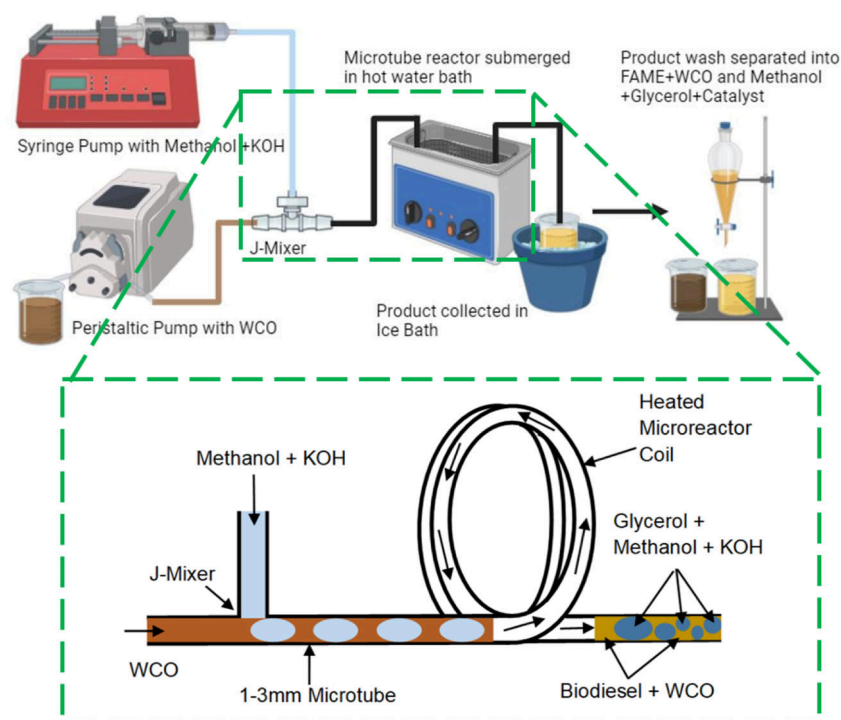


Figure 1. Schematic of the microreactor system.

Once collected, the samples were separated by washing gently with warm water to remove glycerol, methanol and catalyst, leaving FAME, tri-, di- and monoglycerides. This method of separation was chosen as it is simple and affordable and does not require machinery. The washed samples were dried and prepared for Gas Chromatography—Flame Ionisation Detection (GC-FID) analysis.

2.3. Analysis of Fatty Acid Methyl Ester (FAME) Content

The collected biodiesel samples were analysed as described in BS EN 14103:2020 [20] to find the FAME content, as this provides an accepted method to determine the product composition. An7890A GC-FID, Agilent Technologies, Santa Clara, CA, USA, instrument equipped with a G3903-63011 capillary column (30 m × 0.25 mm × 0.25 µm), Agilent Technologies, Santa Clara, CA, USA, was used to analyse the samples for the FAME analysis. Hydrogen was used as a carrier gas, and the column temperature, injection volume and flow rates were selected as described in the aforementioned standard. The ester content of the sample was then calculated using Equation (1) [20]:

$$\text{Ester Content \%} = \frac{\Sigma(A_S R_S) - A_{IS}}{A_{IS}} \times \frac{W_{IS}}{W_S} \times 100 \quad (1)$$

where A_S and A_{IS} are the peak areas of the sample and the internal standard, R_S is the correction factor of the flame ionisation detector for the sample relative to the internal standard, and W_S and W_{IS} are the weights of the sample and internal standard.

2.4. Determination of Reaction Kinetics

The transesterification reaction for biodiesel production involves 3 consecutive reversible reactions, as shown in Equations (2)–(4) [21]:



Here, TG, DG, MG, M, G and ME denote triglycerides, diglycerides, monoglycerides, methanol, glycerol, and methyl esters, respectively. As methanol and oil are immiscible, it is expected that, initially, interfacial mass transfer controls the reaction. However, as the reaction proceeds and methyl esters (biodiesel) are formed, the system transitions to a single phase, where kinetics govern the reaction rate [22]. It is widely recognised that the first step (Equation (2)) is the rate-determining step due to its slower reaction rates compared to the subsequent steps [23]. This understanding forms the basis for the kinetic modelling of biodiesel production.

Although transesterification involves a three-step reaction, the present study adopts a single-step lumped kinetic approach. This approach was selected because, firstly, it is widely recognised that the initial conversion of triglycerides is the rate-determining step, while the subsequent equations proceed considerably faster under homogeneous base-catalysed conditions [24,25]. Consequently, the concentrations of diglycerides and monoglycerides remain considerably low, and the overall reaction rate is governed primarily by triglyceride conversion [26]. Secondly, single-step lumped kinetic models have been successfully applied to describe overall biodiesel production, particularly for reactor design, process optimisation and scale-up, where total FAME conversion is the primary design parameter rather than the concentration profiles of intermediate species [27–30]. In particular, pseudo-homogeneous irreversible second-order models have shown satisfactory prediction of overall biodiesel conversion. Thirdly, the employed analytical method (BS EN 14103:2020) is the standard industrial method for determination of FAME content but does not quantify intermediate glycerides, which would require additional analytical techniques. Consequently, the single-step lumped model should be regarded as an engineering approximation describing the overall conversion process rather than the reaction mechanism.

To evaluate the reaction kinetics, the separated product phase, which is composed primarily of FAME and unreacted WCO, was analysed to determine the FAME content. Based on the product volume and known initial concentrations, mass fractions of individual species were interpolated.

The following assumptions were made to simplify the kinetic analysis:

- The system operates under steady-state conditions.
- Transient effects are neglected.
- The saponification side reaction is considered negligible.
- The transesterification reactions are treated as irreversible.
- The three-step mechanism is approximated as a single-step lumped reaction with the rate-determining step governing overall conversion.
- FAME is assumed to reside solely in the oil (triglycerides) phase; methanol does not contain dissolved FAME.
- Both oil and methanol phases are assumed to be well mixed, with a uniform composition.

- Heat transfer through the PTFE microtube is neglected due to the small scale and controlled operating temperature.

2.4.1. Pseudo-Homogeneous Kinetic Model

The pseudo-homogeneous model assumes that mass-transfer limitations are negligible and that the transesterification reaction occurs within a single, homogeneous phase. In the literature, the base-catalysed transesterification reaction is typically modelled using either a first-order (5) or second-order (6) reaction. The first-order model is particularly suitable under conditions of excess methanol (molar ratio higher than 6:1), where methanol concentration remains effectively constant throughout the reaction [24].

$$-r_a = -\frac{d[TG]}{dt} = k[TG] \quad (5)$$

$$-r_a = -\frac{d[TG]}{dt} = k[TG][M] \quad (6)$$

While the pseudo-homogeneous model offers simplicity and has been shown to provide reasonable accuracy in certain systems [14], it does not account for interfacial effects or mass-transfer limitations, which can lead to deviations in systems with immiscible phases, where mass transfer plays a key role [31]. In addition to the general assumptions outlined in Section 2.4, the following specific assumptions were considered for the pseudo-homogeneous kinetic model:

- The system behaves as a single homogeneous phase.
- The reaction occurs uniformly throughout this homogeneous phase.

2.4.2. Biphasic Kinetic Model

The biphasic model accounts for the immiscibility of methanol and WCO, considering mass transfer across the interface as described by the two-film theory. The two-film theory, originally proposed by Lewis and Whitman [32], considers a thin interfacial layer separating two bulk phases through which mass transfer occurs. The transfer rate is governed by the interfacial area-to-volume ratio and the diffusivity of each species in its respective phase. While the theory is traditionally applied to gas–liquid systems, this framework has been successfully adapted to model liquid–liquid systems, including biodiesel production involving immiscible phases. In this model, the reaction is assumed to occur within the methanol-rich phase, consistent with previously reported biphasic transesterification models [12,18]. Although methanol and triglycerides are largely immiscible, triglycerides that diffuse across the liquid–liquid interface are exposed to the homogeneous KOH catalyst, which is dissolved only in the methanol-rich phase. This assumption provides the basis for modelling the chemical reaction within the methanol phase while explicitly accounting for interphase mass transfer.

The reaction kinetics are modelled using second-order rate expressions, as the assumption of excess methanol is less applicable in a phase-separated system. The governing system of ordinary differential equations (ODEs) (Equations (7)–(12)) is present below:

$$\frac{d[TG]_b}{dt} = -K_{OPa}([TG]_i - [TG]_b) \quad (7)$$

$$\frac{d[M]_b}{dt} = -K_{MPa}([M]_b - [M]_i) \quad (8)$$

$$\frac{d[TG]_i}{dt} = K_{OPa}([TG]_i - [TG]_b) - k[TG]_i[M]_i \quad (9)$$

$$\frac{d[M]_i}{dt} = K_{MPa}([M]_b - [M]_i) - 3k[TG]_i[M]_i \quad (10)$$

$$\frac{d[ME]}{dt} = 3k[TG]_i[M]_i \quad (11)$$

$$\frac{d[G]}{dt} = k[TG]_i[M]_i \quad (12)$$

Here, $[TG]_b$ and $[M]_b$ are the concentrations of triglycerides and methanol in their bulk phases (mol m^{-3}) and $[TG]_i$ and $[M]_i$ are the concentrations of triglycerides and methanol at the interface (mol m^{-3}). The k parameter is the reaction rate constant (s^{-1}), and K_{OP} and K_{MP} are the mass-transfer coefficients for oil and methanol across the oil–methanol interface, respectively. These coefficients were estimated from Sherwood numbers [33] calculated using the Ranz–Marshall correlation [34], together with diffusivity properties of the liquids ($\text{m}^2 \text{s}^{-1}$) estimated using the Wilke–Chang correlation [35]. The interfacial area per unit volume (α , $\text{m}^2 \text{m}^{-3}$) was estimated from the experimentally observed slug geometry using optical images of the slug lengths. These ODEs were solved numerically using MATLAB R2023a to estimate the concentrations and determine the reaction rate constants.

To further refine the model, an enhancement factor (Equation (13) [36]) was also considered, which is a standard practice in two-film theory when assessing whether the process is diffusion- or reaction-limited [36]. The Hatta modulus (Equation (14) [36]) is used to determine if the reaction is diffusion- or reaction-limited and, thus, the enhancement factor can be calculated. The enhancement factor is multiplied by the rate of reaction to provide a more accurate biphasic kinetic model.

$$E = \frac{Ha}{\tanh(Ha)} \quad (13)$$

$$Ha = \frac{\sqrt{kD_{M,OP}[TG]_b}}{K_{MP}} \quad (14)$$

Here, $D_{M,OP}$ is the diffusivity of methanol in the oil phase ($\text{m}^2 \text{s}^{-1}$).

Additional assumptions specific to the biphasic model include the following:

- Methanol and WCO form two immiscible phases.
- The reaction occurs solely in the methanol phase, as the miscibility of oil in the methanol phase is higher than that of methanol in the triglyceride phase [13].

2.5. Error Analysis

The experimental results were compared to model predictions using conventional goodness-of-fit metrics, i.e., the R^2 value, the root mean square error (RMSE) and the mean absolute error (MAE), as described in Equations (15)–(17) [37]. Akaike information criteria (AIC) and Bayesian information criteria (BIC) analyses were also performed to determine the effectiveness of these models while also taking into account model complexity. Unlike goodness-of-fit metrics, AIC and BIC penalise models containing a greater number of fitted parameters, thereby providing a more balanced assessment of predictive capability and model performance. As the present study involved a relatively small dataset, the corrected Akaike Information Criterion (AICc) was used. The corresponding equations for AICc and BIC are given in Equations (18) and (19) [38–40].

$$R^2 = 1 - \frac{\sum_{i=1}^n (\hat{y}_i - \bar{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y}_i)^2} \quad (15)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{n}} \quad (16)$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - \bar{y}_i| \quad (17)$$

$$AIC_c = n \cdot \ln(RMSE^2) + 2k + \left(\frac{2k(k+1)}{n-k-1} \right) \quad (18)$$

$$BIC = n \cdot \ln(RMSE^2) + k \cdot \ln(n) \quad (19)$$

Here, $\hat{y}_i$ is the results of the model, $\bar{y}_i$ represents the mean result, y_i represents the experimental result, n is the number of tests and k is the number of fit parameters used in the model. Each experiment was performed in triplicate, and the corresponding standard deviations were calculated.

3. Results and Discussion

3.1. Transesterification Reaction Conversion

Transesterification of WCO with methanol was performed in a microreactor using KOH as a homogeneous base catalyst. The effects of residence time and temperature (40 °C, 50 °C and 60 °C) on methyl ester (biodiesel) formation were studied. As shown in Figure 2, the conversion of triglycerides followed a logarithmic profile, with methyl ester content reaching a plateau at approximately 100 s. This rapid approach to equilibrium is attributed to the high surface area-to-volume ratio and intensified mixing in the microreactor, which significantly reduces the boundary-layer thickness and accelerates interfacial transport [41]. It can also be seen that temperature had a significant effect on the reaction. At 60 °C, ~99% conversion was achieved, while even at a lower temperature of 40 °C, conversion reached ~93% within 200 s. All performed experiments exhibited slug flow behaviour (inset of Figure 2) at the inlet of the microreactor, which enhanced mass transfer by promoting internal circulation and reduced diffusion paths. This flow regime facilitated efficient mixing and supported the progression of the reaction along the reactor length.

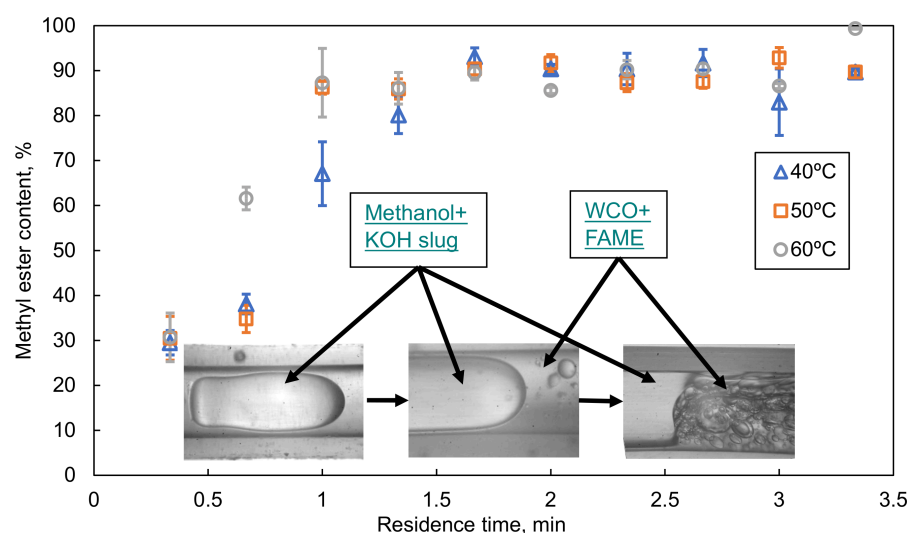


Figure 2. Effect of residence time and temperature on reaction conversion using a 1 mm diameter microtube, 6:1 methanol-to-oil ratio, and 3 wt% KOH catalyst loading. (Images show the flow pattern transition in the microtube during transesterification).

3.2. Transesterification Reaction Kinetics and Mass Transfer Analysis

Two kinetic models were applied to the experimental data to assess their predictive performance: a pseudo-homogeneous model and a biphasic model. Both models assumed a single-step reaction model.

3.2.1. Pseudo-Homogeneous Model

The pseudo-homogeneous kinetic model, based on second-order kinetics, was applied to the data obtained at 60 °C. Figure 3 presents the experimental data alongside the model predictions. While first- and second-order models produced similar results, due to methanol being in excess, the second-order model provided a slightly better fit, as reflected by a higher R^2 value and a lower RMSE (see Table 3). Although the MAE was slightly higher, which suggests reduced sensitivity to outliers, the second-order model was selected for further analysis because it accounts for the methanol in the system more accurately.

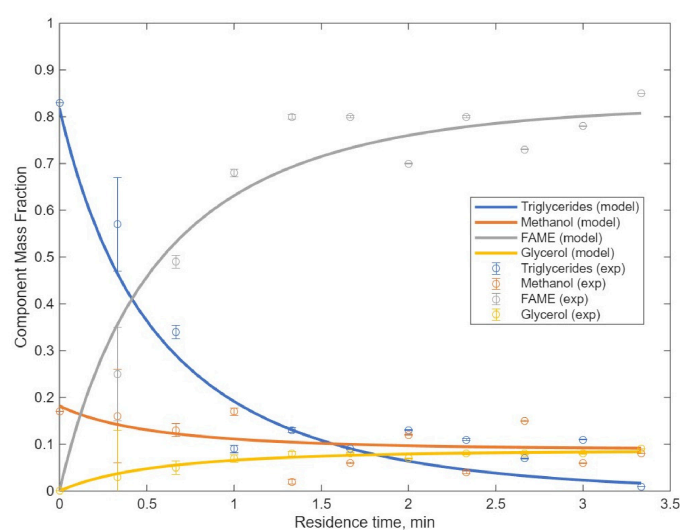


Figure 3. Comparison of experimental data and pseudo-homogeneous second-order kinetic model predictions for the transesterification reaction at a constant 60 °C using a 1 mm diameter microtube, a 6:1 methanol-to-oil ratio, and 3 wt% KOH catalyst loading.

Table 3. Comparison of pseudo-homogeneous and biphasic models with statistical data.

Statistical Metric	Pseudo-Homogeneous First-Order Model	Pseudo-Homogeneous Second-Order Model	Biphasic Model
R^2 value	0.9428	0.9439	0.9603
RMSE	0.0503	0.0483	0.0433
MAE	0.0397	0.0386	0.0344
AIC _C	−120.3	−121.4	−119.0
BIC	−116.2	−117.5	−114.4

3.2.2. Biphasic Model

The biphasic model also assumed a single-step reaction mechanism and was evaluated using the same data from the experiments conducted at 60 °C. As can be seen in Figure 4, there is a strong agreement between experimental and predicted values. Although the trends were similar to those of the pseudo-homogeneous model, the biphasic model provided reasonable predictions of the overall conversion dynamics with a slightly different curve, particularly at early residence times. Both models were tested across all three temperatures (40 °C, 50 °C and 60 °C) and evaluated using the goodness-of-fit metrics, i.e., the average R^2 , the average RMSE, and the average MAE, together with the corrected

Akaike Information Criterion (AICc) and Bayesian Information Criterion (BIC), which account for model complexity. As shown in Table 3, the biphasic model achieved the highest predictive accuracy, exhibiting the highest R^2 value and the lowest RMSE and MAE. When model complexity was considered, the pseudo-homogeneous second-order model produced slightly lower AICc and BIC values than the biphasic model. This indicates that its simpler mathematical formulation provides a marginally better balance between predictive capability and model complexity. However, the differences in AICc and BIC were relatively small (approximately 2–3 units), suggesting that the two models provide statistically comparable descriptions of the experimental data. Consequently, model selection should be guided by the intended application. The pseudo-homogeneous model is suitable for rapid engineering calculations and preliminary reactor design, whereas the biphasic model is more appropriate when an accurate representation of interfacial mass transfer and phase interactions is required.

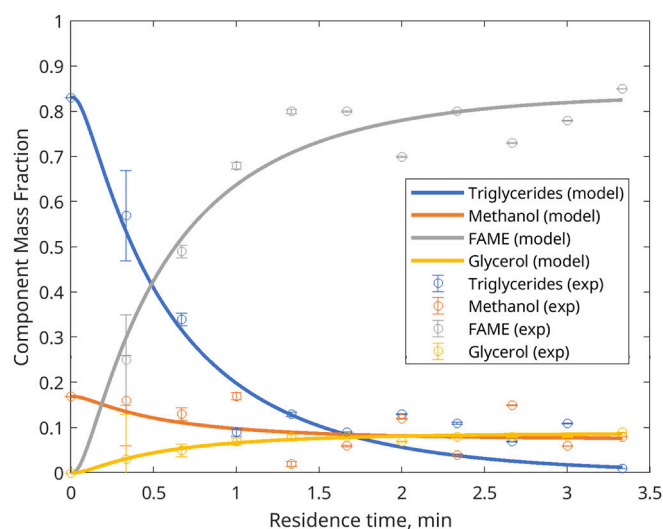


Figure 4. Comparison of experimental data and biphasic kinetic model predictions for the transesterification reaction at a constant 60 °C using a 1 mm diameter microtube, a 6:1 methanol-to-oil ratio, and 3 wt% KOH catalyst loading.

3.2.3. Mass-Transfer Effects

The significance of mass transfer was further evaluated using the Hatta number and enhancement factor (E). Hatta numbers ranging from 1.45 to 1.48 were obtained across the temperature range. Since $0.2 < Ha < 2$, the rate of chemical reaction follows a fast intermediate reaction rate; thus, both reaction and diffusion affect the rate, and neither dominates [36]. Accordingly, the enhancement factor was approximated using Equation (13), finding a range of 1.617–1.645. Although the pseudo-homogeneous model provided reasonably good predictive accuracy and remains useful for simpler, less computationally demanding scenarios, the biphasic model offered more accurate representation of the system, particularly in capturing the roles of mass transfer and phase interaction.

3.3. Thermodynamic Analysis of Pseudo-Homogeneous and Biphasic Models

Utilising the fitted kinetic models, key thermodynamic parameters, such as activation energy and pre-exponential factors, were determined to account for the energy requirements of the transesterification reaction. These values were extracted by varying the reaction rate constants to obtain the best model fit, as summarised in Table 4. The reaction rate constants obtained from the biphasic model differed from those of the pseudo-homogeneous model because the two models define the reaction rate differently. In the pseudo-homogeneous model, concentrations are referenced to the reactor volume, and transport phenomena are

implicitly incorporated into a single apparent reaction rate constant. In contrast, the biphasic model evaluates phase-specific concentrations and explicitly accounts for interfacial area and mass transfer between immiscible phases. Consequently, the reaction rate constants obtained from the two models have different physical meanings. The pseudo-homogeneous model yields a global apparent rate constant that implicitly incorporates transport effects, whereas the biphasic model yields an apparent interfacial rate constant after explicitly accounting for mass transfer and phase interactions. Accordingly, the fitted rate constants should not be interpreted or compared as intrinsic kinetic parameters.

Table 4. Thermodynamic kinetic parameters obtained from pseudo-homogeneous and biphasic transesterification models.

Kinetic Metric	Pseudo-Homogeneous Second-Order Model	Biphasic Model
E_a , kJ mol ^{−1}	11.02 (±24.82)	15.61 (±22.70)
$\Delta H^\ddagger$, kJ mol ^{−1}	8.335 (±24.51)	12.93 (±22.40)
$\Delta S^\ddagger$, J mol ^{−1} K ^{−1}	−241.9 (±75.93)	−272.3 (±69.39)
$\Delta G^\ddagger$, (at 298 K), kJ mol ^{−1}	80.42 (±47.14)	94.08 (±43.08)
Pre-Exponential Factor, m ³ min ^{−1} mol ^{−1}	4.217	0.1090
k at 60 °C, m ³ min ^{−1} mol ^{−1}	0.080	3.933×10^{-4}
k at 50 °C, m ³ min ^{−1} mol ^{−1}	0.068	3.186×10^{-4}
k at 40 °C, m ³ min ^{−1} mol ^{−1}	0.062	2.742×10^{-4}
Enhancement factor	N/A	1.617–1.645
K_{OP} , m s ^{−1}	N/A	9.17×10^{-6} – 1.16×10^{-5}
K_{MP} , m s ^{−1}	N/A	8.76×10^{-6} – 1.31×10^{-5}

95% confidence intervals calculated using $t_{0.025,1} = 12.706$. Due to the limited temperature range ($n = 3$), the confidence intervals are relatively wide, with lower bounds extending to physically unrealistic negative activation energies. These intervals reflect regression uncertainty rather than physically meaningful values; the reported parameters should be interpreted as approximate apparent values.

Kinetic rate constants were determined at three temperatures (40 °C, 50 °C and 60 °C) and used to construct Arrhenius and Eyring plots. As only three temperature points were chosen, the regression analysis has limited degrees of freedom. Therefore, the derived activation energy and thermodynamic activation parameters should be interpreted as approximate values specific to the investigated operating window. To quantify the associated uncertainty, 95% confidence intervals were calculated and are reported for all fitted parameters.

The Arrhenius plots (Figure 5a,b) were used to derive the activation energies and pre-exponential factors for each model. The pseudo-homogeneous model (Figure 5a) resulted in a strong linear correlation ($R^2 = 0.9695$), supporting its validity in describing the temperature dependence of the reaction rate. However, the biphasic model (Figure 5b) demonstrated an even better fit, with higher linearity ($R^2 = 0.9871$), which further supports the strength of this model to capture the underlying kinetics more accurately. To further evaluate the thermodynamic feasibility and energy changes associated with the reaction, the Eyring–Polyani Equation (20) and the Gibbs free energy Equation (21) were applied, following the methodology outlined by Kumar et al. [28]. Eyring plots for both the pseudo-homogeneous and biphasic model are presented in Figure 6. The resulting thermodynamic parameters, activation enthalpy ($\Delta H^\ddagger$), activation entropy ($\Delta S^\ddagger$), and activation free energy ($\Delta G^\ddagger$) are listed in Table 4. It can be seen that both models produced positive values for the activation enthalpy and free energy, indicating that there is an energetic barrier present when the transition state is formed and that the formation of this transition state is endothermic. Furthermore, the negative activation entropy suggests that the transition state is more ordered than the reactants.

$$k = \frac{k_b T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (20)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (21)$$

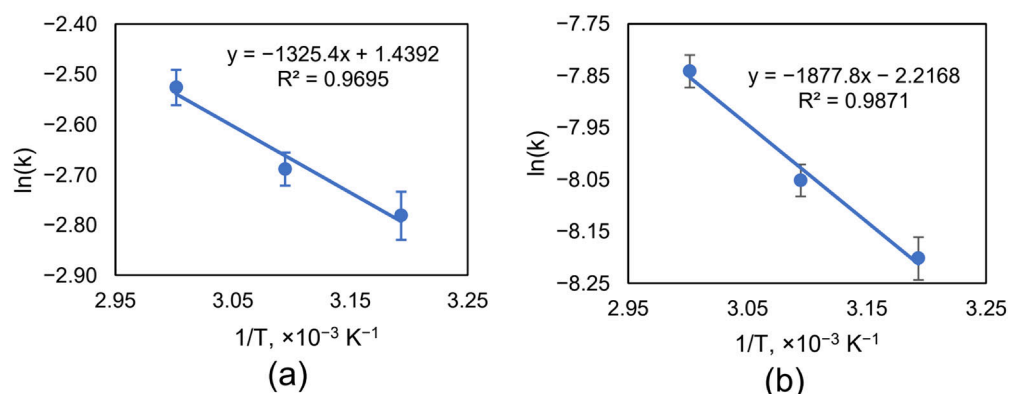


Figure 5. Arrhenius plot for (a) pseudo-homogeneous second-order model and (b) biphasic second-order model for the transesterification of WCO based on experimentally determined rate constants over the temperature range of 40–60 °C. Conditions: 1 mm microtube diameter, 6:1 methanol-to-oil ratio and 3 wt% KOH catalyst loading.

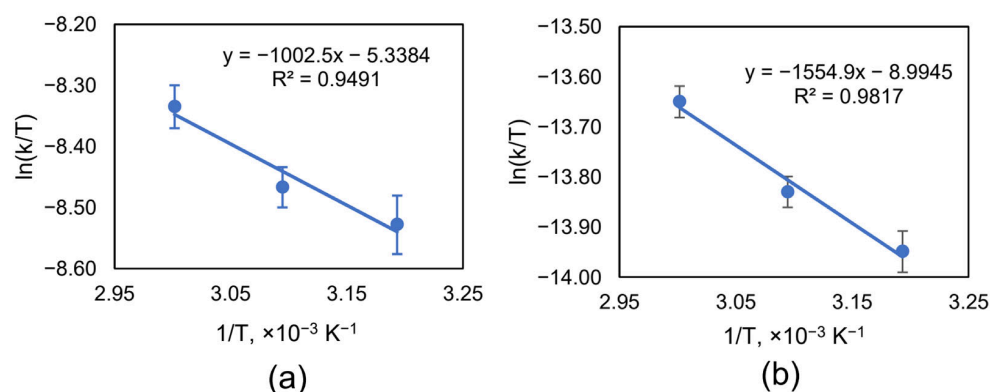


Figure 6. Eyring plot for (a) pseudo-homogeneous second-order model and (b) biphasic second-order model for the transesterification of WCO based on experimentally determined rate constants over the temperature range of 40–60 °C. Conditions: 1 mm microtube diameter, 6:1 methanol-to-oil ratio and 3 wt% KOH catalyst loading.

To evaluate the robustness of the derived thermodynamic parameters, a sensitivity analysis was conducted. The reaction rate constants and the mass-transfer coefficients, as the primary inputs, were varied by up to $\pm 10\%$, and the resulting changes in activation energy, activation enthalpy, activation entropy, and activation free energy were analysed. It should be noted that this evaluation represents a parameter sensitivity analysis to assess the sensitivity of the derived activation parameters to moderate variations in the fitted model parameters.

This analysis was performed at 60 °C, where the largest fluctuations were observed, and the results are summarized in Tables 5–7. The pseudo-homogeneous model showed greater sensitivity to changes in reaction rate constants, with larger percentage deviations observed in the thermodynamic parameters. In contrast, the biphasic model exhibited smaller variations, suggesting that its derived parameters are more stable and less sensitive to small experimental or fitting errors. The mass-transfer coefficients had a minimal effect on the thermodynamic parameters, indicating that the system operates in a regime where mass-transfer resistance is minimised, provided by the microreactor set-up, thereby allowing the reaction to be mainly governed by chemical kinetics. Among all parameters, the change in activation enthalpy was the most affected, showing a maximum deviation of

3.51%. However, across both models and parameters, all percentage variations remained relatively low, indicating that the obtained thermodynamic results are stable and not critically dependent on small changes in the fitted kinetic constants.

Table 5. Sensitivity analysis of thermodynamic parameters for the transesterification reaction at 60 °C, varying the reaction rate constant.

Models	% Variation of k-Values	−10%	−5%	0%	+5%	+10%
Pseudo-homogeneous model	E_a , kJ mol ^{−1}	11.27	11.12	10.98	10.85	10.72
	% Change of E_a	2.66	1.29	0.00	1.23	2.40
Biphasic model	E_a , kJ mol ^{−1}	15.87	15.72	15.58	15.44	15.31
	% Change of E_a	1.87	0.91	0.00	0.87	1.69
Pseudo-homogeneous model	$\Delta H^\ddagger$, kJ mol ^{−1}	8.59	8.45	8.30	8.17	8.04
	% Change of $\Delta H^\ddagger$	3.51	1.71	0.00	1.63	3.18
Biphasic model	$\Delta H^\ddagger$, kJ mol ^{−1}	13.17	13.02	12.88	12.75	12.62
	% Change of $\Delta H^\ddagger$	2.27	1.10	0.00	1.05	2.05
Pseudo-homogeneous model	$\Delta S^\ddagger$, J mol ^{−1} K ^{−1}	−242.7	−242.2	−272.3	−241.4	−241.0
	% Change of $\Delta S^\ddagger$	0.36	0.18	0.00	0.17	0.33
Biphasic model	$\Delta S^\ddagger$, J mol ^{−1} K ^{−1}	−273.58	−272.93	−272.30	−271.70	−271.13
	% Change of $\Delta S^\ddagger$	0.47	0.23	0.00	0.22	0.43
Pseudo-homogeneous model	$\Delta G^\ddagger$ (at 298 K), kJ mol ^{−1}	80.91	80.63	80.36	80.10	79.86
	% Change of $\Delta G^\ddagger$	0.69	0.33	0.00	0.32	0.62
Biphasic model	$\Delta G^\ddagger$ (at 298 K), kJ mol ^{−1}	94.84	94.45	94.08	93.73	93.39
	% Change of $\Delta G^\ddagger$	0.81	0.39	0.00	0.37	0.73

Table 6. Sensitivity analysis of thermodynamic parameters for the transesterification reaction at 60 °C, with the biphasic model varying the oil-phase mass-transfer coefficient.

% Variation of K_{OP}	−10%	−5%	0%	+5%	+10%
E_a , kJ mol ^{−1}	15.37	15.48	15.58	15.67	15.77
% Change of E_a	1.30	0.64	0.00	0.58	1.27
$\Delta H^\ddagger$, kJ mol ^{−1}	12.68	12.78	12.88	12.97	13.08
% Change of $\Delta H^\ddagger$	1.58	0.78	0.00	0.70	1.53
$\Delta S^\ddagger$, J mol ^{−1} K ^{−1}	−271.4	−271.9	−272.3	−272.7	−273.2
% Change of $\Delta S^\ddagger$	0.33	0.16	0.00	0.15	0.32
$\Delta G^\ddagger$ (at 298K), kJ mol ^{−1}	93.55	93.82	94.08	94.32	94.60
% Change of $\Delta G^\ddagger$	0.56	0.28	0.00	0.25	0.55

Table 7. Sensitivity analysis of thermodynamic parameters for the transesterification reaction at 60 °C, with the biphasic model varying the methanol-phase mass-transfer coefficient.

% Variation of K_{MP}	−10%	−5%	0%	+5%	+10%
E_a , kJ mol ^{−1}	15.53	15.55	15.58	15.63	15.66
% Change of E_a	0.32	0.17	0.00	0.32	0.52
$\Delta H^\ddagger$, kJ mol ^{−1}	12.823	12.85	12.88	12.93	12.96
% Change of $\Delta H^\ddagger$	0.39	0.21	0.00	0.38	0.63
$\Delta S^\ddagger$, J mol ^{−1} K ^{−1}	−272.1	−272.2	−272.3	−272.5	−272.7
% Change of $\Delta S^\ddagger$	0.08	0.04	0.00	0.08	0.13
$\Delta G^\ddagger$ (at 298K), kJ mol ^{−1}	93.95	94.01	94.08	94.21	94.30
% Change of $\Delta G^\ddagger$	0.14	0.07	0.00	0.14	0.23

3.4. Comparative Analysis of Reported Literature

This section compares the kinetic and thermodynamic parameters obtained in this study with selected literature. The complexity of transesterification kinetics, especially for waste-derived feedstocks such as waste cooking oil, necessitates robust modelling approaches that account for phase interactions and mass-transfer limitations. Table 8 summarises representative studies relevant to the current work, highlighting feedstocks, catalysts, thermodynamic parameters, kinetic models, and associated mass-transfer characteristics. Because these models employ different reaction orders, kinetic formulations and phase treatments, the reported rate constants have different physical meanings and units. Consequently, the comparison is intended to illustrate the diversity of modelling approaches reported in the literature rather than provide direct quantitative benchmarks between rate constants.

3.4.1. Comparison of Thermodynamic Parameters of WCO and Edible Oils

The activation energy determined in this study ($11.02 \text{ kJ mol}^{-1} \pm 24.82$) is significantly lower than values reported for edible oils. For instance, Nouredini and Zhu [25] reported values ranging from 33.47 to 83.68 kJ mol^{-1} for soybean oil as a feedstock using a three-step pseudo-homogeneous second-order kinetic model in a batch reactor; however, the large confidence intervals due to the limited temperature range mean that statistical significance could not be firmly established. Nevertheless, the significant reduction in activation energy observed in this work suggests that there is a combined effect of intensified transport exhibited in microreactors and WCO properties that facilitate transesterification. The high surface area-to-volume ratios and the intensified mixing reduce the boundary-layer thickness and accelerate interfacial transport, and in traditional batch reactors, mass-transfer resistances can limit the initial reaction rates [6,7,22]. In addition, WCO undergoes thermal and oxidative degradation during cooking, producing shorter-chain and partially oxidised fatty acid derivatives. These species may require less activation energy to transesterify. This is corroborated by Uzun et al. [29], who reported a comparable activation energy of $11.74 \text{ kJ mol}^{-1}$. In the current work, approximately 1–3 wt% of FAME was found to be composed of fatty acids chains shorter than C16:0, suggesting that the presence of low-chain triglycerides may have contributed partly to the observed lower activation energy compared to typical values.

3.4.2. Comparison of Mass-Transfer Coefficients and Solvent Miscibility

Given WCO's high viscosity, mass-transfer limitations were also compared with those of other systems. Richard et al. [19] reported an average mass transfer coefficient of $1 \times 10^{-5} \text{ m s}^{-1}$ sunflower oil in ethanol, which is comparable to the $1.16 \times 10^{-5} \text{ m s}^{-1}$ observed for the methanol–WCO system. Although similar in magnitude, this is not a direct comparison, as ethanol's superior miscibility with triglycerides likely elevates its mass-transfer coefficient. Bannatham et al. [13] reported a higher mass-transfer coefficient ($2.3 \times 10^{-5} \text{ m s}^{-1}$) for palm oil in a microreactor, which can be attributed to the lower viscosity of palm oil relative to WCO. These comparisons underscore the need to account for alcohol choice and feedstock properties when evaluating mass-transfer effects.

3.4.3. Performance of Kinetic Models in the Literature

In this work, the biphasic model and the pseudo-homogeneous model were found to be statistically similar, with the pseudo-homogeneous model providing lower complexity but the biphasic model providing higher accuracy. Zanjani et al. [42] investigated four different kinetic models for transesterification and observed a similar behaviour; they found that a non-linear modified pseudo-homogeneous model was necessary to fit experimental data

with heterogeneous catalysts. Pseudo-homogeneous models oversimplify the existence of concentration gradients across the phase boundary, assuming complete mixing. However, with sufficient residence time and mixing, the performance gap narrows, as also found by Kumar et al. [28], who obtained a maximum R^2 value of 0.9732 using a second-order pseudo-homogeneous model with waste cooking oil feedstock. Similarly, Richard et al. [19] showed that biphasic models can offer excellent agreement when parameters are tuned appropriately. While both models are viable, biphasic modelling better captures early-stage reaction kinetics in immiscible systems, better reflecting initial rate limitations.

3.4.4. Thermodynamic Trends Across Models

The derived thermodynamic parameters, such as activation enthalpy, activation entropy and activation free energy, can provide insight into the reaction's energy profile and were compared with parameters reported in selected studies, particularly those involving WCO-based systems. Compared to the studies by Kumar et al. [28] and Pugazhendi et al. [43], this study reported lower $\Delta G^\ddagger$ values, which may reflect differences in the catalyst concentration, reactor configuration, or feedstock characteristics. Nonetheless, all studies reported positive $\Delta G^\ddagger$ values, indicating that the reaction is thermodynamically unfavourable under standard conditions to achieve the transition state, consistent with the endothermic nature of the formation of the transit and the dependence on external energy input to proceed. The lower activation enthalpy observed in this study may be attributed to enhanced molecular transport and interfacial interactions within the microreactor. Moreover, the more negative $\Delta S^\ddagger$ value suggests that the system evolves toward a more ordered transition stage, possibly due to the alignment of methyl esters at the interface during reaction. Interestingly, the thermodynamic trends observed here align more closely with the findings of Nautiyal et al. [44], who used an algal feedstock and acid catalysis, suggesting that reactor configuration and feedstock composition may have a stronger influence on thermodynamic behaviour than the reaction mechanism itself.

Table 8. Comparison of studies investigating models of reaction kinetics and properties for transesterification reactions.

Feedstock	Catalyst	Kinetic Model	Activation Energy, kJ mol ^{−1}	$\Delta H^\ddagger$, kJ mol ^{−1} ; $\Delta S^\ddagger$, J mol ^{−1} K ^{−1} ; $\Delta G^\ddagger$, kJ mol ^{−1}	Reaction Rate Constant at 60 °C	Mass-Transfer Coefficients at 60 °C, m s ^{−1}	Other Comments	Reference
WCO	KOH	Pseudo-homogeneous and biphasic (both second order)	11.02 (±24.82)/ 15.61 (±22.70)	8.335 (±24.51)/12.93 (±22.4); −241.9 (±75.93)/−272.3 (±69.39); 80.42 (±47.14)/90.48 (±43.08)	0.080/3.933 × 10 ^{−4} m ³ min ^{−1} mol ^{−1}	$K_{OP} =$ 1.16 × 10 ^{−5} $K_{MP} =$ 1.31 × 10 ^{−5}	Microreactor: The biphasic model achieved the best accuracy, with Arrhenius plot yielding an R ² -value of 0.9871.	Current work
Pseudo-Homogeneous Kinetic Models								
Waste frying oil	NaOH	Pseudo-homogeneous first order	11.74	NR	NR	NR	Batch reactor: The Arrhenius plot had an R ² -value of 0.896.	[29]
WCO	Calcinated waste mussel shells or DM water treatment precipitate	Pseudo-homogeneous first order	77.09 79.83	NR	0.0819 hr ^{−1} 0.0932 hr ^{−1}	NR	Batch reactor: The model showed an MRE of 11.68–12.33%; a heterogeneous catalyst allowed for reuse.	[45]
WCO	KOH	Pseudo-homogeneous first order	45.76	43.04; −144.9; 91.32	0.0327 s ^{−1}	NR	Batch reactor: Maximum R ² value of 0.9732 obtained for the kinetic model.	[28]
WCO	Alkaline	Pseudo-homogeneous first order	57.82	55.09; −103; 89.90	0.025–0.092 min ^{−1}	NR	Batch reactor: An average R ² value of 0.955 was obtained from the Arrhenius plot.	[43]
WCO	H ₂ SO ₄ and NaOH	Pseudo-homogeneous first order	88.77	NR	0.0078 min ^{−1}	NR	Batch reactor: A 2-step process combining esterification and transesterification.	[30]
<i>Spirulinaplantensis</i> (algae biomass)	H ₂ SO ₄	Pseudo-homogeneous first order	14.52	16.35; −232.83; 92.71	0.001 min ^{−1}	NR	Batch reactor: High catalyst concentration (60%) required for effective conversion.	[44]
Soybean oil	NaOH	3-step pseudo-homogeneous second order	33.47–83.68	NR	0.050, 0.110, 0.215, 1.228, 0.242, 0.007 for each reaction step	NR	Batch reactor: Reaction exhibited an initial mass transfer-controlled regime, followed by a kinetically controlled regime.	[25]
Palm oil	NaOH	Pseudo-homogeneous reversible second order	76.97 (forward) 106.23 (backward)	NR	0.1032 (forward) 0.0793 (backward) L min ^{−1} mol ^{−1}	NR	Microreactor: The model showed a maximum deviation of 7.6% if reaction equilibrium was reached before droplet coalescence.	[18]
Biphasic Kinetic Models								
Rapeseed and waste sunflower oils	KOH	3-step biphasic second order	47 (forward) 36 (backward) 93 (forward) 48 (backward)	NR	0.0222–0.0879 L min ^{−1} mol ^{−1} for rate determining step	$K_{TG} = 0.2\text{--}1.2 \times 10^{-5}$ m min ^{−1}	Batch reactor: Applied successfully for scale-up to industrial-scale operations.	[46]
Soybean oil	KOH	3-step biphasic first order	NR	NR	0.537–2.518 l ³ min mol ^{−3} for different micromixers and the rate-determining step	$\beta_1 = 0.035\text{--}0.093$, $\beta_2 = 0.184\text{--}1.158$, $\beta_3 = 0\text{--}0.05$ dm min ^{−1} , where $\beta = k_{1,a}$	Micromixing devices (ethanol): Mass transfer increased with lower inner diameters.	[47]
High-oleic sunflower oil	EtONa	3-step biphasic third order	NR	NR	5 × 10 ^{−2} l ² s ^{−1} mol ^{−2} for the rate-determining step	$K_{TG} = 1 \times 10^{-5}$ m/s (averaged)	Microreactor (ethanol): The model was validated experimentally and used to simulate and propose alternative conditions.	[19]
Soybean and sunflower oil	NaOH	Biphasic first order (mass transfer of glycerol included)	NR	NR	5.17–5.78 × 10 ^{−3} s ^{−1}	$K_{TP} =$ 5.18–5.86 × 10 ^{−2} s ^{−1} $K_G = 1.02\text{--}1.$ × 10 ^{−2} s ^{−1} for glycerol	Batch reactor: The mass-transfer rate competed with the reaction rate.	[48]

Single-step lumped kinetics is assumed, unless noted as 3-step reaction. Rate constants reported in this table originate from kinetic models with different reaction orders, mathematical formulations and phase treatments. Consequently, they have different units and physical meanings and are presented for qualitative literature comparison only; they should not be interpreted as directly comparable intrinsic kinetic parameters.

4. Conclusions

This study demonstrated that base-catalysed transesterification of waste cooking oil (WCO) with methanol can be efficiently carried out in a microreactor system, achieving over 90% methyl ester yield within 100 s. The high surface area-to-volume ratio and enhanced mixing characteristics of the microreactor minimized mass-transfer limitations and improved reaction rates, making it a promising platform for sustainable biodiesel production. Two kinetic models were evaluated to describe the reaction: a pseudo-homogeneous second-order model and a biphasic second-order model. While both provided reasonable fits, the biphasic model more accurately represented the reaction system by explicitly accounting for the immiscibility and interfacial mass transfer between WCO and methanol. However, the pseudo-homogeneous model provided a lower AIC_C and BIC value due to its simplicity; therefore, the choice of model is dependent on physical and mechanistic needs. The activation energy derived from the biphasic model ($15.61 \text{ kJ mol}^{-1} \pm 22.70$) was lower than typical values reported for homogeneous systems, reinforcing the hypothesis that microreactors alleviate transport limitations. Thermodynamic analysis revealed positive activation enthalpy and activation free energy and negative activation entropy, indicating that there is a finite energy barrier when reaching the transition state, with the formation of this transition state being endothermic and the transition state being more ordered than the reactants. The presented kinetic models assume a single-step lumped mechanism for transesterification. While this approximation predicts overall FAME yield, it does not capture the evolution of intermediate species, and future work incorporating this analysis would be beneficial to provide a better mechanistic understanding of the system. This research was also limited by obtaining thermodynamic parameters with only three temperatures, resulting in wide confidence intervals; therefore, the parameters should be interpreted as approximate values specific to the experimental conditions, and in the future, additional experiments are required to obtain more statistically robust activation parameters. Overall, this work highlights the viability of integrating waste-derived feedstocks, microreactor technology, and mechanistic kinetic modelling to design intensified, sustainable biodiesel production systems. Future efforts should focus on validating these models under varying conditions and scaling the process while maintaining mass-transfer advantages.

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Abbreviations

The following abbreviations are used in this manuscript:

WCO	Waste cooking oil
FFA	Free fatty acid
FAME	Fatty acid methyl ester
GC-FID	Gas chromatography flame ionisation detection
TG	Triglyceride
DG	Diglyceride
MG	Monoglyceride
M	Methanol
G	Glycerol
ME	Methyl ester
PTFE	Polytetrafluoroethylene
ODE	Ordinary differential equation
RMSE	Root mean square error
MAE	Mean absolute error
NR	Not reported

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