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REVIEW OF CATALYSTS AND PROCESS PARAMETERS IN THE INTERESTERIFICATION REACTION FOR BIODIESEL PRODUCTION

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Interesterification, Methyl Acetate, Biodiesel Production, Heterogeneous Catalysts, Triacetin.

ABSTRACT

This article reviews the development of catalysts and key operating parameters in the interesterification of triglycerides with methyl acetate for biodiesel production. Interesterification offers advantages over conventional methanol-based transesterification, particularly the absence of glycerol formation and the generation of triacetin as a valuable co-product. A systematic narrative review following PRISMA guidelines was conducted on studies published between 2005-2024. The discussion covers homogeneous, heterogeneous, enzymatic, and supercritical systems, as well as kinetic and thermodynamic characteristics. Homogeneous catalysts exhibit rapid reaction rates at mild temperatures but suffer from separation and corrosion issues. Heterogeneous catalysts provide improved stability and reusability, although diffusion limitations are often present. Enzymatic systems offer high selectivity under low-temperature conditions but require long reaction times and incur high costs. Supercritical methyl acetate achieves high conversion without catalysts but demands extreme operating conditions. Comparative analysis indicates that catalyst performance is strongly influenced by feedstock quality, MA:oil ratio, temperature, and process intensification methods. This review highlights research gaps and future directions needed to support efficient and sustainable industrial biodiesel production through methyl acetate–based interesterification.

ABSTRAK

Kata Kunci: Interesterifikasi, Metil Asetat, Produksi Biodiesel, Katalis Heterogen, Triasetin.

Artikel ini mengulas perkembangan katalis dan parameter operasi utama pada reaksi interesterifikasi trigliserida dengan metil asetat untuk produksi biodiesel. Metode interesterifikasi menawarkan keunggulan dibandingkan transesterifikasi berbasis metanol, terutama karena tidak menghasilkan gliserol dan memproduksi triasetin sebagai produk samping bernilai tambah. Kajian ini disusun melalui systematic narrative review berbasis PRISMA terhadap publikasi tahun 2005–2024. Pembahasan mencakup katalis homogen, heterogen, enzimatik, serta proses superkritis, beserta aspek kinetika dan termodinamika. Katalis homogen menunjukkan laju reaksi cepat pada suhu rendah namun memiliki kendala pemisahan dan korosivitas. Katalis heterogen lebih stabil dan dapat digunakan ulang, meskipun kinerjanya sering dibatasi hambatan difusi. Sistem enzimatik memberikan selektivitas tinggi namun membutuhkan waktu reaksi panjang dan biaya besar. Proses superkritis mampu mencapai konversi tinggi tanpa katalis, tetapi memerlukan kondisi operasi ekstrem. Analisis komparatif menunjukkan bahwa performa katalis dipengaruhi kualitas minyak, rasio MA:oil, suhu, dan metode intensifikasi proses. Kajian ini mengidentifikasi gap penelitian serta arah pengembangan untuk mendukung produksi biodiesel yang efisien dan berkelanjutan melalui interesterifikasi berbasis metil asetat.

INTRODUCTION

Energy availability in Indonesia continues to face increasing pressure due to rising national consumption and the declining reserves of fossil fuels. The country’s heavy dependence on petroleum makes the energy sector highly vulnerable to global price fluctuations and supply instability. In this context, biodiesel has emerged as one of the most promising renewable energy alternatives. Biodiesel can be produced from various oil sources, including refined vegetable oils, animal fats, waste cooking oil, and feedstocks with high free fatty acid (FFA) content [1]. This flexibility creates opportunities for utilizing local resources and supports the concept of a circular economy [1], [2], [3].

However, the commonly used biodiesel production pathway—methanol-based transesterification—still presents several limitations, particularly related to glycerol formation, sensitivity to water and free fatty acids, and the need for additional purification steps that increase operational costs [3].

To overcome these challenges, methyl acetate-based interesterification has emerged as a more efficient and process-friendly alternative approach. Unlike methanolysis, which produces glycerol as a byproduct, the interesterification reaction generates triacetin, a compound that is soluble in biodiesel. The absence of a glycerol phase simplifies the process, reduces energy consumption during separation, and enhances economic value since triacetin can be utilized as a fuel additive [7], [8]. Furthermore, interesterification is more tolerant of feedstocks with high FFA content, making it suitable for processing lower-quality oils without requiring pre-esterification [8]. These advantages make interesterification particularly relevant for industrial-scale applications that demand process stability and cost efficiency.

Research on interesterification has grown rapidly over the past two decades, particularly in the development of increasingly diverse catalysts. Early studies focused on homogeneous acid- and base-based catalysts, which exhibit high activity but pose challenges related to corrosivity and separation difficulties [2], [7]. Subsequent research shifted toward heterogeneous catalysts such as CaO, MgO, γ-Al_2O_3, and doped metal oxides, which offer improved thermal stability and reusability potential [10], [11]. In addition, biocatalytic approaches using immobilized lipase have gained attention. Although these systems typically require longer reaction times, they offer advantages in selectivity and milder operating conditions [13], [14]. Other studies have explored supercritical processes without catalysts, which can achieve high conversion rates but require substantial energy input and high-pressure equipment.

Despite these significant contributions, reported results remain highly variable in terms of catalyst durability, surface activity, optimal temperature range, and triacetin formation. This variability highlights the need for a comprehensive reassessment of existing findings to identify clearer development patterns and research directions.

To date, relatively few publications have provided an integrated and comprehensive review of the relationships among catalyst type, operating parameters, and reaction performance in methyl acetate-based interesterification. Most previous reviews have focused on a single catalyst group or emphasized kinetic aspects without systematically comparing different approaches. This gap is critical because the success of interesterification is determined not only by catalyst properties but also by reaction conditions such as molar ratio, temperature, reaction time, and process intensification methods (e.g., ultrasound, co-solvents, and supercritical conditions). Without a systematic scientific synthesis that maps these approaches comprehensively, it becomes challenging for researchers to determine the most effective optimization strategies, particularly for industrial-scale development.

In response to this need, this article aims to provide a comprehensive overview of research developments in methyl acetate-based interesterification for biodiesel production. The discussion focuses on the classification and characteristics of various catalyst types, analysis of the effects of reaction parameters on FAME conversion and triacetin formation, and evaluation of the advantages and limitations of each approach. In addition, this article highlights recent research trends, including biomineral-based catalysts, magnetic catalysts, and reaction intensification strategies. By presenting a critical synthesis and cross-study comparison, this review is expected to serve as a valuable reference for both researchers and industry practitioners in designing more efficient, adaptive, and sustainable interesterification processes.

RESEARCH METHODS

This article was prepared using a systematic narrative review approach, with the PRISMA framework serving as the basis for the literature selection process. The literature search was conducted through ScienceDirect, Scopus, SpringerLink, and Google Scholar using the keywords “interesterification,” “methyl acetate,” “biodiesel,” “glycerol-free,” “biodiesel production,” “heterogeneous catalyst,” “homogeneous catalyst,” “lipase,” and “triacetin.” The publication period was limited to 2005–2024 to capture both early developments and recent research trends.

The selection process included the stages of identification, screening, eligibility assessment, and final inclusion in accordance with the PRISMA flow diagram. The number of articles at each stage is presented in Figure 1. Selection was based on the following inclusion criteria: (1) articles discussing the interesterification of triglycerides using methyl acetate; (2) studies providing data on reaction conditions or catalyst performance; and (3) publications in reputable scientific journals. Articles deemed irrelevant or those focusing solely on methanol-based transesterification were excluded.

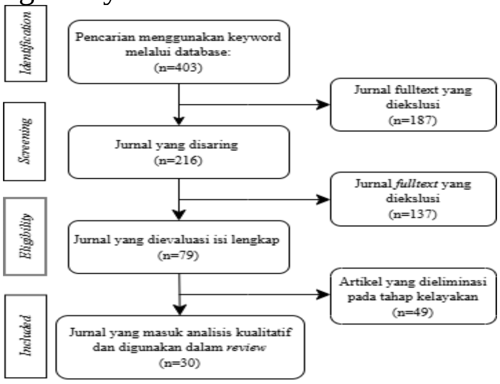

Figure 1. Literature Selection Flow Based on the PRISMA Method

From the overall selection process, a number of eligible articles were included for qualitative analysis. The extracted data comprised catalyst type, activation technique, methyl acetate-to-oil (MA:oil) molar ratio, intensification method, reaction temperature and time, FAME conversion, and triacetin formation. This information was categorized into six groups: homogeneous catalysts, heterogeneous catalysts, enzymatic/biocatalytic systems, supercritical processes, kinetic analyses, and technical studies, in order to facilitate thematic discussion in the subsequent sections.

RESULTS AND DISCUSSION

Mechanism and Basic of Interesterification Reaction

The interesterification reaction is an acyl group exchange process between triglycerides (TG) and a simple ester such as methyl acetate (MA). In general, the reaction mechanism can be described as follows.

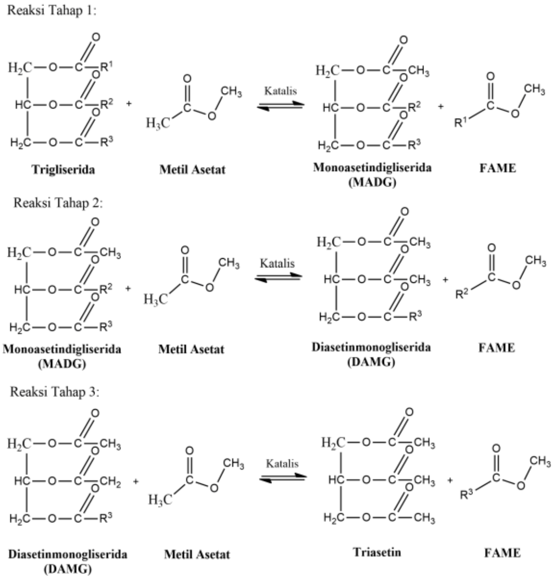

Figure 2. Interesterification reaction stages

Figure 2 shows that the reaction occurs through three stages, namely the formation of monoacetin diglycerides (MADG), followed by diacetin monoglycerides (DAMG), and finally the formation of triacetin. Unlike transesterification reactions, this process does not produce free glycerol, so phase separation and emulsification can be minimized. The main challenge arises in the final stage of triacetin formation due to limited accessibility of the carbonyl groups and diffusion barriers, especially when using solid catalysts. The type of catalyst, solvent polarity, and thermal conditions greatly influence the efficiency of interesterification. Strong base catalysts accelerate the initial stage of the reaction but are susceptible to deactivation by free fatty acids (FFA) and water. Acid and enzymatic catalysts are more tolerant of low-quality oils but require longer reaction times.

Kinetic studies indicate that interesterification is reversible, following a pseudo-second-order reaction model within the temperature range of 50–70°C, both in homogeneous systems and in reactions with ultrasonic intensification. Activation energies ranging from 45–55 kJ/mol suggest that the mechanism is chemically controlled but still affected by diffusion barriers, especially in heterogeneous catalysts. Under extreme conditions such as supercritical states, the reaction rate increases dramatically, but thermal degradation of FAME (fatty acid methyl esters) can occur when temperatures exceed 300°C. Overall, the effectiveness of interesterification is determined by two factors: the stepwise reactivity of MADG–DAGM–triacetin and the interphase diffusion barriers. These two factors explain the significant variability among studies and form the basis for developing more selective and more stable catalysts against FFA. The following is a summary of several related journal articles on interesterification reactions.

Table 1. Research summary from 30 references

Reference	**Type of Catalyst**	**Reaction System**	**MA:Oil**	**Suhu (°C)**	**Waktu (jam)**	**Yield/ Konversi (%)**	**Kelebihan & Keterbatasan**
[2]	H_2SO_4 0,1%	Asam homogen (RSM-optimized)	12:1	55	1,7	142 (total FAME + TA)	Cheap catalyst but corrosive and needs neutralization
[3]	KOH 1% + *co-solvent* 0, 5, 10, 15, 20%	Basa homogen	n.r	60	0,5-1,5	92,43 (*co-solvent* 20%)	No co-solvent separation is required, the biodiesel quality is good, the reaction time is short, and it is glycerol-free; there is a slightly higher density, and the analysis is not yet complete.
[6]	K-metoksida	*Ultrasound-assisted* (UAI)	15:1	55	0,083-0,333	81-90	Short time, Ea=50.5 kJ/mol; requires large-scale validation
[8]	Lipozyme TLIM	Enzimatik	6-12:1	35-45	4-6	85-92	Low temperature, selective; expensive enzyme
[9]	Biokatalis Eugenol	Green biokatalis	6:1	60	0,25	83,16	Environmentally friendly; limited biocatalyst stability.
[10]	5% niobium phosphate	Heterogen	30:1	250	2,5	52,7 FAME dan 0,1 TA	Providing clear optimization of the biodiesel process with an effective RSM model; limited experimental validation and no discussion of biodiesel quality aspects or process scalability.
[11]	Mg-Al hidrotalsit kalsinasi	Basa heterogen	50:1	200	4	95,9	Reuse catalyst: water-sensitive / FFA
[7]	Tanpa katalis	Superkritis	30:1	399	1	97,6	High conversion without a catalyst; high energy and pressure are required..
[12]	Tanpa katalis	Superkritis kontinu (packed bed)	5:1	250-325	0,75	44-83	Continuous, clean; degraded product at high pressure
[13]	Penambahan aditif CH_3COOH/ H_2O	Superkritis dengan aditif	10%wt CH_3COOH	300	0,75	109,7	Lower pressure; controlling composition is important
[14]	$Fe_2(SO_4)_3$	Simulasi proses asam heterogen	10:1; kontinyu	n.r	n.r	n.r	High NPV; suitable industry; limited experimental data
[15]	10% tin	Homogen	18:1	210	20	90 FAME	High catalytic

	octoate					dan 60 TA	performance; high operating temperature and difficult to separate catalysts
[16]	21.3% $S_2O_8^{2-}/ZrO^{2-}$ TiO_2-Fe_3O_4	Heterogen	13,8:1; 50°C	50	20,8	98,5 FAME	High activity and reusable; requires high temperature and catalyst amount, and leaching occurs, resulting in incomplete separation.
[17]	5% niobium oxide	Heterogen	30:1	250	2	45,77 FAME dan 0,21 TA	The active catalyst is reusable; at high temperatures, some catalysts experience a decrease in activity.
[18]	$KOCH_3$	Homogen dengan ultrasound	15:1	50	3	98,12	High mass transfer; Difficult separation
[19]	Lipozyme TLIM	Enzimatik dengan ultrasound	9:1	50	3	96,1	Short time; high cost
[20]	Novozym 435	Enzimatik	6:1; 40°C	40	n.r	n.r	Model ping pong Bi-Bi; slow reaction
[21]	-	*Pressurized*	n.r	375	0,25-0,583	66,49	Without a catalyst; moderate yield
[22]	$NaOCH_3$, lipase, superkritis	Enzimatik dan superkritis	12-20:1	60-350	1-6	92 FAEE	Without glycerol, the mixed product is homogeneous; slow kinetics at low temperatures and high costs for supercritical conditions.
[23]	1% y-alumina	Heterogen	9:1	50	0,83	69,3 FAME	Ultrasound enhances mixing and accelerates reactions; however, the yield is still moderate and the process has not yet been tested on a large scale.
[24]	2% y-alumina	Heterogen	20:1	300	1	48,96 FAME dan 1,84 TA	Provides a broad overview of the role of colloids in energy conversion; the discussion remains general with limited in-depth experimental data.
[10]	5% y-alumina	Heterogen	30:1	250	1	50,61 FAME dan 1,88 TA	Providing clear optimization of the biodiesel process with an effective RSM model; limited experimental validation and no discussion of biodiesel quality aspects or process scalability.
[25]	10% Novozyme 435	Enzimatik	14:1	48	24	64 FAME	Improving biodiesel conversion through pulsed ultrasound and metal

							oxide catalysts; optimization is still limited and has not yet included biodiesel quality evaluation or large-scale feasibility.
[26]	CaO	Heterogen	9:1	60	1,5	87,50	Providing an overview of the selection process, the final product meets almost all ASTM parameters; catalyst quality is lacking, cannot be reused.
[27]	NaOH: 1%, 1,5%, 2%	Homogen	n.r	n.r	3-6	81,79-84,84 FAME	Focus on the interest verification method; the catalyst is less accurate and FAME is far below standard.
[28]	Sn-based, y-Al2O3 support, dan SnO@y-Al2O3	Heteregon	6-12:1	210	0,5-2	90,6 FAME (Katalis Al/Sn = 2,0)	Providing a comprehensive review of triglyceride interesterification using methyl acetate; does not present complete experimental data
[10]	5% Ca-Mg-Al mixed oxide	Heterogen	40:1	325	1,33	61,74 FAME dan 6,81 TA	Providing clear optimization of the biodiesel process with an effective RSM model; limited experimental validation and no discussion of biodiesel quality aspects or process scalability..
[29]	10% CaO	Heterogen	40:1	325	4	62,3 FAME	Active catalyst and reusable; high temperature required and activity decreases due to leaching
[30]	0,69 mol Tin (II) oxide	Heterogen	40:1	210	4	90 FAME dan 70 TA	High reaction selectivity and catalysts that are easy to separate as solids; conversion is not yet optimal and their performance decreases after several cycles.

Abbreviations: TA, triasetin; n.r, not reported

Homogeneous Catalyst System

Homogeneous catalysts are the simplest systems used in interesterification reactions. Homogeneous catalysts such as H_2SO_4, KOH, and $NaOCH_3$ have been proven to provide high activity at low temperatures. Acidic homogeneous catalysts show high tolerance to oils with high FFA content because they can simultaneously activate methyl acetate carbonyl groups and triglycerides. Youssef et al.'s 2024 study reported that 0.1% H_2SO_4 catalyst (w/w) with a molar ratio of MA:oil of 12:1 at 55°C for 1.7 hours produced a yield of 142% (total FAME + triacetin). This study also applied Response Surface Methodology (RSM) and ANOVA to determine optimal conditions.

The results showed that increasing the molar ratio and reaction temperature accelerated triacetin formation and suppressed glycerol formation. However, its use is limited due to corrosiveness and the need for extensive post-processing.

Homogeneous base catalysts such as KOH and NaOH have higher activity compared to acid catalysts at low temperatures (50-70°C) through a strong nucleophilic mechanism, but they are very sensitive to water and high FFA levels. In oils with FFA >2%, soap formation is unavoidable, which reduces conversion and complicates separation. Ansori's 2025 research used K-methoxide as a base catalyst in an ultrasound-assisted interesterification (UAI) system. Ultrasound acts as microturbulence that enhances mass transfer between non-miscible phases (oil:MA), thus reducing reaction time from hours to minutes. Under conditions of 55°C, a molar ratio of 15:1, and a duration of 20-50 minutes, triglyceride conversion of 91-90% was achieved with a pseudo-second-order kinetic model and an activation energy of 50.5 kJ/mol.ol.

Through several studies, homogeneous catalysts have proven to be effective for simple systems and pure raw materials, but their main drawbacks include difficulty in product separation, high corrosiveness, high sensitivity and instability to FFA, as well as environmental issues due to the need for post-reaction neutralization. Therefore, modern research tends to shift toward heterogeneous catalyst systems that are more environmentally friendly and reusable.

Heterogeneous Catalyst System

Heterogeneous catalysts offer advantages such as ease of separation, thermal stability, and the potential for reuse. Commonly used materials include metal oxides, zeolites, and mineral-based materials such as calcium oxide (CaO), magnesium oxide (MgO), or alumina (γ-Al2O3). The activity of heterogeneous catalysts is highly influenced by the specific surface area, the distribution of acid or base sites, and the efficiency of contact between the solid phase and the liquid reactant. Therefore, differences in activation methods and oil properties often result in seemingly inconsistent performance across studies.

Ribeiro et al. (2018) demonstrated that $\gamma\text{-}Al_2O_3$ as a solid acid catalyst can provide a good balance between conversion and energy efficiency in the interesterification reaction of macaúba oil with methyl acetate. Under optimal conditions of 300°C, 2% w/w catalyst, a molar ratio of 20:1, and a duration of 60 minutes, a high FAME yield was obtained with triacetin as the main product. Its stability is also quite good, as it can be reused up to six cycles before activity declines in the seventh cycle. This finding shows that solid acid catalysts are relatively tolerant of high FFA content oils and are not easily deactivated by moisture.

A different approach was demonstrated by Dhawan et al. (2020), who utilized calcined Mg–Al hydrotalcite as a heterogeneous base catalyst. The layered structure of hydrotalcite provides strong basic sites (O^{2-}) that effectively activate the carbonyl group of methyl acetate, achieving a triglyceride conversion of 95.9% at 200°C with a molar ratio of 50:1 over four hours. However, this catalyst remains sensitive to water and free fatty acids (FFA), which can reduce activity through the formation of carbonates or by blocking active sites—an effect that is common in solid base catalysts.

Several studies in Indonesia utilize biomineral sources such as CaO from shell shells, fish bones, and rice husk ash. The abundant $CaCO_3$ content can be converted into active CaO through calcination. This catalyst is inexpensive, widely available, and strongly basic, making it an attractive candidate for large-scale biodiesel production. However, CaO easily re-carbonates back to $CaCO_3$ when exposed to humid air, and it is less suitable for oils with high FFA content. Another challenge is the consistency of catalytic properties, as biomineral sources tend to be heterogeneous.

From a kinetic perspective, most heterogeneous systems exhibit a lower reaction rate compared to homogeneous catalysts due to diffusion barriers to the particle surface. However, the overall process efficiency is often better. The products are easier to purify, no soap formation occurs, and the catalyst can be reused with relatively low activity loss. In some systems, such as Mg-Al modification or γ-Al2O3, stability can be maintained over many cycles without major regeneration. These findings confirm that heterogeneous catalysts work more slowly, but in terms of economics and sustainability, they are far superior to homogeneous systems.

Enzymatic and Biocatalytic System

The enzymatic system provides a more selective and environmentally friendly alternative in the interesterification process because lipase can catalyze the breaking and forming of ester bonds without requiring extreme reaction conditions. Unlike chemical catalysts, enzymes work specifically on triglyceride ester bonds without the need for extreme conditions, making them more suitable for oils with high FFA content. Immobilized lipase, such as Lipozyme TLIM (Thermomyces lanuginosa lipase), is a biocatalyst widely applied in interesterification systems. Halim et al. (2022) reported that this enzyme works effectively at relatively low temperatures (35–45 °C), with a molar ratio of methyl acetate to oil of 6:1 to 12:1, reaction times of 4–60 hours, and enzyme loading of 1–10%. Under optimal conditions, biodiesel conversion can reach 85–92%, accompanied by the formation of triacetin as a consistent byproduct.

The main advantages of lipase lie in its selectivity and stability. In immobilized form, the enzyme can be reused up to about ten cycles with a gradual decrease in activity. This enhances the economic value of the process despite the relatively high initial cost of the biocatalyst. However, the duration of the reaction time remains a significant limitation, especially for industrial applications requiring high throughput.

In addition to lipase, research on biocatalysts based on bioactive compounds is also developing. Daryono et al. (2024) examined the use of eugenol and eucalyptus oil as biocatalytic agents that have a dual function, namely increasing interphase reactivity while also acting as natural cofactors. At a temperature of 60°C with a reactant ratio of 6:1 and a reaction time of 15 minutes, a yield of 83.16% was obtained with a reduction in acid number to 0.5 mg KOH/g. The proposed mechanism involves the formation of a transient complex between eugenol and triglycerides that accelerates the ester bond cleavage process. Although still in the early stages of development, this approach offers potential for utilizing renewable biological sources as alternative catalysts.

Overall, enzymatic and biocatalytic systems have strong prospects in the context of green chemistry because they can operate at low temperatures, do not produce hazardous waste, and have a high level of reaction selectivity. However, the relatively high cost of enzymes and long reaction times remain major obstacles in industrial-scale applications. Future development directions include optimizing enzyme stability through more efficient immobilization techniques, engineering biocatalysts to enhance activity, and integrating with continuous flow reactors such as continuous stirred-tank reactors (CSTR) to improve overall process efficiency.

Supercritical System and Additive

The supercritical process based on methyl acetate is a non-catalytic approach that offers significant advantages over conventional methods. Under conditions above the critical point of methyl acetate (239°C; 4.7 MPa), the oil and reactant mixture are in a single homogeneous phase. This eliminates the interphase diffusion barrier, which is the main limiting factor in heterogenous systems, thereby substantially increasing the reaction rate. Tan et al. (2010) and Dona et al. (2013) reported that triglyceride interesterification at 399°C for 59 minutes with a molar ratio of 30:1 can achieve nearly complete conversion with FAME yields reaching 97.65%. The absence of free glycerol and the presence of triacetin as a byproduct are additional advantages, as this system produces a more stable and valuable product mixture.

Future research efforts should focus on reducing temperature and pressure requirements to make the process more energy- and economically viable. Goembira and Saka (2014) demonstrated that adding additives such as acetic acid and small amounts of water can lower the operating temperature to around 300°C. These additives increase the system's polarity and promote alternative reaction pathways through partial hydrolysis of triglycerides into more reactive free fatty acids (FFAs). Additionally, the formation of acid-assisted acyl exchange conditions accelerates the formation of triacetin. The results indicate that optimizing the mixture composition of reactants can significantly reduce energy needs without compromising conversion efficiency.

Several studies also report semi-supercritical approaches that combine supercritical fluid properties with the presence of solid catalysts. Ribeiro et al. (2018) showed that γ-Al_2O_3 can accelerate conversion under moderate supercritical conditions without adding complexity to product purification, resulting in a more thermally efficient system. This approach opens opportunities to reduce operating pressure while maintaining high reaction rates.

Overall, supercritical processes have long-term potential as clean and efficient technologies, but their industrial feasibility still depends on engineering innovations capable of lowering energy requirements and infrastructure costs. Relevant research directions include reducing the critical point through co-solvents, designing lower-energy reactors, and integrating with sustainable biodiesel production systems.

Kinetics and Thermodynamics

The interesterification reaction of triglycerides with methyl acetate generally follows a pseudo-second-order kinetic model, both in homogeneous and heterogeneous systems. This model explains that the reaction rate is controlled by the concentrations of both reactants simultaneously, which differs from methanolysis that tends to follow a pseudo-first-order under certain conditions. Youssef et al. (2024) reported that the activation energy (Ea) value for interesterification ranges between 45–55 kJ/mol, indicating that this process is primarily controlled by chemical kinetics, although diffusion barriers can become significant when using solid catalysts with narrow pores. In heterogeneous systems, intra-sit and inter-particle diffusion become important determinants.

Studies on CaO, MgO, and γ-Al_2O_3-based materials show that increasing temperature accelerates the reaction but not always linearly, because the diffusion of reactants toward active sites limits the rate at moderate temperatures. Conversely, in homogeneous acid catalyst systems, the reaction rate is more sensitive to temperature increases and tends to follow the Arrhenius pattern more consistently. From a thermodynamic perspective, interesterification reactions are classified as mildly endothermic.

Therefore, increasing temperature generally shifts the equilibrium toward the formation of methyl esters and triacetin. However, at excessively high temperatures (>300°C), especially under supercritical conditions, thermal degradation, oil depolymerization, and the formation of light side products can occur, making the selection of an optimal temperature crucial to maintain product selectivity. In supercritical systems, the decreasing fluid density at high temperatures increases diffusivity and accelerates the reaction, but overly reducing reactant density can decrease the frequency of effective collisions. Understanding these kinetic and thermodynamic aspects is essential for evaluating the performance of various catalyst categories. Basic catalysts work quickly in the initial stages but are susceptible to inhibition by free fatty acids (FFA); acid catalysts are stable but slow; solid catalysts face diffusion limitations; while supercritical systems rely on optimizing fluid density. Thus, kinetic and thermodynamic analyses provide a comparative framework that clarifies the reasons behind the performance variations reported in various studies.

TabLE 2. Kinetics summary from 10 journals

Referensi	**Catholic System**	**Main condition (T, MA: Oil, time))**	**Model Kinetika**	**Activation Energy (Ea, $kJ\cdot mol^{-1}$)**	**Important note**
[6]	*Ultrasound-assisted*; K-*methoxide* (homogen)	55°C; 15:1; 5–20 menit	Pseudo-order two	50.5	Ultrasonik meningkatkan transfer massa; kinetika dikendalikan secara kimiawi + efek intensifikasi.
[11]	Mg–Al *hydrotalcite* (heterogen, kalsinasi)	200°C; 50:1; 4 jam	Two-stage: rapid reaction + slow reaction (adsorption-desorption)	~52.3	The model shows the involvement of the diffusion process at the final stage.
[2]	H_2SO_4 (asam homogen)	55 °C; 12:1; 1.7 jam (RSM *optimized*)	Reported as an acid mechanism; kinetics are reported empirically (pseudo-second order under certain conditions)	n.r.	The RSM report presents the optimized reaction rate; the results show a high total yield (FAME + triacetin).
[7]	Superkritis (MA, tanpa katalis)	399 °C; 30:1; 1 jam	In supercritical conditions, rapid kinetics, the model is often presented as a higher-order/empirical kinetics.	n.r.	Minimal diffusion barrier; extreme conditions → thermal challenge.
[12]	Superkritis *kontinu* (*packed bed*)	250–325 °C; beragam rasio	The kinetic model is reported to be based on an empirical continuous reactor experiment.	n.r.	Performance depends on pressure and residence time; degradation at high pressure has been reported.
[31]	γ-Al_2O_3 (padat asam)	300 °C; 20:1; 1 jam	Empirical kinetics (rapid conversion at high T conditions), specific kinetic models are not always reported.	n.r.	The catalyst can be reused (approximately 6 cycles) before activity declines; effective on non-edible oil.
[10]	*Screening* heterogen (beberapa oksida)	Berbagai kondisi	Some studies report pseudo-order two or empirical models; the details of the kinetics per catalyst vary.	n.r.	Focus on comparing catalyst activities; complete kinetics are not always provided.

[18]	*Ultrasound-assisted* (homogen)	50 °C; 15:1; waktu singkat	The reaction rate is significantly affected by intensification; the commonly adopted kinetic models are pseudo-second order or empirical models.	n.r.	UAI lowers the mass transfer limit; kinetic parameters are exposed per condition.
[20]	Enzimatik (lipase)	35–45 °C; rasio bervariasi	Enzymatic model: ping-pong Bi–Bi or Michaelis–Menten for some lipase systems	n.r.	The enzyme kinetics model differs from conventional chemistry; parameters Km and Vmax are often reported.
[21]	*Pressurized methyl acetate* (semi-kontinyu)	Kondisi bertekanan; durasi 15–35 menit	Experimental (empirical) kinetics, some studies report that second-order models are effective	n.r.	Shows the trade-off between speed and energy; relevant for continuous reactor design.

Abbreviation: n.r, not reported

Comparative Evaluation

A comparative analysis of more than thirty publications shows that the performance of methyl acetate interesterification is highly influenced by the type of catalyst and operating conditions. Homogeneous catalysts provide the fastest reaction rates at relatively low temperatures (50–60 °C) with conversions of 81–98%, but are very sensitive to water and free fatty acids (FFA). Heterogeneous catalysts achieve conversions of 60–98% at higher temperatures and offer advantages such as ease of separation and potential for reuse. The enzymatic system is the most energy-efficient but requires longer reaction times and high enzyme costs. Supercritical processes can reach conversions of up to 97% in a short time but require extreme temperatures and pressures. The optimal MA:oil ratio is between 9:1 and 20:1 for homogeneous and enzymatic systems, and 30:1 to 50:1 for heterogeneous and supercritical systems. No approach is entirely superior overall; the choice of system depends on oil quality, target conversion, energy efficiency, and separation strategy.

Techno-Economic Analysis and Future Research Directions

The technical and economic aspects (techno-economic analysis, TEA) play an important role in determining the feasibility of commercializing the methyl acetate-based interesterification process. Process simulations by Dougher et al. (2023) using Aspen Plus show that the heterogeneous acid system is more cost-efficient compared to the base system because it does not require a neutralization step and is tolerant of high FFA content [12]. At a production capacity of 30,000 tons/year, with a MA:oil ratio of 10:1 and ferric sulfate catalyst, a Net Present Value (NPV) of approximately USD 34 million is obtained over a 20-year project lifespan, with biodiesel prices around USD 0.78/kg [12].

The supercritical process offers advantages in product purity and simplified separation but requires significant investment in high-pressure reactors and consumes substantial energy at temperatures above 350°C and pressures above 20 MPa [9], [11]. Therefore, the development of hybrid processes such as semi-supercritical systems assisted by solid catalysts or ultrasonic heating becomes an attractive alternative to reduce energy needs without compromising conversion [30]. In the context of sustainability, the utilization of catalysts based on biomineral waste, such as rice husk ash, shell, and bones, is increasingly studied due to their abundant availability and support for the circular economy concept [31].

Additionally, continuous flow reactors and magnetic catalysts like Fe_3O_4-doped CaO/TiO_2 are predicted to be important directions for development to increase reaction rates, facilitate catalyst separation, and reduce energy consumption [32], [33]. This literature review also indicates that standardization of reaction parameters and mapping the influence of chemical characteristics on interesterification pathways remain limited. Furthermore, the integration of kinetic modeling and transport phenomena, as well as long-term validation in continuous reactors, has not been widely conducted. Strengthening these aspects is necessary so that methyl acetate-based interesterification can be applied more precisely, stably, and in accordance with industrial needs.

CONCLUSION

Interesterification based on methyl acetate has proven to be a competitive pathway for producing glycerol-free biodiesel, with better reaction stability compared to conventional transesterification. The success of methyl acetate-based interesterification is primarily determined by the system's ability to manage two main aspects: the stepwise chemical reactivity of MADG–DAGM–triasetin formation and the diffusion barriers that arise at the oil–catalyst interface. Evaluation of various catalytic approaches shows that each catalyst category has advantages specific to its purpose. Homogeneous systems excel in accelerating the initial stage, heterogeneous catalysts are more stable and easier to separate, enzymatic catalysts provide high selectivity, and supercritical processes achieve maximum conversion without producing free glycerol. Therefore, the effectiveness of interesterification is not determined by a single type of catalyst but by the compatibility between the oil characteristics, operating conditions, and separation strategies employed.

Overall, this review confirms that methyl acetate interesterification is a technically feasible biodiesel production pathway because it can maintain reaction stability and produce value-added byproducts. Optimal implementation at an industrial scale depends on the system's ability to reduce diffusion barriers, maintain catalyst consistency during repeated use, and minimize energy requirements in the chosen process configuration.

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