

Experimental and kinetic study for the production of biodiesel from waste cooking oil by microwave assisted system

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ABSTRACT

Serious problems in the current decades are the ensuring of enough energy supply and mitigating the consequences of global warming. Considered as a substitute for exhaustible fossil fuels in recent years, biodiesel may help to lower world temperature and considered as renewable source of energy. In this work, the feasibility of using calcium oxide (CaO) nano catalyst derived from falling willow leaves extraction, with microwave assistance as a heating source to produce biodiesel from waste cooking oil was investigated. We investigated the effects of fundamental parameters including the amount of microwave power, the ratio of methanol to oil, the time and temperature of the reaction, and the amount of catalyst used. The results show that the best yield, 96.31%, was reached at 65 °C in 20 minutes with a 3 wt.% catalyst loading, 10% power, and a 70 wt.% methanol: oil ratio. The activation energy for the catalyzed transesterification process, which was 24.266 kJ/mol, indicates that the reaction is under chemical control. The importance of this study goes beyond the academic aspect, as it represents a practical model for biodiesel production at the industrial level by utilizing biomass waste as catalysts and inedible oils as raw materials, using microwave-based heating systems, which contributes to the application of green and environmentally friendly chemistry. The study also relies on the use of economical raw materials that are not suitable for human consumption, utilizing biomass waste to produce biofuel, which supports environmental sustainability and the sustainable management of biomass waste, and enhances modern and advanced research in the field of biofuel production.

Keywords: biodiesel, microwave, CaO nano catalyst, willow leaves extract, waste cooking oil, transesterification.

INTRODUCTION

Traditional and non-sustainable energy sources such as coal and crude oil are important, especially after the increase in population and industrial development that has occurred, which has increased the demand for them to meet energy requirements. However, these sources tend to be subject to depletion and not environmentally friendly where they caused greenhouse gas emissions that cause pollution such as calcium dioxide and leads to a phenomenon of global warming (Abd et al., 2024; Linggawati, 2016; Rozina et al., 2024). Biodiesel can be used as a sustainable energy source to replace or supplement petroleum-based energy sources (Tippayawong and Sittisun, 2012).

Biodiesel shows promise as a fossil fuel substitute because of its similarity to fossil diesel in

many physical and chemical aspects, including viscosity, energy, and ignition characteristics. The presence of two oxygen atoms and one or more unsaturated bonds distinguishes biodiesel from its counterpart (Muley and Boldor, 2018). Biodiesel has many advantages over conventional diesel, where its: (1) biodegradable (2) renewable (3) environmentally friendly as the emissions of toxic gases from conventional diesel are very low (4) provides the possibility of direct use without need to modify the engine (Mohammed and Jabbar, 2015). But the main drawback is that its production cost is high in both the raw material and the process of converting oil into biodiesel (Mahmood and Al-Yaqoobi, 2025; Ong and Nomanbhay, 2018a; Subramaniam et al., 2024a).

Generally, Biodiesel is a methyl ester of long chain fatty acids (Hussain et al., 2011), wherefore it's called fatty acid methyl ester (FAME).

Biodiesel is usually produced from oil drawn out from algae, fungi, animal fat, vegetable oil, or other sources such as junk cooking oil. Production costs for biodiesel's primary ingredients contributes approximately more than 70% of the total cost (Meng et al., 2008; Phan and Phan, 2008). Since oils is the most essential raw material, using use fats and oils in homes and restaurants reduces the cost of producing biodiesel and will also help with garbage disposal (Banković-Ilić et al., 2012).

The process of producing biodiesel is the conversion of oil by several chemical and physical methods including (pyrolysis, micro emulation, dilution, and transesterification (Ong and Nomanbhay, 2018b). In the dilution or direct mixing process (physical method) raw diesel is mixed with vegetable oil in different proportions, but this process is unsuccessful due to the increasing of the viscosity of diesel, which leads to solidification of vegetable oil when the temperature drops. as well as increased content of FFAs and the decreasing of volatility of vegetable oil and the formation of gum. that leads to engine failure and incomplete combustion of the fuel (Bashir et al., 2022). The method of combining oil with a short-chain alcohol, like methanol, is known as micro-emulsions. However, this approach has drawbacks because it results in carbon deposits in the engine and incomplete fuel combustion. Pyrolysis, also known as catalyst cracking, is the process of converting vegetable or animal fats without the presence of oxygen or air into fuels like diesel (Carlucci, 2022).

The most popular process for producing biodiesel is transesterification, which involves triglycerides and alcohol reacting with a catalyst. This procedure has the benefit of producing inexpensive, straightforward, and high-yield biodiesel. (Subramaniam et al., 2024b). Transesterification reactions possible to be catalytic processes, non-catalytic. Heterogeneous catalysts, homogeneous catalysts, ionic liquids, and biocatalysts are usually utilized (Tran et al., 2017). as mentioned, it's possible not to use catalysts in the transesterification, but this process requires supercritical conditions of high temperature and pressure, so its commercial use has decreased. Therefore, catalysts are used to reduce energy activation and fast the reaction rate (Sahu et al., 2023).

Heterogeneous catalysts are environmentally friendly catalysts because they are solid catalysts that can be used more the once and thus reduce

the cost of the process (Colombo et al., 2017; Kouzu and Hidaka, 2012). Acidic catalysts are suitable for the reaction catalytic process if the FFA ratio is high in oil and water, but this process requires a higher concentration, a large ratio of alcohol to oil, and a high reaction time of the catalyst, and the equipment could be corroded due to the the catalyst acidity (Marinković et al., 2016). To get rid of these problems, basic heterogeneous catalysts are used where they are low cost, easily detach from the final product, and highly effective (Kouzu and Hidaka, 2012). An example of these heterogeneous catalysts is oxides. Among the many heterogeneous catalysts utilized in biodiesel production, calcium oxide stands out for its unique combination of low cost, mild reaction conditions, and peculiar characteristics. The fact that it is a highly efficient catalyst means that the reaction time is minimal (Almadani et al., 2023).

It has been found that the use of short-chain alcohol produces a higher conversion and more stable result (methanol, ethanol) than long-chain alcohols. Although Ethanol comes from agricultural products, is a sustainable alternative, and good solvent for oil. However, methanol was used because ethyl esters have greater pour and cloud points and thicker viscosities than methyl esters, and therefore they give higher torque and rotational force than those produced by ethyl ester (Jachuck et al., 2009; Jongsomjit et al., 2010).

Traditional heating method involves heat transfer by (convection, thermal conduction) from the surface of the container to the internal materials. this method leads to a large loss of energy because the rise in temperature lead to heat transfer from the surface to the inside of sample, and the heating is inhomogeneous as it depends on thermal conductivity, specific heat, and density (Gude et al., 2013; Groisman and Gedanken, 2008) On the other hand, the waves used in microwaves are a(electromagnetic) ranging in frequency from (0.3–300) GHz. Since biodiesel consists of oil and alcohol, it is difficult to mix to gather so these waves are suitable for solution that are difficult to mix (Yunsari et al., 2019). microwave energy is used in many applications as it accelerates chemical reactions because it works by polar molecules (Varma, 2001). Heating in the microwave is fast and homogenous where the heat transfer by microwaves is through wave absorption, so the temperature of The sample is above the reactor's surface, so the heat transfer process in the microwave doesn't take place through the surface (Abd et

al., 2024; Abd and Al-Yaqoobi, 2025) unlike the utilization of microwave radiation in the manufacturing of biodiesel offers numerous benefits in comparison to traditional methods, as it decreases the reaction period (fast reactions) due to the radiation energy, this energy is clean, so it doesn't produce waste, it is more efficient than traditional methods, so it gives the best way to manufacture biodiesel, it is safer, and also provides better way to separate products (Iyyaswami et al., 2013; Win and Khine, 2017).

Analyzing the transesterification reaction's kinetics plays a crucial role in deciding the optimal conditions for this reaction with the aim of enhancing biofuel (biodiesel) production. Kinetic models contribute to providing accurate insights into the behavior of the reaction, as they can take into account the effects of mass and heat transfer, as well as thermal dynamic equilibrium, which enables the improvement of process efficiency and more accurate prediction of its outcomes (Aljendeel et al., 2022).

This investigation concentrates on the synthesis of biodiesel utilizing leftover cooking oil as an oil source and a nanoscale calcium oxide (CaO) catalyst synthesized from willow leaf extract using microwave technology. As part of the study, an analysis was conducted to determine the impact that several operational elements had on the manufacturing process. These factors included the ratio of methanol to oil (by weight), the quantity of catalyst and the length of the reaction, the impact of microwave power, and the temperature of the reactant. To check the quality and effectiveness of the biodiesel that is generated, the fuel characteristics and physical characteristics of biodiesel were also analyzed.

MATERIALS AND METHODS

Materials

A range of pure chemicals were used in the experiments, including high-concentration calcium nitrate tetrahydrate, sodium hydroxide from Thomas Baker, India, and nearly 100% pure methanol purity of 99.8%, originating from Chem-lab NV in Belgium and ethanol was purchased from RCI Labscan with a minimal analysis of 99.9%, high-purity deionized water and phenolphthalein reagent from BDH Chemicals Ltd, England were

also used for analysis. The cooking oil used was obtained from local restaurants.

Treatment of used cooking oil

To get rid of contaminants and food residues, the used cooking oil was processed by filtering it through a fine sieve. The free fatty acid content was then determined using an alkaline titration technique. A specific amount of the oil was mixed with ethanol, and a small amount of a color indicator was added. The oil was then titrated with an alkaline solution until the color changed, revealing that the free fatty acid content was 2.4%. The moisture content was estimated by drying a sample of the oil in a constant-temperature oven for two hours, followed by calculating the mass loss, which revealed that the water content of the oil was 0.05%.

Preparation of CaO nano-catalyst

The process began with preparing willow leaves, which were thoroughly washed and dried at a constant temperature of 100 °C for six hours. They were then ground by electrical ground into a fine powder. This powder was then heated in deionized water at 60 °C for half an hour, allowed to cool, and filtered to extract the aqueous solution. The aqueous extract was heated to 55 °C, and alkali and a calcium source were added, resulting in a yellow paste indicating the completion of the reaction. The resulting material was subsequently heated to a calcined state at 600 °C for two hours, resulting in a calcium oxide nano catalyst.

Catalyst characterization

An EDX analysis of the willow leaves extract at a concentration of 10% was performed. The results showed a high presence of calcium and oxygen, reflecting the extract's active compounds that interact with calcium salts. FTIR analysis of the extract also confirmed active functional groups, including carboxyl and hydroxyl groups, which contribute to the stabilization of metal ions. The prepared catalyst was examined using XRF, showing that the calcium oxide content was 82.54%. It was characterized using XRD, SEM-EDX, FTIR, and BET methods. The catalyst's specific surface area was 12.097 m²/g, its pore volume was 0.0237 cm³/g, and its typical pore diameter ranged from 2 to

10 nm, according to BET analysis, indicating its nanostructure. The EDX results for the catalyst revealed a calcium content of 49.31% and oxygen content of 45.08%, further confirming the formation of nano-calcium oxide. FTIR analysis of the catalyst also showed characteristic peaks confirming the formation of Ca–O bonds.

Transesterification reaction

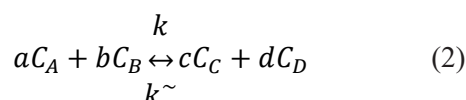
All trials were conducted in batches using a WB20230745 microwave chemical reactor operating at atmospheric pressure. This reactor, manufactured by Gongyi Yuhua Instrument Co., Ltd., has microwave power that may be adjusted between 80 and 800 W. Figure 1 shows an illustration of the experimental setup used, which includes a three-necked glass flask that is attached to a temperature sensor and condenser, allowing precise control of reaction conditions. For each of the experiments, thirty grams of used cooking oil were utilized, and the weight ratio of methanol to oil was varied to be 50%, 60%, 70%, and 80%. The influence of the concentration of the catalyst was also investigated at 1%, 2%, 3%, and 4% of the used cooking oil weight. The microwave radiation power was set at two levels: 10%, and 20% of the total device power, while different reaction times were chosen: 10, 15, 20, and 25 minutes reaction and different reaction temperature at

45 °C, 55 °C, 65 °C, and 75 °C. Upon completion of the reaction, the mixture was left to settle overnight, resulting in the clear separation of three layers: a bottom layer containing catalyst residues, a middle layer of glycerin, and an upper layer representing biodiesel. The fuel layer was collected and separated from the catalyst using centrifugation, subsequently, it had been dried in an oven that was set at 65 °C for a day to eliminate any residual methanol. After that, the conversion ratio to biodiesel was calculated using Equation 1.

$$\text{Yield\%} = \frac{\text{weight of biodiesel}}{\text{weight of waste cooking oil}} \times 100\% \quad (1)$$

Kinetic analysis of the response

The complete equation of product biodiesel can be written as Equation 2:



Since the reaction is a pseudo-homogenous, its rate can be written as follows:

$$\begin{aligned} -r_A &= -\left(\frac{dC_A}{dt}\right) = \\ &= kCA^aCB^b - k^{\sim}CC^cCD^d \end{aligned} \quad (3)$$

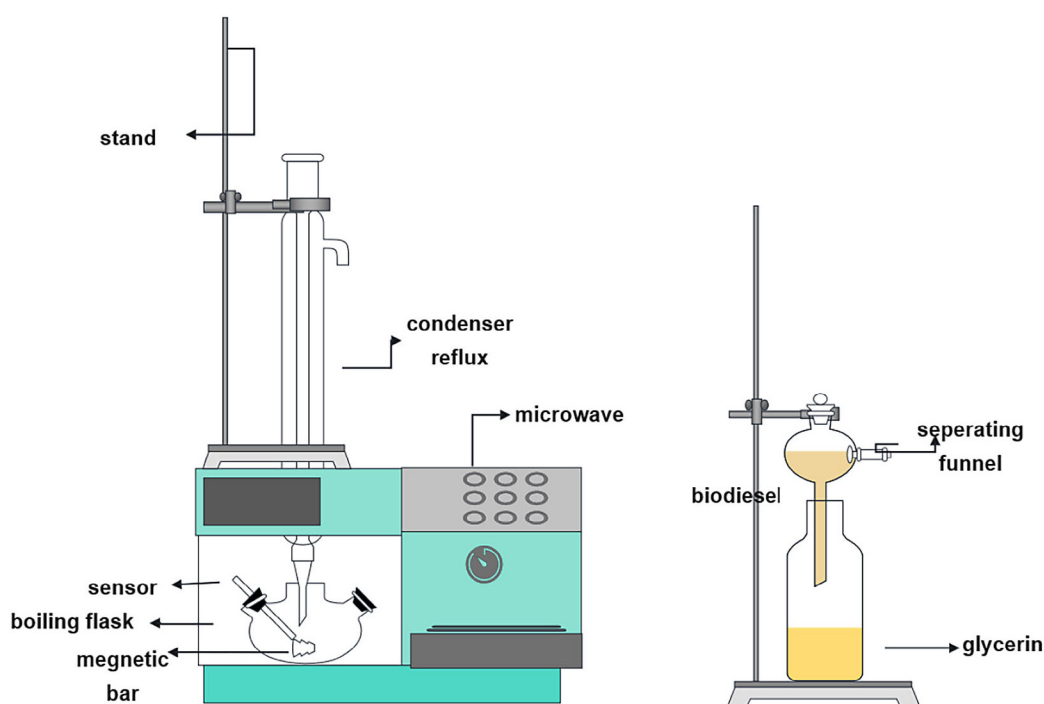


Figure 1. Scheme diagram of laboratory microwave for experimental setup

Where the appropriate reaction orders are denoted by a, b, c, and d, The amounts of waste cooking oil, methanol alcohol, the fatty acid methyl esters, and glycerin are denoted by CA, CB, CC, and CD, respectively, and the reaction rate constants are denoted by k and k^{-} . CB^b is regarded as constant since the methanol concentration is excessively high in relation to the other concentration terms. Additionally, since k is greater than k^{-} , Equation 3 can be simplified to Equation 4.

$$\left(\frac{dCA}{dt}\right) = -kCA^n \quad (4)$$

$$CA = CA_0 (1 - X_A) \quad (5)$$

The terms CA_0 and X_A stand for the initial waste cooking oil concentration and fractional biodiesel yield, respectively. Additionally, Equation 5 can be expressed as Equation 6.

$$-\left(\frac{dx_A}{dt}\right) = \left(\frac{k}{CA_0}\right) = k_1 CA_0 (1 - X_A)^n \quad (6)$$

$$\ln(1 - X_A) = -k_1 t \quad (7)$$

where: $\left(\frac{k}{CA_0}\right) = k_1$, and Equation 6, can be integrated as Equation 7, for $n = 1$.

The Arrhenius equation, as per Equation 8, was utilized to determine the activation energy (E_a) of the reaction by utilizing the rate constants at different temperatures (10–25 °C).

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (8)$$

In this case, T stands for the reactant temperature with A and R represent the pre-exponential factors, which are $8.314 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

To estimate the kinetics, the microwave's temperature was raised at 25-minute intervals from 45 °C to 75 °C.

RESUL AND DISCUSSION

Reaction parameters that effect transesterification of used cooking oil

Methanol to oil ratio

The present investigation examines the impact of the methanol-to-oil weight ratio on biodiesel production was evaluated under fixed operational conditions, which included a catalyst

concentration of 3 wt.%, a microwave power of 10% and at temperature 65 °C, and an exposure time of 20 minutes. The ratio of methanol to oil ranged between 50 wt.% and 80 wt.%, where the results showed in Figure 2a that the biodiesel yield reached 77.54% at a 50 wt.% ratio. With the rise in the ratio of methanol, the yield gradually rose to its maximum value of 96.31% at a 70 wt.% ratio. However, continuing to increase the methanol ratio beyond this point led to a decline in yield, as it dropped to 87.38% to an 80% ratio. This decrease in productivity at high methanol ratios can be explained by several factors, the most notable of which are: the increased solubility of glycerol in the biodiesel, making separation difficult, the formation of foam that hinders the separation process between the components, and the excess amounts of methanol that may deactivate the catalyst's effectiveness and promote the reverse reaction, thereby reducing conversion efficiency. These results are in accordance with prior research, including (Sharma et al., 2019a) and (Erchamo et al., 2021), indicating that the optimal ratio of methanol to oil for generating the greatest quantity of biodiesel production under the specified conditions is 70 wt.%.

The impact of varying the percentage of methanol to oil at various microwave power levels

The influence of ratio of methanol oil on biodiesel yield was examined at two microwave power settings (10%, and 20%) constant temperature 65 °C, with both exposure time 20 minutes and catalyst concentration 3 wt.% kept constant. The study included methanol-to-oil ratios of 50 wt.%, 60 wt.%, 70 wt.%, and 80 wt.%. The results, as shown in Figure 2b, indicated that the highest productivity of 96.31% was achieved at a 70 wt.% ratio of methanol to oil, using a microwave power of 10%. When the power increased to 20%, the maximum productivity decreased to 94.60% at the same ratio (70 wt.%). This decrease is attributed to the rapid higher temperature resulting from the increased energy to reach the reaction temperature, leading to the rapid evaporation of methanol and a reduction in its actual quantity in the reaction system, thereby decreasing productivity (Mahmood and AL-Yaqoobi, 2025).

Irradiation time

The influence of microwave exposure duration on biodiesel production was studied under

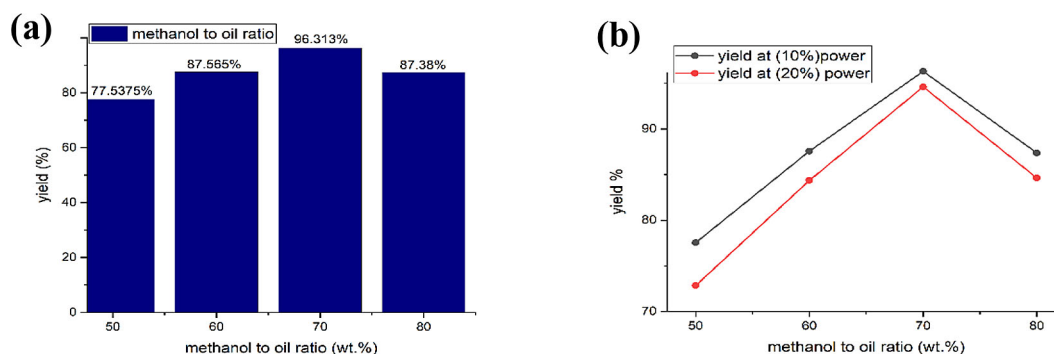


Figure 2. Methanol to oil ratio effect at 10% power 65 °C temperature, time 20 min, and catalyst loading 3 wt.% (a); ratio of methanol to oil effect with various microwave power at temperature 65 °C, time 20 min, and catalyst loading 3 wt.% (b)

constant operating conditions, which are: microwave power at 10%, temperature of reaction 65 °C, The catalyst quantity is set at 3 wt.%, and the methanol/oil ratio is 70 wt.%. The results showed in Figure 3a that the production yield of biodiesel rose from 81.43% after ten minutes of exposure to its highest value of 96.31% after 20 minutes. But after this optimal time, the yield began to gradually decrease, reaching 84.75% at 25 minutes. This is attributed to the reaction reaching equilibrium after approximately 20 minutes, suggesting that because the ester exchange reaction is reversible, the opposite reaction will occur, lowering the yield (Laskar et al., 2020; Rahman et al., 2019). Furthermore, extending the reaction time may result in soap formation due to the hydrolysis of esters by water, reducing the efficiency of biodiesel.

The impact of irradiation period at various microwave power levels

Figure 3b illustrates that the duration needed to get the maximum biodiesel yield fluctuates with microwave power. The maximum yield of 96.31%

was attained at 10% power within 20 minutes of exposure. When the power was increased to 20%, the time required to reach the maximum yield (94.60%) at also 20 minutes. It is clear from this that increasing the microwave power negatively affects the final yield quantity. This is attributed to the significant increase in the temperature of the mixture with the increase in power. This rapid increase in temperature to reach the reaction temperature leads to the accelerated evaporation of methanol and affects the activity of the catalyst.

Catalyst loading

Determining the precise concentration of the catalyst is regarded as a crucial step in the transesterification technique is employed to accelerate the reaction rate. Figure 4a illustrates how the production of biodiesel is affected by varying catalyst concentrations. Fixed parameters of 10% microwave power, temperature 65 °C, 20 minutes of irradiation time, and 40 wt.% methanol to oil ratio were used in this series of tests. The yield rises from 81.25% at a catalyst

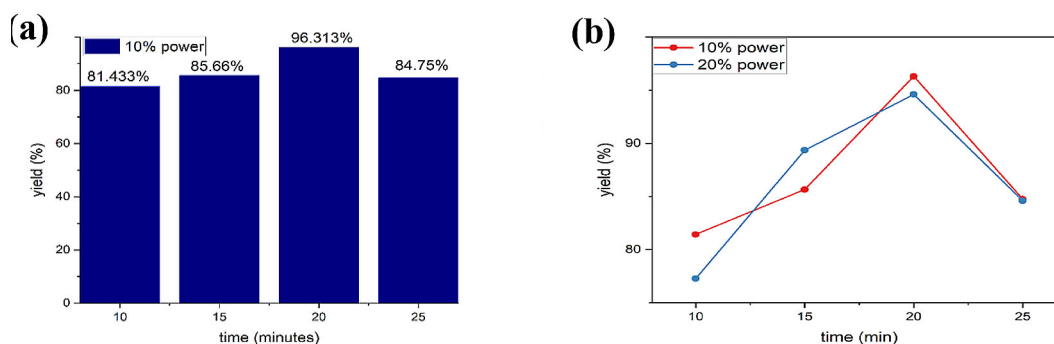


Figure 3. Irradiation time effect at reaction temperature 65 °C, methanol to oil ratio 70 wt.%, 10% power, catalyst loading 3 wt.% (a); irradiation time effect with different microwave power (b)

concentration of 1% to 84.88% at 2% and then reaches its maximum yield of 96.31% at a concentration of 3%, as can be observed. After that, the yield began to decline as the catalyst concentration rose, reaching 89.77% at a catalyst concentration of 4%. The biodiesel output undergoes reduction when the concentration of the catalyst is increased above the ideal level, promoting a saponification reaction (Chen et al., 2012). Furthermore, the utilization of too much base catalyst caused the development of an organic layer, that in turn motivates the free fatty acid to react with the catalyst, resulting in the formation of a gel. Consequently, the amount of biodiesel produced is reduced (Ansori et al., 2019).

Temperature effect

An investigation into the impact of temperature on the production of biodiesel was conducted by means of microwave-assisted catalysis under particular operating conditions. These conditions involve a molar ratio of 70 wt.% of methanol to oil, a catalyst concentration of 3 wt.%, a reaction time of 20 minutes, a constant temperature of 65 °C, and a microwave power of 10%. Results Figure 4b showed that increasing the temperature from low values up to 65 °C led to a gradual increase in biodiesel productivity, with the highest productivity recorded at this temperature. However, exceeding this temperature caused a decline in yield. This observation is accorded to several factors; while some studies indicate that the exteriority and symmetry reaction is an endothermic reaction (Basumatary et al., 2021), other researchers believe it is slightly exothermic (Lawan et al., 2020; Rathore et al., 2015). It is well known that an increase in temperature raises molecular activity, which in turn accelerates the

rate of reaction. However, raising the temperature to approximately 65 °C, that's the boiling temperature of methanol, causes some of the methanol to evaporate, which ultimately results in a decline in the concentration of methanol in the reaction mixture and has a detrimental impact on the equilibrium of the reaction, thereby decreasing the final yield of biodiesel. Additionally, exceeding this temperature may promote the occurrence of triglyceride saponification reactions, which are undesirable reactions that caused soap formation, hindering the separation of the pure product and reducing the overall efficiency of the process (Tang et al., 2018).

The physical characteristics of biodiesel

The fundamental physical features of the generated biodiesel were examined by the (batch process) microwave-assisted transesterification reaction, with the findings summarized and contrasted against the ASTM D6751-09 standard and EN 14214, as presented in Table 1. The findings indicated that density, viscosity, and flash points conform to allowed norms, demonstrating the appropriateness of this biodiesel for application in diesel engines. At 40 °C, kinematic viscosity was found to be 5.47 mm² s⁻¹, aligning with the ASTM standards for biodiesel. The result obtained aligned with the value of 5 mm²/s published by (Mahmood and AL-Yaqoobi, 2025) in prior investigations concerning biodiesel created from waste cooking oil. The created biodiesel was calculated to possess a flash point of 90 °C, comparable to diesel, thus ensuring safe handling. Previous investigations have indicated this flash point, with (Degfie et al., 2019) documenting a flash point of 96 °C. At 15 °C, the measured density was found

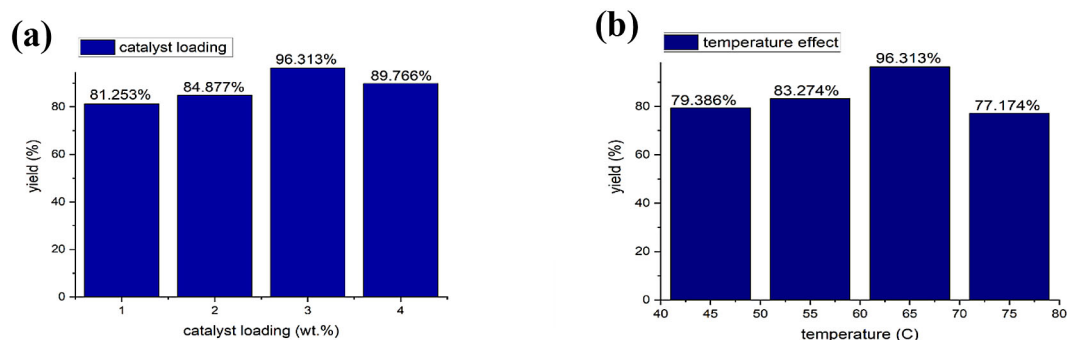


Figure 4. Catalyst loading effect at power 10%, methanol to oil ratio 70 wt.%, temperature 65 °C, and time 20 min (a); temperature effect at methanol to oil ratio 70 wt.%, 10% power, catalyst loading 3 wt.%, and 20 min (b)

0.9005 g cm⁻³, falling within EN 14214 standard range for biodiesel shown in Table 1.

Kinetics and energy activation of the transesterification process

The kinetics of the transesterification process were analyzed to evaluate the effect of different temperatures at a different reaction time. The experiments were conducted under ideal operating conditions, where the reaction was tested at temperatures of 45, 55, 65, and 75 °C and time at 10, 15, 20, 25 minutes. The graphs in Figure 5a showed a linear correlation between time and $-\ln(1-X)$, indicating that the reaction conforms to pseudo-first-order kinetic models, based on Equation 7. The energy of activation (E_a) was calculated using the rate constants extracted from the experimental data and the Arrhenius equation (Eq. 8). From the graph shown in Figure 5b) which relates $\ln(k)$ and $1/T$, the value of E_a was determined using the line's slope ($-E_a/R$), while the pre-exponential factor (A) was determined from the intercept on the $\ln(k)$ axis. The activation energy was 24.22 kJ/mol, which falls within the typical range for transesterification reactions (24.7–84.1 kJ/mol). This value was compared with the results of previous studies that used heterogeneous catalysts and different raw materials as shown in Table 2. For example, (Mazubert et al., 2014) recorded a low activation energy (9.7 kJ/mol) when using used cooking oil in a microwave heating method, while Gupta and Rathod (Gupta and Rathod, 2018) reported an energy of 26.56 kJ/mol using the same oil and a solid catalyst. The values in additional studies, for example Pavlovic et al. (2020) recorded relatively high activation energies of 67 and 58 kJ/mol. As for (Mahmood and Al-Yaqoobi, 2024, and (Amesho et al., 2022) they recorded the same activation energy (38 kJ/mol) using the traditional heating method and microwave heating. These differences in activation energy values indicate the significant impact of the type of catalyst, the nature of the feedstock, and the heating method used on the reaction kinetics. The value

calculated in this study falls within the medium range, reflecting a good balance between energy requirements and reaction efficiency, which highlights the effectiveness of the system used in biodiesel production through the transesterification reaction.

A comparative investigation of the catalyst produced

The outcome indicated that the catalyst prepared in this study achieved high performance, with a biodiesel production rate of 96.31% over 20 minutes of reaction, under ideal condition including a 70 wt.% methanol to oil ratio, 3 wt.% concentration of catalyst, and temperature of reaction of 65 °C. To compare these results with prior research employing CaO heterogeneous catalysts noted in Table 3. Research carried by Hsiao et al. (2020), used heterogeneous solid base catalysts CaO to produce biodiesel derived from used frying oil, but they required a long time to produce (60 min) to achieve 98.2% yield. Although Mahmood and Al-Yaqoobi (2025) achieved 96% yield in 15 min with using the same feedstock but the reaction required high temperature. In other studies, conducted by Ye et al. (2016), Amesho et al. (2022) and Hsiao et al. (2011), used different feed stock and almost the same catalyst concentration (4 wt.% and 5 wt.%) with longer reaction times (60 hours), likely due to the lower surface area of the catalysts used. In contrast, Khemthong et al. (2012), Hindarso et al. (2015) and Sharma et al. (2019b), indicated that heterogeneous CaO catalysts exhibited high catalytic efficiency, with a low catalyst concentration. But it required a high power to achieve the reaction temperature. In the current study, the catalyst derived from fallen willow leaves (FWL) has demonstrated high catalytic efficiency, as confirmed by the EDS analysis, which showed a high content of calcium, a primary CaO source. Calcium oxide is known for its effectiveness as a heterogeneous catalyst and is widely used in various industrial applications, especially in the manufacturing of biodiesel (Foroutan et al., 2021; Teo et al., 2017).

Table 1. Physical characteristics of biodiesel

Physical properties	Biodiesel of waste cooking oil	ASTM D 6751	EN 14214
Density (mm ² /s)	5.472	1.9–6	3.5–5
Viscosity (mm ² /s)	0.9005	0.87–0.89	0.86–0.90
Flash point (°C)	90	130 minimum	>101

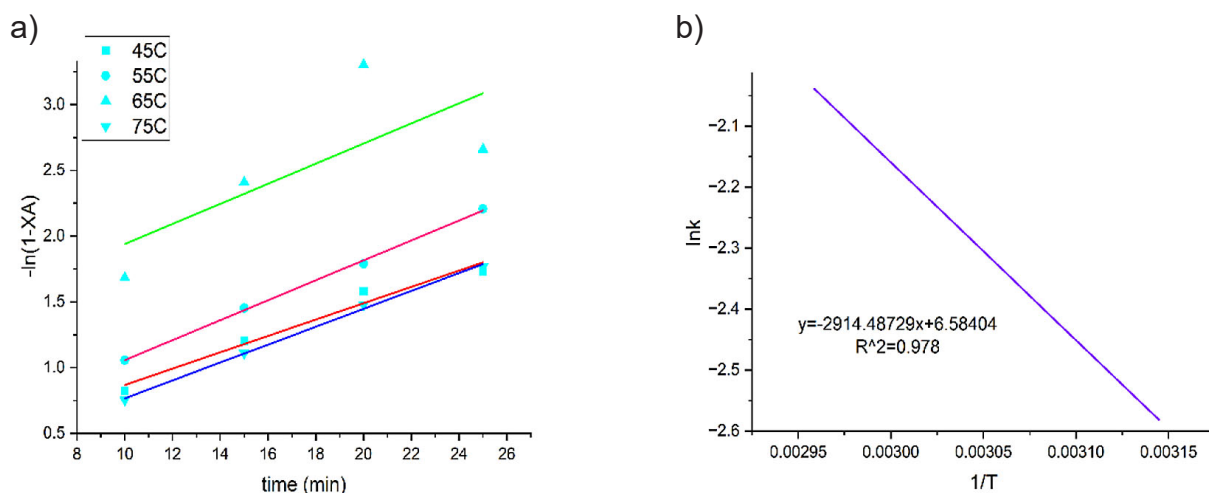


Figure 5. (a) $-\ln(1-x_A)$ versus time at four reaction temperature for the transesterification, (b) $\ln k$ versus $1/T$ of Arrhenius plot

Table 2. Activation energy comparative between different studies

Raw material	Method of heating	Catalyst	Energy activation (kJ/mole)	References
Waste cooking oil	Microwave	–	9.7	(Mazubert et al., 2014)
Waste cooking oil	Microwave	Diglycerides of calcium (CaDG)	26.56	(Gupta and Rathod, 2018)
Waste cooking oil	Conventional	Calcium oxide prepares from fallen mango leaves	38	(Mahmood and Al-Yaqobi, 2024)
Sunflower oil	Rotating miniature autoclave reactor system	CaO/zeolite-based catalyst made from coal fly ash and leftover chicken eggshell	67.17 and 58.03	(Pavlović et al., 2020)
Jatropha curcas oil	Microwave	Eggshell-derived CaO catalyst	38.5	(Amesho et al., 2022)
Waste cooking oil	Microwave	CaO catalyst prepared from fallen willow leaves	24.226	Current study

Table 3. Comparative different studies of product CaO catalyst

Feedstock	Methanol to oil ratio	Reaction time (min)	Temperature (°C)	Catalyst	Power (W)	Yield (%)	References
Palm oil	1:9	60	65	CaO (5 wt.%)	150	89.9	(Ye et al., 2016)
Waste cooking oil	1:8	75	65	CaO (4 wt.%)	–	98.2	(Hsiao et al., 2020)
Jatropha curcas oil	1:9	180	65	CaO (5 wt.%)	800	91.1	(Amesho, Lin, Chen, Cheng, & Shangdiar, 2022)
Soybean oil	1:7	60	65	CaO (3%)	300	96.6	(Hsiao et al., 2011)
Palm oilien oil	1:18	4	60	CaO (15 wt.%)	900	96.7	(Khemthong et al., 2012)
Waste cooking oil	40 wt.%	15	–	CaO (3 wt.%)	80	96	(Mahmood & AL-Yaqobi, 2025)
Microalgae Nannochloropsis	1:6	3	60	CaO (3 wt.%)	–	96.46	(Hindarso et al., 2015)
Waste cotton-seed cooking oil	1:9.6	9.7	50 °C	CaO (1.33 wt.%)	180	89.94	(Sharma et al., 2019b)
Waste cooking oil	70 wt.%	20	65	CaO (3 wt.%)	80	96.313	Current study

CONCLUSIONS

In this research, a sustainable solid-based heterogeneous catalyst that is derived from biowaste (fallen willow leaves) was developed to produce biodiesel. The prepared catalyst demonstrated high catalytic efficiency. Results of this investigation emphasize the potential of the developed catalyst in industrial biodiesel production processes using inedible oils as feedstock and biowaste as a catalyst source, within microwave-based heating systems. The impacts of microwave power, time of reaction, and methanol/oil ratio on the production yield were assessed. The finding indicated that the use of microwave significantly improved the reaction efficiency, reducing the reaction time required for the ester exchange process compared to conventional heating, with yields reaching 96.31% at 10% power at 65 °C and a reaction time of 20 minutes. Therefore, this study not only contributes academically, but also provides a practical model for sustainable biofuel production technologies and represents an advanced step towards effective and economical biowaste management strategies.

REFERENCES

1. Abd, M. F., AL-yaqoobi, A. M. (2025). The potential significance of microwave-assisted catalytic pyrolysis for valuable bio-products driven from Albizia tree. *Applied Science and Engineering Progress*, 18(1), 7454.
2. Abd, M. F., Al-yaqoobi, A. M., Abdul-Majeed, W. S. (2024). Catalytic microwave pyrolysis of albizia branches using Iraqi bentonite clays. *Iraqi Journal of Chemical and Petroleum Engineering*, 25(2), 175–186.
3. Aljendeel, H., Borhan, E., Al-Ani, M. J. (2022). Kinetic study of transesterification reaction of edible oil using heterogeneous catalyst. *Iraqi Journal of Chemical and Petroleum Engineering*, 23(3), 11–16. <https://doi.org/10.31699/ijcpe.2022.3.2>
4. Almadani, E. A., Abdelghani, K. A., Omar, F. A. (2023). Calcium oxide as an efficient heterogeneous catalyst for production of biodiesel. *The Scientific Journal of University of Benghazi*, 36(2). <https://doi.org/10.37376/sjuob.v36i2.4303>
5. Amesho, K. T. T., Lin, Y. C., Chen, C. E., Cheng, P. C., Ponnusamy, V. K. (2022). Optimization and kinetics studies of biodiesel synthesis from *Jatropha curcas* oil under the application of eco-friendly microwave heating technique: an environmentally benign and sustainable bio-waste management approach. *Sustainable Environment Research*, 32(1). <https://doi.org/10.1186/s42834-022-00151-w>
6. Amesho, K. T. T., Lin, Y.-C., Chen, C.-E., Cheng, P.-C., Shangdiar, S. (2022). Kinetics studies of sustainable biodiesel synthesis from *Jatropha curcas* oil by exploiting bio-waste derived CaO-based heterogeneous catalyst via microwave heating system as a green chemistry technique. *Fuel*, 323, 123876.
7. Ansori, A., Wibowo, S. A., Kusuma, H. S., Bhuana, D. S., Mahfud, M. (2019). Production of biodiesel from nyamplung (*Calophyllum inophyllum* L.) using microwave with CaO catalyst from eggshell waste: optimization of transesterification process parameters. *Open Chemistry*, 17(1), 1185–1197.
8. Banković-Ilić, I. B., Stamenković, O. S., Veljković, V. B. (2012). Biodiesel production from non-edible plant oils. *Renewable and Sustainable Energy Reviews*, 16(6), 3621–3647.
9. Bashir, M. A., Wu, S., Zhu, J., Krosuri, A., Khan, M. U., Aka, R. J. N. (2022). Recent development of advanced processing technologies for biodiesel production: A critical review. *Fuel Processing Technology*, 227, 107120.
10. Basumatary, S., Nath, B., Das, B., Kalita, P., Basumatary, B. (2021). Utilization of renewable and sustainable basic heterogeneous catalyst from *Heteropanax fragrans* (Kessuru) for effective synthesis of biodiesel from *Jatropha curcas* oil. *Fuel*, 286, 119357.
11. Carlucci, C. (2022). An overview on the production of biodiesel enabled by continuous flow methodologies. In *Catalysts* 12(7). MDPI. <https://doi.org/10.3390/catal12070717>
12. Chen, K.-S., Lin, Y.-C., Hsu, K.-H., Wang, H.-K. (2012). Improving biodiesel yields from waste cooking oil by using sodium methoxide and a microwave heating system. *Energy*, 38(1), 151–156.
13. Colombo, K., Ender, L., Barros, A. A. C. (2017). The study of biodiesel production using CaO as a heterogeneous catalytic reaction. In *Egyptian Journal of Petroleum* 26(2), 341–349. Egyptian Petroleum Research Institute. <https://doi.org/10.1016/j.ejpe.2016.05.006>
14. Degfie, T. A., Mamo, T. T., Mekonnen, Y. S. (2019). Optimized biodiesel production from waste cooking oil (WCO) using calcium oxide (CaO) nanocatalyst. *Scientific Reports*, 9(1), 18982.
15. Erchamo, Y. S., Mamo, T. T., Workneh, G. A., Mekonnen, Y. S. (2021). Improved biodiesel production from waste cooking oil with mixed methanol–ethanol using enhanced eggshell-derived CaO nanocatalyst. *Scientific Reports*, 11(1), 6708.
16. Foroutan, R., Mohammadi, R., Razeghi, J., Ramavandi, B. (2021). Biodiesel production from edible oils using algal biochar/CaO/K₂CO₃ as a

- heterogeneous and recyclable catalyst. *Renewable Energy*, 168, 1207–1216.
17. Gnanaswar Gude, V., Patil, P., Martinez-Guerra, E., Deng, S., Nirmalakhandan, N. (2013). *Micro-wave energy potential for biodiesel production*. <http://www.sustainablechemicalprocesses.com/content/1/5/5>
 18. Groisman, Y., Gedanken, A. (2008). Continuous flow, circulating microwave system and its application in nanoparticle fabrication and biodiesel synthesis. *Journal of Physical Chemistry C*, 112(24), 8802–8808. <https://doi.org/10.1021/jp801409t>
 19. Gupta, A. R., Rathod, V. K. (2018). Waste cooking oil and waste chicken eggshells derived solid base catalyst for the biodiesel production: Optimization and kinetics. *Waste Management*, 79, 169–178.
 20. Hindarso, H., Ayliaawati, A., Sianto, M. E. (2015). Biodiesel production from the microalgae nanochloropsis by microwave using CaO and MgO catalysts. *International Journal of Renewable Energy Development*, 4(1), 72.
 21. Hsiao, M.-C., Kuo, J.-Y., Hsieh, S.-A., Hsieh, P.-H., Hou, S.-S. (2020). Optimized conversion of waste cooking oil to biodiesel using modified calcium oxide as catalyst via a microwave heating system. *Fuel*, 266, 117114.
 22. Hsiao, M.-C., Lin, C.-C., Chang, Y.-H. (2011). Microwave irradiation-assisted transesterification of soybean oil to biodiesel catalyzed by nanopowder calcium oxide. *Fuel*, 90(5), 1963–1967.
 23. Hussain, H. K., Kareem, A., Jendeel, A., Naife, T. M., Abdul, H., Al, K., Tariq, J., Naife, M. (2011). Production of Biodiesel Fuel from Used vegetable Oil. In *Journal of Engineering* (Vol. 17).
 24. Iyyaswami, R., Halladi, V. K., Yarramreddy, S. R., Malur Bharathaiyengar, S. (2013). Microwave-assisted batch and continuous transesterification of karanja oil: Process variables optimization and effectiveness of irradiation: Microwave-assisted transesterification of karanja oil. *Biomass Conversion and Biorefinery*, 3(4), 305–317. <https://doi.org/10.1007/s13399-013-0080-8>
 25. Jachuck, R., Pherwani, G., Gorton, S. M. (2009). Green engineering: Continuous production of biodiesel using an alkaline catalyst in an intensified narrow channel reactor. *Journal of Environmental Monitoring*, 11(3), 642–647. <https://doi.org/10.1039/b807390m>
 26. Jongsomjit, B., Phisalaphong, M., Watcharathamrongkul, K. (2010). Calcium oxide based catalysts for ethanolysis of soybean oil. In *Article in Songklanakarin Journal of Science and Technology* 32(6). <https://www.researchgate.net/publication/279580036>
 27. Khemthong, P., Luadthong, C., Nualpaeng, W., Changsuwan, P., Tongprem, P., Viriya-Empikul, N., Faungnawakij, K. (2012). Industrial eggshell wastes as the heterogeneous catalysts for microwave-assisted biodiesel production. *Catalysis Today*, 190(1), 112–116.
 28. Kouzu, M., Hidaka, J. S. (2012). Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review. In *Fuel* 93, 1–12. <https://doi.org/10.1016/j.fuel.2011.09.015>
 29. Laskar, I. B., Gupta, R., Chatterjee, S., Vanlalveni, C., Rokhum, S. L. (2020). Taming waste: Waste Mangifera indica peel as a sustainable catalyst for biodiesel production at room temperature. *Renewable Energy*, 161, 207–220.
 30. Lawan, I., Garba, Z. N., Zhou, W., Zhang, M., Yuan, Z. (2020). Synergies between the microwave reactor and CaO/zeolite catalyst in waste lard biodiesel production. *Renewable Energy*, 145, 2550–2560.
 31. Linggawati, A. (2016). Preparation and Characterization of Calcium Oxide Heterogeneous Catalyst Derived from Anadara Granosa Shell for Biodiesel Synthesis. *KnE Engineering*, 1. <https://doi.org/10.18502/keg.v1i1.494>
 32. Mahmood, S. S., Al-Yaqoobi, A. M. (2024). Production of biodiesel by using CaO nano-catalyst synthesis from mango leaves extraction. *International Journal of Renewable Energy Development*, 13(6), 1025–1034. <https://doi.org/10.61435/ijred.2024.60469>
 33. Mahmood, S. S., AL-Yaqoobi, A. M. (2025). Microwave-assisted production of biodiesel using CaO nano-catalyst produced from mango fallen leaves extract. *Journal of Ecological Engineering*, 26(1), 248–259. <https://doi.org/10.12911/22998993/195650>
 34. Marinković, D. M., Stanković, M. V., Veličković, A. V., Avramović, J. M., Miladinović, M. R., Stamenković, O. O., Veljković, V. B., Jovanović, D. M. (2016). Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives. In *Renewable and Sustainable Energy Reviews* 56, 1387–1408. Elsevier Ltd. <https://doi.org/10.1016/j.rser.2015.12.007>
 35. Mazubert, A., Taylor, C., Aubin, J., Poux, M. (2014). Key role of temperature monitoring in interpretation of microwave effect on transesterification and esterification reactions for biodiesel production. *Bioresource Technology*, 161, 270–279.
 36. Meng, X., Chen, G., Wang, Y. (2008). Biodiesel production from waste cooking oil via alkali catalyst and its engine test. *Fuel Processing Technology*, 89(9), 851–857.
 37. Mohammed, W. T., Jabbar, M. F. A. (2015). Esterification of free fatty acid with high chain alcohol for biodiesel production using semi-batch reactive distillation. *Iraqi Journal of Chemical and Petroleum Engineering*, 16(4), 11–19.
 38. Muley, P. D., Boldor, D. (2018). *Process*

- intensification and parametric optimization in biodiesel synthesis using microwave reactors.*
39. Ong, M. Y., Nomanbhay, S. (2018a). Design and modeling of an enhanced microwave reactor for biodiesel production. *International Journal of Scientific and Research Publications (IJSRP)*, 8(12). <https://doi.org/10.29322/ijssrp.8.12.2018.p8465>
40. Ong, M. Y., Nomanbhay, S. (2018b). Design and modeling of an enhanced microwave reactor for biodiesel production. *International Journal of Scientific and Research Publications (IJSRP)*, 8(12). <https://doi.org/10.29322/ijssrp.8.12.2018.p8465>
41. Pavlović, S. M., Marinković, D. M., Kostić, M. D., Janković-Častvan, I. M., Mojović, L. V., Stanković, M. V., Veljković, V. B. (2020). A CaO/zeolite-based catalyst obtained from waste chicken eggshell and coal fly ash for biodiesel production. *Fuel*, 267, 117171.
42. Phan, A. N., Phan, T. M. (2008). Biodiesel production from waste cooking oils. *Fuel*, 87(17–18), 3490–3496.
43. Rahman, W. U., Fatima, A., Anwer, A. H., Athar, M., Khan, M. Z., Khan, N. A., Halder, G. (2019). Biodiesel synthesis from eucalyptus oil by utilizing waste egg shell derived calcium based metal oxide catalyst. *Process Safety and Environmental Protection*, 122, 313–319.
44. Rathore, V., Tyagi, S., Newalkar, B., Badoni, R. P. (2015). Jatropha and Karanja oil derived DMC–biodiesel synthesis: A kinetics study. *Fuel*, 140, 597–608.
45. Rozina, Emmanuel, O., Ahmad, M., Waseem, A., Ahuchao, A. A. (2024). Repurposing *Citrus paradisi* L. waste seed oil in the renewable production of biodiesel using phytosynthesized lead oxide nanoparticles. *Waste Management Bulletin*, 2(2), 335–348. <https://doi.org/10.1016/j.wmb.2024.05.012>
46. Sahu, S., Saikia, K., Gurunathan, B., Dhakshinamoorthy, A., Rokhum, S. L. (2023). Green synthesis of CaO nanocatalyst using watermelon peels for biodiesel production. *Molecular Catalysis*, 547. <https://doi.org/10.1016/j.mcat.2023.113342>
47. Sharma, A., Kodgire, P., Kachhwaha, S. S. (2019a). Biodiesel production from waste cotton-seed cooking oil using microwave-assisted transesterification: Optimization and kinetic modeling. *Renewable and Sustainable Energy Reviews*, 116, 109394.
48. Sharma, A., Kodgire, P., Kachhwaha, S. S. (2019b). Biodiesel production from waste cotton-seed cooking oil using microwave-assisted transesterification: Optimization and kinetic modeling. *Renewable and Sustainable Energy Reviews*, 116, 109394.
49. Subramaniam, K., Wong, K. Y., Wong, K. H., Chong, C. T., Ng, J. H. (2024a). Enhancing biodiesel production: a review of microchannel reactor technologies. In *Energies* 17(7). Multidisciplinary Digital Publishing Institute (MDPI). <https://doi.org/10.3390/en17071652>
50. Subramaniam, K., Wong, K. Y., Wong, K. H., Chong, C. T., Ng, J. H. (2024b). Enhancing biodiesel production: a review of microchannel reactor technologies. In *Energies* 17(7). Multidisciplinary Digital Publishing Institute (MDPI). <https://doi.org/10.3390/en17071652>
51. Tang, Z.-E., Lim, S., Pang, Y.-L., Ong, H.-C., Lee, K.-T. (2018). Synthesis of biomass as heterogeneous catalyst for application in biodiesel production: State of the art and fundamental review. *Renewable and Sustainable Energy Reviews*, 92, 235–253.
52. Teo, S. H., Islam, A., Masoumi, H. R. F., Taufiq-Yap, Y. H., Janaun, J., Chan, E.-S. (2017). Effective synthesis of biodiesel from Jatropha curcas oil using betaine assisted nanoparticle heterogeneous catalyst from eggshell of Gallus domesticus. *Renewable Energy*, 111, 892–905.
53. Tippayawong, N., Sittisun, P. (2012). Continuous-flow transesterification of crude jatropha oil with microwave irradiation. *Scientia Iranica*, 19(5), 1324–1328. <https://doi.org/10.1016/j.scient.2012.08.004>
54. Tran, D. T., Chang, J. S., Lee, D. J. (2017). Recent insights into continuous-flow biodiesel production via catalytic and non-catalytic transesterification processes. In *Applied Energy* 185, 376–409. Elsevier Ltd. <https://doi.org/10.1016/j.apenergy.2016.11.006>
55. Varma, R. S. (2001). Solvent-free accelerated organic syntheses using microwaves. *Pure and Applied Chemistry*, 73(1), 193–198.
56. Win, T. T., Khine, M. M. (2017). Synthesis and characterization of CaO and KF Doped CaO (KF/CaO) derived from chicken eggshell waste as heterogeneous catalyst in biodiesel production. *Technology, and Sciences (ASRJETS) American Scientific Research Journal for Engineering*, 38(2), 134–151. <http://asrjetsjournal.org/>
57. Ye, W., Gao, Y., Ding, H., Liu, M., Liu, S., Han, X., Qi, J. (2016). Kinetics of transesterification of palm oil under conventional heating and microwave irradiation, using CaO as heterogeneous catalyst. *Fuel*, 180, 574–579.
58. Yunsari, S., Rusdianasari, Husaini, A. (2019). CPO based biodiesel production using microwaves assisted method. *Journal of Physics: Conference Series*, 1167(1). <https://doi.org/10.1088/1742-6596/1167/1/012036>