Microwave assisted continuous flow transesterification of waste cooking oil for biodiesel production

Abstract

Biodiesel is a major renewable energy source derived from vegetable oils. Modern techniques are now required to produce biofuels, particularly biodiesel, to improve the process's efficiency and sustainability due to technological advancements. This study focuses on continuous biodiesel production from waste cooking oil through transesterification in a flow process with microwave heating. Calcium oxide prepared from willow leaves extract was used as a catalyst at concentrations ranging from 1% to 4%, with a microwave power of 20% from a total 800W and an irradiation time of 0.5-7 min. The oil-to-methanol ratio was 50wt.%-80wt.% and reaction temperature of 45-75℃. The results reviled that the waste cooking oil can be converted to biodiesel with a yield of (93.43%) in 5 min. with a 70wt.% oil/methanol molar ratio and 3wt.% catalyst. Also, the results indicated that the production of high-quality biodiesel, which followed ASTM standard specifications, was facilitated by all operational conditions. The results suggest that microwave heating is a viable approach for achieving high yields of biodiesel with shorter reaction times, even in continuous reactions. This is attributed to reduced energy activation. This method is promising for industrial use in the production of high-quality biodiesel, with methanol as the preferred alcohol.

Keyword: biodiesel, continuous, microwave, CaO nano catalyst, willow leaves extraction, waste cooking oil.

1.Introduction

Environmental and economic issues have drawn increased attention to renewable energy in recent years The global economy has been significantly impacted by the substantial Fossil fuel depletion and rising pricing[1]. Many nations have developed alternative energy sources like wind, water, and biomass that can be converted into biofuel to lower their fuel usage, which is projected to increase by approximately 60% over the period of 25 years [2,3].

The issue of finding other sources of energy to supplant diesel fuel is a critical concern in the quest for sustainability. The oils of vegetables and fats from animals serve as significant raw materials for fuel alternatives in diesel engines [4]. Short-term engine tests have shown the possibility of using them directly without significant modifications. However, long-term use has faced many challenges, the most notable being the high viscosity and the presence of impurities in these biofuels, which lead to engine performance degradation, increased harmful emissions, and reduced engine lifespan[5].

The transesterification process was used to solve the technical issue of high viscosity in vegetable oils. This procedure depends on the reaction of one form of alcohol, typically methanol or ethanol with triglycerides, the primary constituent of vegetable oils, in the presence of a chemical catalyst. Triglycerides progressively change into diglycerides, monoglycerides, and glycerol during these reactions. The main product used as biodiesel, fatty acid ester, is produced at each stage[6].

Biodiesel extracted from renewable and biodegradable sources is an effective option for reducing carbon and sulfur oxide emissions, contributing to improved combustion efficiency[7] . Biodiesel receives a lot of attention since it is different from petroleum diesel in that it is non-toxic, breaks down quickly, has a higher cetane number, and has a higher flash point. [8,9].

In general, biodiesel is a mono-alkyl ester of long chain fatty acids[10], so it is called fatty acid methyl ester (FAME). Typically, Biodiesel is derived from oils obtained from algae,

animal fats, fungi, vegetable oils, or alternative sources such used cooking oil[11]. The expense of raw ingredients utilized in biodiesel production accounts for more than 70% of the whole expenditure [12,13]. Utilizing waste oils and fats in homes and restaurants lowers the cost of producing biodiesel while simultaneously solving the problem of trash disposal because oil is essential raw material used [14].

Depending on the chemicals involved, transesterification reactions can employ either homogenous (acid, base) or heterogeneous (acid, base) catalysts. Heterogeneous catalysts are typically solid and, in a phase, different from the reaction mixture, whereas homogenous catalysts are liquids in the reaction phase. The drawbacks of homogenous catalysts include their inability to separate from the product, their inability to create a stable emulsion, and the production of copious amounts of wastewater. Apart from that, the heterogeneous catalysts are safe for the environment because they are made using green synthesis and don't corrode. Their main benefit is that they are cheap and can be reused [15,16].

Acidic catalysts are appropriate for the reaction catalytic process if the FFA ratio in the oil and water is high; however, this process necessitates a long time of reaction, a high concentration of catalyst, and a high alcohol/oil ratio. Because the catalyst is acidic, it causes corrosion in the equipment [17]. To address these issues, basic heterogeneous catalysts will be used because they are inexpensive, simple to separate from the product, and extremely effective [18].Oxides, including calcium oxide, constitute a heterogeneous catalyst that is widely employed in the synthesis of biodiesel because of their unique properties, such as low cost, moderate reaction conditions, and short reaction time due to their high effectiveness [19].

A catalyst is also required for the transesterification process to lower the energy activation and drive the reaction [20]. So, using fallen willow leaves, which are considered waste, decreases the total expense associated with producing biodiesel.

Microwaves are a form of electromagnetic radiation, with frequencies ranging between infrared and radio waves, specifically between 0.3 and 300 gigahertz, and a wavelength range of 0.01 to 1 meter. To avoid interference with communication and mobile phone frequencies, The standard frequency for most home microwave ovens is 2.45 gigahertz. In industrial applications, common frequencies used are 915 and 2450 megahertz. In laboratories and chemical experiments, microwave devices are often used at a frequency of 2450 megahertz and a wavelength of 12.24 centimeters[21,22].

The energy of microwave is used in a variety of applications because it speeds up chemical reactions by utilizing polar molecules[23]. Heating in the microwave is fast and homogeneous because microwaves transfer heat via wave absorption, so the temperature of the sample is higher than the surface of the reactor, so the heat transfer process in the microwave does not occur through the surface [2,24]. Unlike traditional methods, Heat moves from the exterior of the container to the items inside. via thermal conduction (convention). This method will result in a significant loss of energy because the rise in temperature will cause Heat moves from the sample's outside to its inside, and the heating will be inhomogeneous due to thermal conductivity, specific heat, and density[25]. Microwave radiation offers many benefits over traditional methods in the manufacture of biodiesel , including reduced reaction time (fast reactions) due to radiation energy, clean energy that does not produce waste, greater efficiency than traditional methods, which provides the best way to manufacture biodiesel, safety, and a better way to separate products[26].

For producing biodiesel using the method of batch transesterification, you need a big reactor and a large methanol /oil ratio. In addition, the process must be water-free and excess glycerin and catalyst must be removed from process[27]. Therefore, a system has been developed that

can address these problems using continuous reactor technology. This system has proven to be efficient and effective. The continuous flow reactor has many advantages, including reducing the methanol-to-oil ratio, reducing reaction time, and giving high biodiesel yields[28,29]. The most important advantage of this system is that it is able to process large quantities of reactants and at the same time withdraw samples from the system without the need to stop the process. In addition, it mixes the materials as a result of its flow through the tubes, and it cost is low due to the small reactor size[30]. The continuous flow system also operates under stable conditions in terms of giving stable products, the methyl esters concentration is also stable[31]. The main purpose of using the continuous flow system instead of the batch system in industry is safety. Because in a relatively large reactor inside the microwave under pressure can cause many problems that lead to a malfunction in the reactor and can cause disaster. Therefore, to avoid these problems, continuous flow reactors are used inside the microwave because they are relatively safe and can be used with many reagents [30].

The examination of the transesterification reaction's kinetics is crucial for establishing optimal conditions to enhance biofuel (biodiesel) production. Kinetic models offer precise insights into reaction behavior by considering mass and heat transfer effects, along with thermodynamic equilibrium, hence enhancing process efficiency and improving outcome predictions [32].

This research aimed to study the feasibility of using a continuous microwave transesterification of waste cooking oil to enhance the production of biodiesel. Also, the study highlights the impact of catalyst concentration, reaction time in microwave irradiation, reaction temperature and oil-to-methanol molar ratio on the production yield and determining best conditions for biodiesel yields. Finally, the kinetic of reaction and determine the activation of energy were also investigated.

2. Material and method

2.1 Material

The experiments made use of a wide variety of pure chemicals, such as sodium hydroxide, calcium nitrate tetrahydrate from India, Thomas Baker and phenolphthalein reagent from BDH Chenicals Ltd. in England were utilized for analysis, Thomas Baker and nearly one hundred percent pure methanol with a purity of 99.8 percent, which originated from Chem-lab NV in Belgium. Additionally, ethanol was purchased from RCI Labscan with a minimal analysis of 99.9 percent. Additionally, high-purity deionized water and. The cooking oil that was utilized came from places of business in the neighborhood.

2.2 pretreatment of used cooking oil

To eliminate any impurities and food particles, the waste cooking oil is filtered through a strainer. The titration of the oil with 0.1N KOH was used to measure the free fatty acid content (FFA). The oil was mixed with 50ml of ethanol alcohol and a few drops of phenolphthalein indicator. The oil weighed 4g. The FFA% in the oil was determined to be 2.4%, and the mixture was titrated with 0.1N KOH until it reached a pink color. The water content was determined by placing a 20 g sample of oil in an oven at 110℃ for 2 hours. The water content was determined to be 0.051% by measuring weight losses.

2.3 CaO nano-catalyst preparation and characterization

After being cleaned and washed, the willow leaves were dried for six hours at 100 °C. After that, they were ground into a fine powder by crushing them. The powdered leaves were boiled for 30 minutes at 60 °C in deionized water. To get an aqueous extraction, it is then filtered and

exposed to cold temperatures. After heating the aqueous extract to 55 °C, calcium nitrate tetrahydrate and NaOH were added The formation of a yellow paste indicated the completion of the reaction, and the process was then stopped. A CaO nano catalyst was created by calcining the catalyst at 600°C in a muffle furnace for two hours. Initially, the extract was analyzed using FT-IR and EDX techniques to identify its active components. FT-IR results revealed distinct absorption peaks indicating the presence of calcium-containing compounds, while EDX results of the extract showed a high percentage of elemental calcium (10%), indicating that the raw material is rich in calcium and capable of being converted into efficient calcium oxide (CaO). Next, a CaO nano catalyst was produced using the preparation method described in the literature. The catalyst was analyzed using XRF, which revealed that the calcium oxide content in the sample was 82.542%, indicating a high degree of purity. The catalyst was characterized using BET, FT-IR, and SEM-EDX techniques. EDX results of the CaO catalyst revealed that calcium constituted 49.31% and oxygen 45.08%, the expected proportions for calcium oxide formation. BET analysis also showed that the catalyst had a specific surface area of 12.097m^2/g and a pore volume of 0.023711 cm^3/g, with an average pore diameter ranging from 2–10 nm. The crystal structure was confirmed using XRD analysis.

2.4 Transesterification reaction in continuous reactor

Experiments were carried out continuously in laboratory microwave of type WB20230745, manufactured by Gongyi Yuhua Instrument Co., Ltd., with a power output ranged from 80 to 800 Watt. Figure 1 illustrates the scheme diagram of the experimental setup. In this study, a three-neck glass flask was used as the source for preparing the reaction mixture. A mixture of used oil, methanol, and catalyst was placed inside the flask. A condenser was installed on one neck to prevent the methanol from evaporating and returning it to the system. A thermometer was installed in the other neck to monitor the temperature of the mixture during preparation. A pump was used to draw the mixture from the flask and pump it into a Teflon tubular reactor constructed from a 2-meter-long tube with an inner diameter of 8 mm. The reaction proceeded as the mixture flowed through the tube under controlled temperature conditions. A sensor was installed at the end of the tube to measure the temperature of the outgoing mixture to ensure stable reaction conditions. The microwave heating device was also inspected before the experiments to ensure no radiation leakage, ensuring safety and accurate results. The Teflon tube wound into the microwave in a coil shape and connected to the outflow separating funnel.

Methanol (based on oil weight) was used with (30g) of waste cooking oil and CaO nano catalyst; the resulting solution was then put into a three necked glass flask and heated to reaction temperature. To avoid phase separation, the reactants were stirred at 700 rpm using a magnetic stirrer that was put in vessel. The irradiation time was then adjusted by continuously pumping the reactants with varying flow rates into the Teflon tubular reactor. The experiment's independent variables were the amount of catalyst, and methanol to oil ratio. The weight ratio of methanol to oil varying between 50%, 60%, 70%, and 80%. The effect of catalyst concentration was also investigated at 1%, 2%, 3%, and 4% of the waste cooking oil weight. The microwave radiation power was set at 20% of the total device power, with different reaction times (0, 0.5, 1, 2, 3, 4, 5, and7 minutes) and reaction temperatures (45℃, 55℃, 65℃, 75℃) .Following the completion of the reaction, the combination was left to have a rest for the entire night, revealing three distinct layers: : a layer at the bottom with catalyst leftovers, a layer of glycerin in the middle, and a layer of biodiesel on top. Centrifugation was used to separate the fuel layer from the catalyst. The mixture was then dried in an oven at 65°C for 24 hours to get rid of any methanol that was still there. Following that, the conversion ratio to biodiesel was calculated using equation (1).

$$yield\% = \frac{weight\ of\ biodiesel}{weight\ of\ waste\ cooking\ oil} * ١٠٠٪ \quad (1)$$

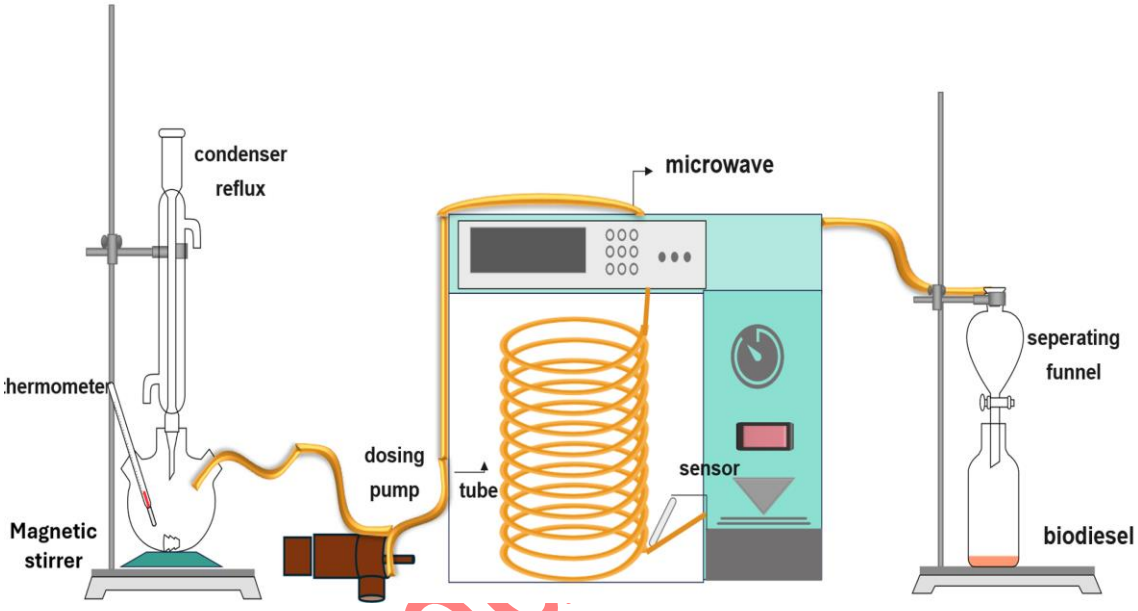

Figure1. scheme diagram of continuous process in microwave of biodiesel production

2.6 kinetic study

the total equation of product fatty acid methyl ester from triglyceride shown in Eq. (2).

$TG + ٣\square\square\square \xrightleftharpoons{\Delta catalyst} GL + ٣\square\square\square\square\square$ (2) Due to excess methanol, the transesterification reaction was predicted to have pseudo-first-order kinetic. When the amount of a reactant (methanol) exceeds the amount of another (TG), the second-reaction kinetics become pseudo first order [33] , with negligible reversible reactions. The reaction rate (r) can be calculated using Eq. (3).

$$-r_A = \frac{d_{CA}}{dt} = kC_A \quad (3)$$

In equation (3), C_A, k, and t represent TG concentration, rate constant, and reaction time, respectively. Rate constants were calculated using Eq. (4) and observed at various reaction times.

$$-\ln(١ - X_A) = kt \quad (4)$$

In the above equation (4), X represents the product conversion at time t. The activation energy (Ea) was calculated using Arrhenius' equation (5).

$$lnk = -\frac{E_a}{RT} + lnA \quad (5)$$

T represents the reaction temperature, while A and R are the pre-exponential factors٨.٣١٤ ∗ ١٠.$^{-٣}$ $\frac{KJ}{K.mole}$.

To calculate the kinetics, the microwave's temperature increased at 5-minute intervals from 318.15K (45°C) to 348.15K (75°C).

3. Results and discussion

3.1 The parameters effect on Biodiesel product

3.1.1 methanol to oil ratio effect

The molar ratio of alcohol to WCO is a key factor in determining methyl ester yield. The stoichiometric molar ratio of WCO to methanol is typically 1:3, but this does not always result in a complete reaction. To achieve higher yields of methyl esters, a higher molar ratio is needed to reach equilibrium and complete the reaction [34]. This study examined how different methanol-to-oil ratios (50 wt.%, 60wt.%, 70wt.%, and 80wt.%) affect biodiesel yield. The following parameters were kept constant: temperature of 65°C, catalyst loading of 3wt.%, microwave power of 20%, and reaction time of 5 minutes. The molar ratio of 70wt.% resulted in the highest biodiesel yield reached 93.43), as shown in Figure 2(a). However, increasing the methanol ratio beyond this limit resulted in no further yield improvement, indicating the achievement of a quasi-stable equilibrium[26].

3.1.2 Catalyst Loading Effect

The WCO conversion and yield are significantly influenced by the catalyst loading. for this set of experiments, the temperature was maintained at 65°C, the oil-to-methanol ratio was maintained at 70 wt.%, the reaction time was 5 minutes, and the microwave power was 20%. The CaO catalyst was adjusted from 1 to 4 wt.%. As illustrated in Figure 2(b), the catalyst loading increased from 1 to 3wt.%, resulting in a rise in yield from 79.73 to 93.43 wt.%. Nevertheless, the percentage of biodiesel was reduced because of the increased soap formation, which was brought about by an additional rise in concentration of catalyst (from 1 to 4 wt.%). Consequently, the highest yield of biodiesel was achieved at 3 wt.%, yielding 93.433%.

3.1.3 Temperature effect

The influence of the temperature was investigated by adjusting the temperature of the reaction between 45 to 75°C while keeping all the other variables constant (3 wt.% concentration of catalyst, 70 wt.% ratio of methanol to oil, 20% microwave power, and 5-minutes of reaction period). Temperature influences the yield, as seen in Figure 2(d). The yield increased from 65.57% to 94.16% when the temperature rose from 45 to 65°C. Nevertheless, successive temperature increases resulted in a drop in yield. The cause for this is the evaporation of methanol at temperatures surpassing 64.7°C (methanol boiling point), which results in a 75°C loss in yield. This is consistent with the findings of Gimbun et al. (2013) [35]. Methanol generates bubbles in the solution that exceed its boiling point, which can impede the reaction, as per Wang et al. [36]. Additionally, the saponification of glycerides is accelerated by a higher temperature, which results in an increase in the production of glycerol. The outcome of this investigation is in accordance with the findings of prior investigations[37,38].

3.1.4 Time effect

To explore the effect that reaction time has on the process of producing biodiesel, the catalyst concentration was set at 3wt.%, and the ratio of methanol to oil was set at 70wt.%, the temperature at 65℃, and the microwave irradiation power at 20%,

while maintaining the other reaction conditions constant. The reaction duration varied between 0.5 and 7 minutes. The results, as illustrated in Figure2(c), demonstrate that the biodiesel yield experienced substantial improvements as the reaction time increased from 0.5 to 5 minutes. The maximum value was 93.433%. Nevertheless, indicators experienced a decline when the reaction time was extended to more than 5 minutes.

This decrease is associated with the potential for esters to undergo hydrolysis, resulting in the formation of soap rather than continuing the conversion process[39]. This process has a detrimental impact on the reaction's efficiency. The optimal reaction time for achieving the highest yield and conversion rate in subsequent reactions within this study was determined to be 5 minutes based on these results.

3.1.5 Improvement rate of reaction

In this part of the study, a narrow-channel tubular reactor measuring (2 meters) in length and (5 mm) in internal diameter was used, which is smaller in diameter compared to the reactor used in previous experiments. The experiment was conducted under the same optimal operating conditions that yielded the best results in the larger reactor, including methanol-to-oil ratio, catalyst concentration, temperature, and residence time. Although the narrow-channel reactor offers theoretical advantages in terms of improved diffusion mixing and better control of heat and mass transfer [٤٠], the results showed a lower yield (٨٦٪) compared to the larger reactor (٩٣،٤٣), even under constant operating conditions including ٣wt.% catalyst concentration, ٧٠wt.% methanol to oil ratio ,٦٥°Creaction temperature, and ٢٠٪ microwave power. This decrease is attributed to several engineering and behavioral factors associated with the new reactor design, most notably Exceeding optimal conditions in the engineering context of a small reactor. Even if the temperature and residence time are identical, the flow distribution within the narrow channel may be irregular or lead to localized stagnation zones, negatively impacting the reaction efficiency. Excessive transfer rates: In small, narrow-channel reactors, the mass and heat transfer rates are very high. This can lead to rapid product separation within the reactor before the reaction is complete, especially since the conversion process relies on continuous contact between the oil and methanol. Difference in flow regime: A smaller reactor may tend toward a non-optimal flow regime (such as inhomogeneous plug flow or localized mixing) compared to a larger reactor, which provides greater homogeneity, impairing reaction efficiency. Premature product separation: The narrow design contributed to rapid separation of methanol or glycerol from the reaction medium, leading to the reaction being interrupted before reaching maximum conversion. Thus, it is concluded that the optimal conditions achieved in a larger reactor cannot be directly transferred to a smaller reactor without modification, as the reactor's engineering characteristics play a crucial role in determining reaction efficiency.

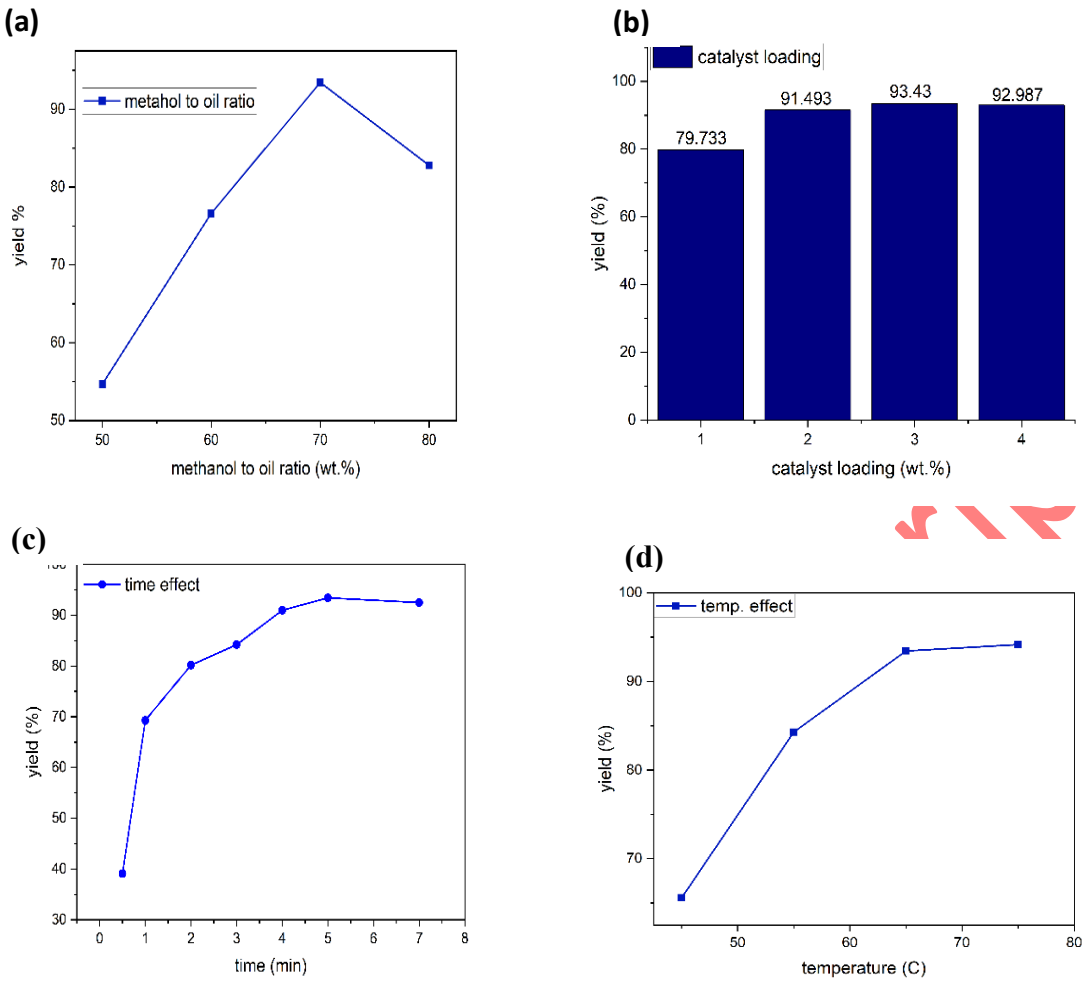

Figure 2. The parameters effect on transesterification reaction (a) Methanol to oil ratio effect(b) Catalyst loading effect (c) Time reaction effect (d) Temperature reaction effect .

3.2 Properties of biodiesel product

The basic characteristics of the biodiesel that was produced were studied utilizing microwave-assisted transesterification process (continuous systems), with the results being summarized and compared to the ASTM D6751-09 standard and EN 14214 14214, as shown in Table (1).

The findings indicated that density, viscosity, and flash point are within permissible limits according to the standards, indicating the suitability of this type of biodiesel for utilizing in diesel engines. The biodiesel produced was determined to have a viscosity of 5. ٠٩٤mm²/s. The result obtained agreed with the value of 5.2 mm²/s reported by [41] in other studies on biodiesel extracted from used cooking oil. The biodiesel produced was estimated to have a flash temperature of ٩٣.٥ °C, which is comparable to diesel and renders it safe to handle. The same previous studies have reported this flash point, with [41] reporting a flash point of 96 °C in comparison to 60 °C for mineral diesel. The density of biodiesel produced from waste cooking oil was 0.908, which is approximately equivalent to the maximum of the English studies.

Table1. physical properties of biodiesel product

property	Biodiesel product	ASTM D 6751	EN 14214
Viscosity(mm^2/s)	5.094	1.9-6	3.5-5
Density (g/cm^3)	0.9128	0.87-0.89	0.86-0.90
Flash point (°C)	93.5	130 minimum	>101

3.3 kinetic study and activation energy

The kinetics of the transesterification reaction were investigated to determine the influence of varying temperatures at different reaction times. The studies were conducted under optimal operating conditions, with temperatures of 45, 55, 65, and 75°C and time intervals of 1, 2, 3, 4, and 25 minutes. Figure 3(a) shows a linear relationship between −ln(1−X) and time, showing the reaction follows pseudo-first-order kinetic models based on equations (4).The activation energy (Ea.) was estimated using the rate constants obtained from the experimental data and the Arrhenius equation (Equation 5). Figure 3(b) shows a graph between ln(k) and 1/T. The slope of the line (−Ea./R) was used to compute Ea., and the intercept on the ln(k) axis was used to derive the pre-exponential component (A). The activation energy was 15 kJ/mol, which is less than common for transesterification processes (24.7-84.1 kJ/mol).

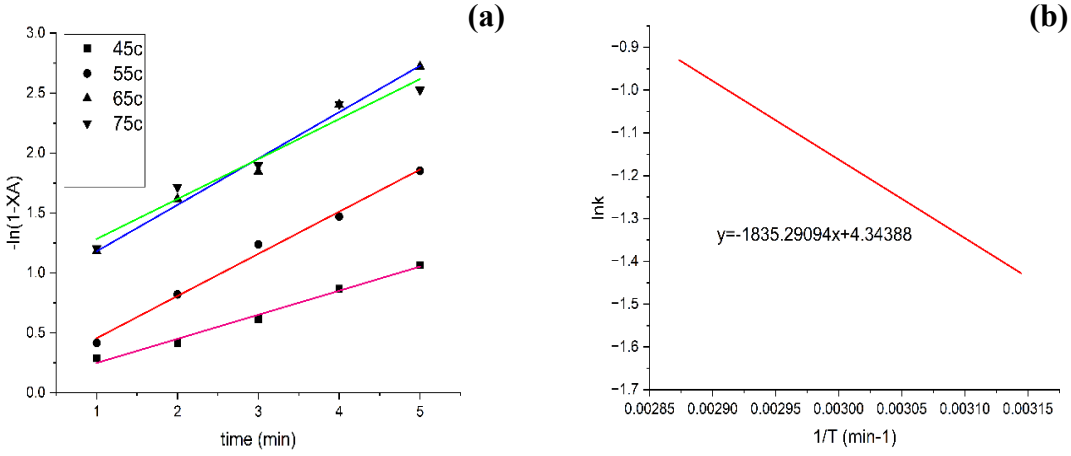

Figure 3. (a) linear relationship between −ln(1−X) and time (b) graph between ln(k) and 1/T

3.4 Comparison between Batch and Continuous Processes under the Same Conditions

A comparison was conducted between batch and continuous processes using the same feedstock and under identical operating conditions in terms of temperature, catalyst type and quantity, and methanol-to-oil ratio, power to evaluate the performance of the continuous process. The results showed that both systems achieved good conversion rates, but the continuous process demonstrated a clear advantage in reducing the reaction time required to achieve maximum conversion. The continuous flow of reactants contributed to improved reaction efficiency by enhancing mixing and temperature stability, which accelerated the conversion process. Therefore, the continuous process can be considered a more efficient option

for biofuel production compared to the batch process, especially in applications that require reduced operating time without compromising conversion efficiency.

Table 2. comparative study between batch and continuous process

Optimum condition	Methanol to oil ratio(wt.%)	Reaction time	Reaction temperature (℃)	Catalyst loading (wt.%)	Power%	yield
Batch study	70	20	65	3	20	94.606
Continuous study	70	5	65	3	20	93.43

3.5 comparative between other studies

Although the biodiesel conversion rate in this study was lower than in prior studies, what sets it apart is the use of a new natural catalyst, CaO Nano catalyst derived from willow leaves extract, which was used for the first time in this context. This catalyst is inexpensive, locally available, and ecologically friendly, making it a more sustainable option than traditional industrial catalysts. Previous experiments, such as those using example: NaOH, achieved conversion rates of 95% under operational settings such as a temperature of 60℃ and a reaction time of 0.5 minutes used waste soyabean oil as a feedstock [42]. While in other studies that use NaOH as a Catalyst achieved conversion rate of 99.04% in 21.04 minutes as a result of used coconut oil as feedstocks [43]. The [44] and [45] found that utilizing KOH and NaOH as a catalyst at a similar concentration (1wt.%) and different feed stocks (used vegetable oil and used palm oil) resulted in a high yield in both catalysts 98.9% and 97% although used the different alcohol to oil ratio. In a prior study, $NaOCH_3$ catalyst was employed with Jatropha oil, and under operational settings that included a reaction period of 0.5, an 96.5% conversion rate was attained[5]. In this investigation, was combined with CaO under various conditions 5 minutes reaction time,65℃ reaction temperature, and 70 wt.% methanol to oil ratio to get a conversion rate of 93.43.

The efficiency discrepancy can be explained by a variety of factors, including the natural catalyst's features, such as surface area, catalytic activity, and chemical composition. However, the findings represent a promising first step toward creating alternative and more sustainable natural catalysts. This study indicates the possible use of atypical catalysts for biodiesel generation, paving the way for further improvements in performance via structural modifications or operating conditions.

Table 3. The comparative between different catalysts applied in continuous process.

Process type	Feed stock	Alcohol to oil ratio	Temperature (℃)	Reaction time (min)	catalyst	Yield %	references
continuous	Jatropha oil	1:6	-------	0.5	NaOCH3 (1.0wt.%)	96.5	[5]
continuous	Used vegetable oil	1:6	--------	1	KOH (1.0wt.%)	98.9	[44]
continuous	Coconut oil	1:7 methanol	65	21.04	NaOH (1 wt.%)	99.04	[43]

continuous	Used palm oil	1:12 Ethanol	50	0.5	NaOH (1wt.%)	97	[45]
continuous	Waste soyabean oil	1:6 methanol	60	0.5	NaOH (1wt.%)	95	[42]
continuous	Waste cooking oil	70wt.%	65	5	CaO (3wt%)	93.43	Current study

4. Conclusions

A continuous process for biodiesel production has been developed by applying process, using a narrow-channel reactor unit in microwave to study the effects of Cao nano catalyst concentration derived from fallen willow extract, temperature, reaction duration, and the ratio of methanol to oil. The results showed that increasing the catalyst concentration from 1% to 3% by weight led to a significant increase in yield of (biodiesel. Additionally, increasing the reaction time also contributed to improving the reaction efficiency. The specialized continuous microwave-assisted reactor developed for this study successfully facilitates the conversion of waste cooking oil to biodiesel. The maximum yield (93.43%) was attained at a temperature of 65 °C, a molar ratio of oil to methanol of 70wt.%, a catalyst loading of 3wt.% CaO catalyst, and a reaction time of 5 minutes. The biodiesel generated in this study is consistent with the specifications outlined in ASTM D6751. Additionally, the design used helped enhance the separation process between biodiesel and glycerin, thanks to the reliance on gravitational separation within the reaction tube.

Nomenclature

- **Roman symbols**

Symbols	***Description***	***Units***
A	Pre-exponential Factor	mol/g. min
dC_A/dt	Rate of change of concentration	mole/L.min
$Ea.$	Activation Energy	KJ/mol
k	Rate constant	1/min
R	Gas Constant	J/mol.K
r_A	Rate of reaction	Mole/L.min
t	Reaction Time	min
T	Reaction Temperature	℃
X_A	Conversion of A	%

- **Abbreviations**

symbol	Description
ASTM	American society of Testing and Materials
BET	Brunauer-Emmett-Teller
CaO	Calcium oxide
EDX	Energy Dispersive X-Ray Spectroscopy
EN	European Norm
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FTIR	Fourier Transform Infrared Spectroscopy
GL	Glycerol
KOH	Potassium hydroxide
$NaCH_3$	Sodium methoxide
NaOH	Sodium hydroxide
RCOOR	Ester (FAME)
ROH	alcohol
SEM-EDX	Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy
TG	Triglycerides
XRD	X-Ray Diffraction
WCO	Waste cooking oil

References

1. Al-Yaqoobi AM, Al-Rikabey MN, Al-Mashhadani MKH. Electrochemical harvesting of microalgae: Parametric and cost-effectivity comparative investigation. Chemical Industry and Chemical Engineering Quarterly. ٢٠٢١;٢٧(٢):١٢١–٣٠. https://doi.org/10.2298/CICEQ191213031A.

2. Abd MF, AL-yaqoobi AM. The potential significance of microwave-assisted catalytic pyrolysis for valuable bio-products driven from Albizia tree. Applied Science and Engineering Progress. 2025;18(1):7454. https://doi.org/10.14416/j.asep.2024.07.016.

3. Abd MF, Al-yaqoobi AM, Abdul-Majeed WS. Catalytic microwave pyrolysis of albizia branches using iraqi bentonite clays. Iraqi Journal of Chemical and Petroleum Engineering. ٢٠٢٤;٢٥(٢):١٧٥–٨٦. https://doi.org/10.31699/IJCPE.2024.2.16.

4. Haryono H, Ishmayana S, Fauziyah I. Synthesis and Characterization of Calcium Oxide Impregnated on Silica from Duck Egg Shells and Rice Husks as Heterogeneous Catalysts for Biodiesel Synthesis. Baghdad Science Journal. ٢٠٢٣;٢٠:١٩٧٦–٨٤. https://doi.org/10.21123/bsj.2023.7895.

٥. Tippayawong N, Sittisun P. Continuous-flow transesterification of crude jatropha oil with microwave irradiation. Scientia Iranica. ٢٠١٢;١٩(٥):١٣٢٤–٨. https://doi.org/10.1016/j.scient.2012.08.004

6. Kumar R, Ravi Kumar G, Chandrashekar N. Microwave assisted alkali-catalyzed transesterification of Pongamia pinnata seed oil for biodiesel production. Bioresour Technol. ٢٠١١ Jun;١٠٢(١١):٦٦١٧–٢٠. . https://doi.org/١٠,١٠١٦/j.biortech.٢٠١١,٠٣,٠٢٤.

7. Sahu S, Saikia K, Gurunathan B, Dhakshinamoorthy A, Rokhum SL. Green synthesis of CaO nanocatalyst using watermelon peels for biodiesel production. Molecular Catalysis. 2023 Aug 1;547. https://doi.org/10.1016/j.mcat.2023.113342.

8. Abbas AS, Abbas RN. Preparation and characterization of NaY zeolite for biodiesel production. Iraqi Journal of Chemical and Petroleum Engineering. ٢٠١٥;١٦(٢):١٩–٢٩. https://doi.org/10.31699/IJCPE.2015.2.3.

٩. Abbas RA, Flayeh HM. Bioethanol (biofuel) production from low grade dates. Iraqi Journal of Chemical and Petroleum Engineering. ٢٠١٩;٢٠(٤):٤١–٧. https://doi.org/10.31699/IJCPE.2019.4.7

10. Hussain HK, Kareem A, Jendeel A, Naife TM, Abdul H, Al K, et al. Production of Biodiesel Fuel from Used vegetable Oil. Vol. 17, Journal of Engineering. 2011. https://doi.org/10.31026/j.eng.2011.05.25.

١١. Haryono H, Ishmayana S, Fauziyah I. Synthesis and Characterization of Calcium Oxide Impregnated on Silica from Duck Egg Shells and Rice Husks as Heterogeneous Catalysts for Biodiesel Synthesis. Baghdad Science Journal. ٢٠٢٣;٢٠:١٩٧٦–٨٤. https://doi.org/10.21123/bsj.2023.7895.

١٢. Phan AN, Phan TM. Biodiesel production from waste cooking oils. Fuel. ٢٠٠٨;٨٧(١٧–١٨):٣٤٩٠–٦. https://doi.org/١٠,١٠١٦/j.fuel.٢٠٠٨,٠٧,٠٠٨

13. Meng X, Chen G, Wang Y. Biodiesel production from waste cooking oil via alkali catalyst and its engine test. Fuel processing technology. ٢٠٠٨;٨٩(٩):٨٥١–٧.. https://doi.org/10.1016/j.fuproc.2008.02.006

14. Tan KT, Lee KT, Mohamed AR. Potential of waste palm cooking oil for catalyst-free biodiesel production. Energy. ٢٠١١;٣٦(٤):٢٠٨٥–٨. https://doi.org/10.1016/j.energy.2010.05.003.

15. Ani FN, Said NH, Said MFM. Optimization of biodiesel production using a stirred packed-bed reactor. International Journal of Technology. ٢٠١٨ Apr ١;٩(٢):٢١٩–٢٨. https://doi.org/10.14716/ijtech.v9i2.1386.

16. Subramaniam K, Wong KY, Wong KH, Chong CT, Ng JH. Enhancing Biodiesel Production: A Review of Microchannel Reactor Technologies. Vol. 17, Energies.

Multidisciplinary Digital Publishing Institute (MDPI); 2024. https://doi.org/10.1007/s12155-021-10333-w

17. Marinković DM, Stanković M V., Veličković A V., Avramović JM, Miladinović MR, Stamenković OO, et al. Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives. Vol. 56, Renewable and Sustainable Energy Reviews. Elsevier Ltd; ٢٠١٦. p. ١٣٨٧–٤٠٨. https://doi.org/10.1016/j.rser.2015.12.007.

18. Kouzu M, Hidaka JS. Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review. Vol. ٩٣, Fuel. ٢٠١٢. p. ١–١٢. https://doi.org/١٠,١٠١٦/j.fuel.٢٠١١,٠٩,٠١٥.

19. Almadani EA, Abdelghani KA, Omar FA. Calcium Oxide as an Efficient Heterogeneous Catalyst for Production of Biodiesel. The Scientific Journal of University of Benghazi. 2023 Dec 6;36(2). https://doi.org/10.37376/sjuob.v36i2.4303.

20. Subramaniam K, Wong KY, Wong KH, Chong CT, Ng JH. Enhancing Biodiesel Production: A Review of Microchannel Reactor Technologies. Vol. 17, Energies. Multidisciplinary Digital Publishing Institute (MDPI); 2024. https://doi.org/10.3390/en17071652.

21. Abd Maha F, Al-Yaqoobi AM. The feasibility of utilizing microwave-assisted pyrolysis for Albizia branches biomass conversion into biofuel productions. International Journal of Renewable Energy Development. 2023;12(6):1061. https://doi.org/10.14710/ijred.2023.56907.

٢٢. Gude VG, Patil P, Martinez-Guerra E, Deng S, Nirmalakhandan N. Microwave energy potential for biodiesel production. Sustainable Chemical Processes. ٢٠١٣;١:١–٣١. https://doi.org/10.1186/2043-7129-1-5

٢٣. El Sherbiny SA, Refaat AA, El Sheltawy ST. Production of biodiesel using the microwave technique. J Adv Res. ٢٠١٠ Oct;١(٤):٣٠٩–١٤. https://doi.org/10.1016/j.jare.2010.07.003.

٢٤. Abd MF, Al-yaqoobi AM, Abdul-Majeed WS. Catalytic microwave pyrolysis of albizia branches using iraqi bentonite clays. Iraqi Journal of Chemical and Petroleum Engineering. ٢٠٢٤;٢٥(٢):١٧٥–٨٦. https://doi.org/10.31699/IJCPE.2024.2.16.

25. Gnaneswar Gude V, Patil P, Martinez-Guerra E, Deng S, Nirmalakhandan N. Microwave energy potential for biodiesel production [Internet]. 2013. Available from: http://www.sustainablechemicalprocesses.com/content/1/5/5.https://doi.org/10.1186/2043-7129-1-5.

26. Iyyaswami R, Halladi VK, Yarramreddy SR, Malur Bharathaiyengar S. Microwave-assisted batch and continuous transesterification of karanja oil: Process variables optimization and effectiveness of irradiation: Microwave-assisted transesterification of karanja oil. Biomass Convers Biorefin. ٢٠١٣;٣(٤):٣٠٥–١٧. https://doi.org/10.1007/s13399-013-0080-8.

27. Acevedo-Quiroz A, Carrera-Avendaño E de J, Acevedo-Quiroz N, Alvarez-Gutiérrez PE, Borunda M, Adam-Medina M. Experimental Study on Biodiesel Production in a Continuous Tubular Reactor with a Static Mixer. Processes. 2024;12(12):2859. https://doi.org/10.3390/pr12122859.

28. He BB, Singh AP, Thompson JC. EXPERIMENTAL OPTIMIZATION OF A CONTINUOUS-FLOW REACTIVE DISTILLATION REACTOR FOR BIODIESEL PRODUCTION. Transactions of the ASAE. ٤٨(٦):٢٢٣٧–٤٣. https://doi.org/10.13031/2013.20071.

29. Serhan M, Sprowls M, Jackemeyer D, Long M, Perez ID, Maret W, et al. Total iron measurement in human serum with a smartphone. In: AIChE Annual Meeting, Conference Proceedings. American Institute of Chemical Engineers; 2019. https://doi.org/10.1039/x0xx00000x.

30. Groisman Y, Gedanken A. Continuous flow, circulating microwave system and its application in nanoparticle fabrication and biodiesel synthesis. Journal of Physical Chemistry C. ٢٠٠٨ Jun ١٩;١١٢(٢٤):٨٨٠٢–٨. https://doi.org/١٠,١٠٢١/jp٨٠١٤٠٩t.

31. Tran DT, Chang JS, Lee DJ. Recent insights into continuous-flow biodiesel production via catalytic and non-catalytic transesterification processes. Vol. ١٨٥, Applied Energy. Elsevier Ltd; ٢٠١٧. p. ٣٧٦–٤٠٩. https://doi.org/١٠,١٠١٦/j.apenergy.٢٠١٦,١١,٠٠٦.

32. Aljendeel H, Borhan E, Al-Ani MJ. Kinetic Study of Transesterification Reaction of Edible Oil Using Heterogenous Catalyst. Iraqi Journal of Chemical and Petroleum Engineering. ٢٠٢٢ Sep ٣٠;٢٣(٣):١١–٦. https://doi.org/١٠,٣١٦٩٩/ijcpe.٢٠٢٢,٣,٢.

33. Pauline JMN, Sivaramakrishnan R, Pugazhendhi A, Anbarasan T, Achary A. Transesterification kinetics of waste cooking oil and its diesel engine performance. Fuel. 2021;285:119108. https://doi.org/10.1016/j.fuel.2020.119108

34. Encinar JM, Gonzalez JF, Rodriguez JJ, Tejedor A. Biodiesel fuels from vegetable oils: transesterification of Cynara c ardunculus L. oils with ethanol. Energy & fuels. ٢٠٠٢;١٦(٢):٤٤٣–٥٠. https://doi.org/١٠,١٠٢١/ef٠١٠١٧٤h.

35. Gimbun J, Ali S, Kanwal CCSC, Shah LA, Muhamad NH, Cheng CK, et al. Biodiesel production from rubber seed oil using activated cement clinker as catalyst. Procedia Eng. ٢٠١٣;٥٣:١٣–٩. https://doi.org/١٠,١٠١٦/j.proeng.٢٠١٣,٠٢,٠٠٣.

٣٦. Wang B, Li S, Tian S, Feng R, Meng Y. A new solid base catalyst for the transesterification of rapeseed oil to biodiesel with methanol. Fuel. ٢٠١٣;١٠٤:٦٩٨–٧٠٣. https://doi.org/10.1016/j.fuel.2012.08.034.

37. Azcan N, Yilmaz O. Microwave assisted transesterification of waste frying oil and concentrate methyl ester content of biodiesel by molecular distillation. Fuel. ٢٠١٣;١٠٤:٦١٤–٩. https://doi.org/١٠,١٠١٦/j.fuel.٢٠١٢,٠٦,٠٨٤.

٣٨. Zhang H, Ding J, Zhao Z. Microwave assisted esterification of acidified oil from waste cooking oil by CERP/PES catalytic membrane for biodiesel production. Bioresour Technol. ٢٠١٢;١٢٣:٧٢–٧. https://doi.org/١٠,١٠١٦/j.biortech.٢٠١٢,٠٦,٠٨٢.

39. Uzun BB, Kılıç M, Özbay N, Pütün AE, Pütün E. Biodiesel production from waste frying oils: Optimization of reaction parameters and determination of fuel properties. Energy. ٢٠١٢;٤٤(١):٣٤٧–٥١. https://doi.org/١٠,١٠١٦/j.biortech.٢٠١٢,٠٦,٠٨٢

40. Jachuck R, Pherwani G, Gorton SM. Green engineering: Continuous production of biodiesel using an alkaline catalyst in an intensified narrow channel reactor. Journal of Environmental Monitoring. ٢٠٠٩;١١(٣):٦٤٢–٧. https://doi.org/١٠,١٠٣٩/b٨٠٧٣٩٠m.

41. Degfie TA, Mamo TT, Mekonnen YS. Optimized biodiesel production from waste cooking oil (WCO) using calcium oxide (CaO) nano-catalyst. Sci Rep. 2019;9(1):18982. https://doi.org/10.1038/s41598-019-55403-4

42. Lin CH, Chang YT, Lai MC, Chiou TY, Liao CS. Continuous biodiesel production from waste soybean oil using a nano-Fe3O4 microwave catalysis. Processes. 2021;9(5):756. **https://doi.org/10.3390/pr9050756**

٤٣. Kumar G, Kumar D, Singh S, Kothari S, Bhatt S, Singh CP. Continuous low cost transesterification process for the production of coconut biodiesel. Energies (Basel). ٢٠١٠;٣(١):٤٣–٥٦. https://doi.org/١٠,٣٣٩٠/en٣٠١٠٠٤٣

٤٤. Barnard TM, Leadbeater NE, Boucher MB, Stencel LM, Wilhite BA. Continuous-flow preparation of biodiesel using microwave heating. Energy & Fuels. ٢٠٠٧;٢١(٣):١٧٧٧–81. https://doi.org/10.1021/ef0606207

45. Sarvi A, Fogelholm CJ, Zevenhoven R. Emissions from large-scale medium-speed diesel engines: ٢. Influence of fuel type and operating mode. Fuel Processing Technology [Internet]. ٢٠٠٨;٨٩(٥):٥٢٠–٧. Available from: https://www.sciencedirect.com/science/article/pii/S٠٣٧٨٣٨٢٠٠٧٠٠٢١٥٩. https://doi.org/10.1016/j.fuproc.2007.10.005