TRANSESTERIFICATION OF SUNFLOWER OIL IN AN ATOMIZATION SYSTEM

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ABSTRACT

Difficulties in mass transfer have been widely reported as challenges to be overcome in biodiesel production. In this context, the present study proposes using atomization to improve the transesterification of sunflower oil via the ethyl route. Preliminary experiments were carried out using different dosages of sodium hydroxide (0.1%-2.0%, w/w) and modes of operation (batch, dripping, and atomization). An experimental design was also carried out to evaluate the effects of atomization pressure (0.5-1.5 bar) and oil flow (3-9 g/min) on the conversion into ethyl ester. Generally, the highest conversion values were obtained during the first moments of operation (15 min) and under the highest ethanol: oil ratios. The conversion values followed the following feeding order: atomization > dripping > batch by reducing oil size. Under the ethanol: oil ratio of 60:1, 98.3% conversion was achieved in the atomization system using a pressure of 1.5 bar and an oil flow rate of 3 g/min, showing that this reactor design is attractive for biodiesel production.

KEYWORDS: *biodiesel, ethanol, ethyl ester, reactor, batch system.*

I. INTRODUCTION

The growth of the world population has required increasing energy consumption, which puts great pressure on the planet's ecological balance due to the use of non-renewable resources. With the increase in population and the development of modern life, exhaustible energy resources have been exploited indiscriminately, worrying government agencies and challenging society in the search for alternatives that can meet this growing energy demand [1].

One of the main bases for sustainable development is using renewable energy sources. In this context, replacing conventional petroleum-based liquid fuels for transportation with green fuels or liquid biofuels has been the focus in recent years [2]. Different types of biofuels exist at different stages of development, such as biodiesel, bioethanol, biomethane, hydrotreated vegetable oils and fats, and lignocellulosic-based fuels [3]. Biodiesel is composed of monoalkyl esters of fatty acids with long chains that are obtained from renewable sources of lipids such as animal fats and vegetable oils, the most used in the industry being soybean oil, sunflower oil, palm oil, among others, and waste cooking oils, through a transesterification process [4]. One of the main advantages of replacing biodiesel with conventional fossil fuels is the lower level of pollution and toxicity [5].

Despite the advantages, the biodiesel production area still requires studies to make its processes more sustainable, improve its physical-chemical characteristics compared to diesel, and mitigate its possible environmental impacts. Currently, the high cost of biodiesel is induced by the high costs of the raw

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material, and the process is the main obstacle that hinders its widespread commercialization, resulting in the need to develop techniques to intensify the production chain [6].

Reactor technology can scale up the biodiesel production process, which contributes greatly to ensuring large-scale production. Therefore, to ensure operational control, increase production efficiency, and produce cost-effectively, it is necessary to adopt scale-up processes, in which atomization represents a technology that has shown progress in production scenarios [7].

In general, atomization studies used for biofuels aim to determine appropriate atomization regimes to reduce droplet size and, therefore, increase the surface area of the liquid, which is necessary to improve evaporation and mixing of the fuel, thus promoting Such action improves conversion rate and product features [8].

In this context, the present study investigated the production of biodiesel via transesterification using an atomization system. The experiments were conducted in an atomization reactor at a fixed temperature of 50 °C, containing ethanol, sodium hydroxide and sunflower oil. Initially, analyzes were carried out through experimental planning, aiming to observe the conversion rate through the transesterification reaction with changes in the operating variables. Transesterification performance was compared with batch and drip tests. Finally, the effects of atomization operating conditions (atomization pressure and oil flow rate) on the conversion results were evaluated.

II. MATERIALS AND METHODS

2.1. Chemicals

Sodium hydroxide in microbeads (purity > 99%) and acetic acid (purity = 99.7%) were purchased by Synth (São Paulo, Brazil), and anhydrous ethanol (99.5%) was purchased by Dinâmica (São Paulo, Brazil). Sunflower oil was purchased from the local market, and distilled water was used for the experiments and analysis.

2.2. Atomization system

The atomization system (Fig. 1) used in the transesterification experiments is composed of different modules, including (1) jacketed reactor, (2) diaphragm pump of 80 psi and maximum flow of 3.1 L/min, type E thermocouple, stainless steel dual-fluid mixing chamber with 0.45 mm outlet, (3) sunflower oil reservoir, (4) peristaltic pump, (5) 2 hp air compressor and (6) solenoid valve for modulating the mixing time opening and closing of atomization. Other modules include (7) 0.5 hp centrifugal pump, (8) refrigerant reservoir, (9) 1000 W immersion electrical resistors, (10) circular coil, (11) control system with relays, (12) computer, and (13) condenser. An Arduino microcontroller controlled all pump, compressor, resistance, and solenoid drives.

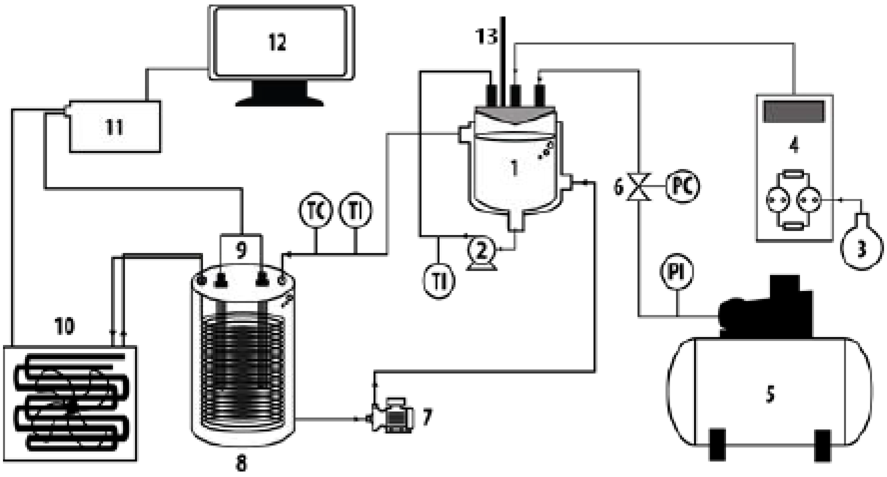

Fig. 1. Schematic of the atomization system used in transesterification reactions. 1- reactor, 2- diaphragm pump, 3-sunflower oil reservoir, 4- peristaltic pump, 5- compressor, 6- solenoid valve, 7- centrifugal pump, 8- water reservoir, 9- electrical resistances, 10- condenser, 11-control box, 12-computer, 13-condenser; TI-temperature indicator, TC-temperature controller, PI-pressure indicator, PC-pressure controller.

2.3. Preliminary transesterification tests

Before starting tests on the atomization system, batch and semi-batch tests were carried out by dripping sunflower oil and sodium hydroxide. These experiments were carried out in a three-way reactor with 72 g of ethanol and different dosages of sodium hydroxide (0.1%, 0.5%, 1.0%, and 2.0%, w/w about the mass of sunflower oil) under magnetic stirring and temperature of 50 °C. In batch operation, 120 g of sunflower oil was previously added to the reactor, leading to an initial molar ratio of 9:1. In semi-batch operation, sunflower oil was added to the system at a flow rate of 4 g/min using a high-pressure pump (LDC Analytical, ConstaMetrica 3200). The final molar ratio of the experiment was also 9:1. In both experiments, analyses were performed at 15, 30, and 60 min. The reaction efficiency was evaluated based on the conversion of sunflower oil into ethyl ester.

2.4. Transesterification in the atomization system

When operating in an atomization system, the experiments were conducted in a reactor at a fixed temperature of 50 °C, in which 300 mL of ethanol containing 0.5% (w/w) sodium hydroxide (based on the mass of sunflower oil). The sunflower oil feeding system was activated only after the ethanol-sodium hydroxide mixture reached the desired temperature. The oil was pumped to the atomization nozzle at flow rates of 10.0 and 16.7 g/min, which correspond to final ethanol: sunflower oil molar ratios of 15:1 and 9:1, respectively. The atomization pressure of sunflower oil was maintained at 1.0 bar, while the opening and closing time of the solenoid valve was 0.25 s with time intervals of 0.5 s. Reactions were observed for 60 min. When the total mass of sunflower oil had just been injected, there were still 30 min left until the end of the investigation. Therefore, the reaction occurred in two stages: the first 30 min in semi-batch and the last 30 min in batch. Samples (~5 mL) were withdrawn periodically and neutralized with 1 g of acetic acid. Then, the samples were washed three times with distilled water and dried in an air circulation oven at 70 °C for 2 h. Image analyses were also performed to measure the size of droplets generated by atomization. A Python program was developed using the OpenCV and scikit-image libraries (with Blob Detection function) in image processing.

More experiments were conducted to investigate the role of atomization in higher ethanol: oil ratios and the effects of the variables sunflower oil flow rate and atomization pressure. The levels used in each factor in the experimental design 32 are shown in Table 1. At this stage, the experiments were conducted with 400 mL ethanol containing 1.0% (w/w) sodium hydroxide (based on the mass of sunflower oil) and 100 g of sunflower oil. The performance of the reactions was observed over 60 min with a final ethanol: sunflower oil ratio equal to 60:1 in all experiments.

Table 1. Factors and levels used in transesterification in an atomization system using sunflower oil.

Factors	Codes	Values		
		-1	0	+1
Oil flow rate (g/min)	X_1	3.0	6.0	9.0
Atomization pressure (bar)	X_2	0.5	1.0	1.5

2.5. Analytical method

The amount of ethyl ester formed in the experiments was determined by thermogravimetric analysis by Chand et al. [9]. Analysis was performed using a DTG-60AH analyzer (Shimadzu, Japan) and an alumina crucible. The following operating conditions were used: N_2 flow (purge gas) of 50 mL/min, maximum temperature of 1000 °C and use of two heating rates (10 °C/min to 600 °C and 20 C/min to 1000 °C).

III. RESULTS AND DISCUSSIONS

3.1. Comparison between different feeding modes

Table 2 presents the conversion values obtained in preliminary tests using the three-way reactor as the reactor. The excess catalyst promoted intense saponification before 15 min in run G4, which made it impossible to consider the condition for the following stages of the study. In general, the conversion values remained at the level regardless of the reaction time in the batch experiments. On the other hand, higher conversion values were obtained during the semi-batch moments since the oil: ethanol ratio is at its highest level, and the reaction environment contains mainly ethanol and sodium hydroxide. Conversion reached 41.9% in run G2 (0.5% catalyst, w/w) at 15 min, but values declined to 32.1% at times of 30 and 60 min. In run G3, the conversion exceeded 50% after 15 min and reduced slightly to 45.1% and 46.3% after 30 and 60 min of reaction. The reduction in conversion after 30 min was also evidenced by the change in the appearance of the reaction medium. Unlike esters and glycerol, sunflower oil has low miscibility in ethanol [10].

The comparison between the feeding modes already indicates that reducing the oil droplet favors the process performance, especially at the highest catalyst dosages (0.1% and 1.0%, w/w). The results of runs B1 and B3 in 60 min (11.6% and 35.8%) were lower than those of their dripping versions. These results align with transesterification runs with other reactor designs focusing on mass transfer intensification [11].

Table 2. Transesterification of sunflower oil into ethyl ester using different feeding strategies in a three-way reactor and sodium hydroxide as catalyst. The experiments were operated at 50 °C.

Run	Time (min)	Catalyst (%w/w)	Feeding	Ethanol: Sunflower oil (w:w)	Conversion (%)	Appearance
B1	15	0.1	Batch	9:1	11.5	Heterogeneous
B1	30	0.1	Batch	9:1	12.1	Heterogeneous
B1	60	0.1	Batch	9:1	11.6	Heterogeneous
G1	15	0.1	Dripping	18:1	15.7	Homogenous
G1	30	0.1	Dripping	9:1	14.7	Heterogeneous
G1	60	0.1	Dripping	9:1	14.5	Heterogeneous
B2	15	0.5	Batch	9:1	29.3	Heterogeneous
B2	30	0.5	Batch	9:1	30.0	Heterogeneous
B2	60	0.5	Batch	9:1	31.1	Heterogeneous
G2	15	0.5	Dripping	18:1	41.9	Homogenous
G2	30	0.5	Dripping	9:1	32.1	Heterogeneous
G2	60	0.5	Dripping	9:1	32.1	Heterogeneous
B3	15	1.0	Batch	9:1	35.3	Heterogeneous
B3	30	1.0	Batch	9:1	35.8	Heterogeneous
B3	60	1.0	Batch	9:1	35.8	Heterogeneous
G3	15	1.0	Dripping	18:1	51.3	Homogenous
G3	30	1.0	Dripping	9:1	45.1	Heterogeneous
G3	60	1.0	Dripping	9:1	46.3	Heterogeneous
G4	-	2.0	Dripping	-	-	-

Table 3 presents the ethyl ester conversion values using the atomization reactor in two runs. Notably, the same behavior in runs G1, G2, and G3 was recorded in runs A1 and A2. The conversion values at 15 min were higher than those at 30 and 60 min. After 15 min, the results remained practically constant, indicating that the semi-batch reached the conversion limit as a function of the ethanol: oil ratio, temperature, and amount of catalyst.

All conversion values obtained in run A2 were higher than run A1, comparing the same reaction time. This result is also attributed to the higher ethanol: oil molar ratio so that the following reaction order was recorded: 9:1 < 15:1 < 18:1 < 30:1. Erchamo et al. [12] also reported a significant increase in transesterification conversion and an increase in the alcohol: oil ratio.

In 15 minutes of reaction, there is also a jump of almost 40% in conversion between the G2 (41.9%) and A2 (77.1%) runs due to the change in feeding mode. The atomization of the oil led to the formation of droplets of micrometric size, in the order of 20 µm (> 50% of the droplets), as seen in Fig 2. The largest droplets generated were only 55 µm in size. The injection of oil in the form of micrometric droplets should promote intimate contact between the reactants and, consequently, an abrupt increase in conversion. Similarly, stirred reactors also achieved better transesterification results with increased stirring power due to the breakage of droplets by the impeller [13-14]. Even so, no significant differences were observed between the results at 30 and 60 min, indicating that atomization's benefits manifest in higher ethanol: oil ratios.

Table 3. Transesterification of sunflower oil into ethyl ester in an atomization reactor using two feed flows and sodium hydroxide as catalyst. The experiments were operated at 50 °C.

Run	Time (min)	Catalyst (%w/w)	Oil flow rate (g/min)	Ethanol: Sunflower oil (w:w)	Conversion (%)	Appearance
A1	15	0.5	16.7	18:1	77.1	Homogenous
A1	30	0.5	16.7	9:1	32.5	Heterogeneous
A1	60	0.5	16.7	9:1	32.8	Heterogeneous
A2	15	0.5	10.0	30:1	93.5	Homogenous
A2	30	0.5	10.0	15:1	37.5	Heterogeneous
A2	60	0.5	10.0	15:1	37.7	Heterogeneous

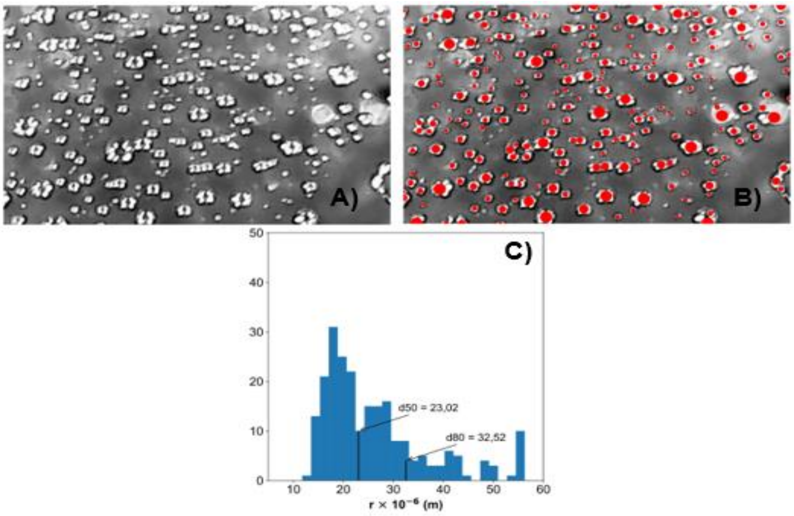

Fig. 2. Images of sunflower oil droplets generated by atomization at 1 bar without (A) and with image processing (B). Droplet size distribution (C).

3.2. Effects of pressure and oil flow on transesterification in an atomization reactor

Table 4 presents the transesterification conversion values of sunflower oil under different operating conditions of the atomization system. Conversions ranged from 96.0% (run AG7) to 98.3% (run AG3), indicating that the ethanol: oil ratio governs the reaction, and that atomization plays a secondary role. Unruean et al. [15] obtained conversion values in the order of 95% under the same ethanol: oil ratio. Although close to 100% conversion, it is possible to observe that the increase in pressure is advantageous since the highest conversion values were obtained in runs AG3, AG6, and AG9. This observation was also confirmed by Pareto chart analysis, as seen in Fig 3. Deus et al. [16] state that increasing atomization pressure forms a narrow jet with smaller droplets, facilitating mass transfer. In this condition, the sunflower oil droplets move faster in the jet and promote a greater degree of mixing with the liquid bulk.

On the other hand, in the Pareto chart, changing the oil flow rate from 3 to 9 g/min caused a reduction in transesterification conversion. As the final ethanol: oil molar ratios were fixed, the effects of oil flow fell solely on droplet size, with a direct correlation between them. In a study on the preparation of zinc oxide nanoparticles, Hidayat et al. [17] observed that increasing the liquid flow rate in the atomizer caused the formation of larger droplets, which would reduce the mass transfer rate.

Table 4. Experimental planning matrix 3^2 for transesterifying sunflower oil via the ethyl route using an atomization reactor. The experiments were conducted with an ethanol: oil ratio of 60:1, 1% (w/w) sodium hydroxide as the catalyst, and a temperature of 50 °C.

Run	Oil flow rate (g/min)	Pressure (bar)	Conversion (%)
AG1	3 (-1)	0.5 (-1)	96.9
AG2	3 (-1)	1.0 (0)	97.3
AG3	3 (-1)	1.5 (+1)	98.3
AG4	6 (0)	0.5 (-1)	96.6
AG5	6 (0)	1.0 (0)	97.6
AG6	6 (0)	1.5 (+1)	98.2
AG7	9 (+1)	0.5 (-1)	96.0
AG8	9 (+1)	1.0 (0)	97.1
AG9	9 (+1)	1.5 (+1)	97.7

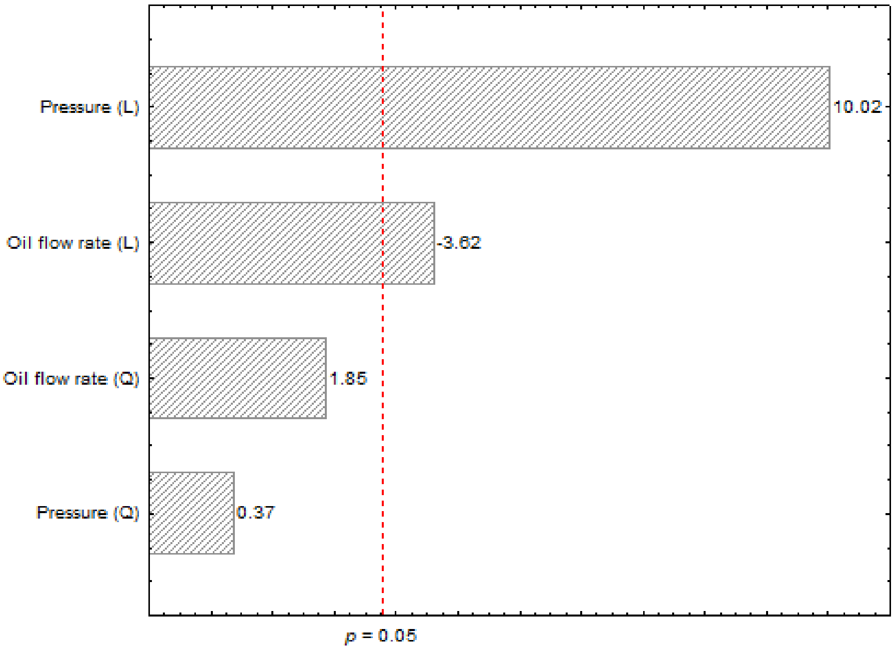

Fig. 3. Pareto chart of experimental planning on converting sunflower oil transesterification using an atomization reactor. The experiments were conducted with an ethanol: oil ratio of 60:1,1% (w/w) sodium hydroxide as a catalyst and a temperature of 50 °C.

IV. CONCLUSIONS

The study on the transesterification reaction using atomization technology is innovative, and exciting information about the process could be extracted. After the batch and semi-batch dripping experiments, increasing the alcohol: sunflower oil molar ratio improved the transesterification performance. Compared to the same dripping conditions, the reduction in the size of sunflower oil droplets by atomization was advantageous to the process. Increasing the atomization pressure led to better conversion results while increasing the sunflower oil flow rate was detrimental to conversion. The highest conversion value found was 98.3% at a temperature of 50 ºC, pressure of 1.5 bar, and oil flow of 3 g/min. In short, the proposed process presents attractive characteristics and can be used as an alternative to batch reactors for producing ethyl ester from ethanol.

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REFERENCES

[1] Manaf, I. S. A.; Embong, N. H.; Khazaai, S. N. M.; Rahim, M. H. A.; Yusoff, M. M.; Lee, T. K.; Maniam, G. P. (2019). A review for key challenges of the development of biodiesel industry. *Energy Conversion and Management*, v. 185, p. 508-517.

[2] Kumar, K.; Roy, K.; Moholkar, V.S. (2021). Mechanistic investigations in sonoenzymatic synthesis of n-butyl levulinate. *Process Biochem.*, 111 pp. 147-158.

[3] Oh, Y. K.; Hwang, K. R.; Kim, C.; Kim, J. R.; Lee, J. S. (2018). Recent developments and key barriers to advanced biofuels: a short review. *Biores Technol.* 257:320–333.

[4] Devarajan, Y. (2019). Experimental evaluation of combustion, emission and performance of research diesel engine fuelled Di-methyl-carbonate and biodiesel blends. *Atmos. Pollut. Res.*

[5] Giakoumis, E. G. et al. (2018). Estimation of biodiesel cetane number, density, kinematic viscosity and heating values from its fatty acid weight composition. *Fuel.*

[6] Bôas, R. N. V.; Mendes, M. F. (2022). A review of biodiesel production from non-edible raw materials using the transesterification process with a focus on influence of feedstock composition and free fatty acids. *J. Chil. Chem. Soc.*, v .67, n.1.

[7] Akubude, V.; Jaiyeoba, K.; Oyewusi, T.; Abbah, E.; Oyedokun, J.; Okafor, V. (2021). Overview on Different Reactors for Biodiesel Production. In *Biodiesel Technology and Applications*; Inamuddin, M.I., Ahamed, R.B., Mashallah, R., Eds.; Scrivener Publishing: Beverly, MA, USA, pp. 341–359.

[8] Phuong, X.; Pham, K. T.; Nguyen, T.; Pham, V.; Nguyen V. H. (2020). Biodiesels Manufactured from Different Feedstock: From Fuel Properties to Fuel Atomization and Evaporation. *ACS Omega*. 5 (33), 20842-20853.

[9] Chand, P., Reddy, C. V., Verkade, J. G., Wang, T., & Grewell, D. (2009). Thermogravimetric quantification of biodiesel produced via alkali catalyzed transesterification of soybean oil. *Energy & Fuels*, *23*(2), 989-992.

[10] Dias, T. P. V. B., Mielke Neto, P., Ansolin, M., Follegatti-Romero, L. A., Batista, E. A. C., & Meirelles, A. J. A. (2015). Liquid-liquid equilibrium for ternary systems containing ethylic biodiesel+ anhydrous ethanol+ refined vegetable oil (sunflower oil, canola oil and palm oil): experimental data and thermodynamic modeling. *Brazilian Journal of Chemical Engineering*, *32*, 699-706.

[11] Laosuttiwong, T., Ngaosuwan, K., Kiatkittipong, W., Wongsawaeng, D., Kim-Lohsoontorn, P., & Assabumrungrat, S. (2018). Performance comparison of different cavitation reactors for biodiesel production via transesterification of palm oil. *Journal of Cleaner Production*, *205*, 1094-1101.

[12] 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 nano-catalyst. *Scientific Reports*, *11*(1), 6708.

[13] Nezhad, A. H., Hashemi, S. J., & Tabatabaie, S. R. (2014). Biodiesel production from waste cooking oil using a stirred batch reactor. *J Nov App Sci*, *3*(10), 1125-1130.

[14] Rashid, A. B., & Kader, M. F. (2022). Performance analysis of an automated biodiesel processor. *Environmental and Climate Technologies*, *26*(1), 84-97.

[15] Unruean, P., Nomura, K., & Kitiyanan, B. (2022). High conversion of CaO-catalyzed transesterification of vegetable oils with ethanol. *Journal of Oleo Science*, *71*(7), 1051-1062.

[16] Deus, M. S., Deus, K. C., Lira, D. S., Oliveira, J. A., Padilha, C. E., & Souza, D. F. (2023). Esterification of Oleic Acid for Biodiesel Production Using a Semibatch Atomization Apparatus. *International Journal of Chemical Engineering*, *2023*.

[17] Hidayat, D., Widiyastuti, W., Ogi, T., & Okuyama, K. (2010). Droplet generation and nanoparticle formation in low-pressure spray pyrolysis. *Aerosol Science and Technology*, *44*(8), 692-705.