Vol. 24, No. 1(2025) IE244
Revista Mexicana de Ingeniería Química

Obtention of methyl esters fractions through distillation and pour point evaluation of the obtained fractions

Obtención de fracciones de ésteres metílicos mediante destilación y evaluación del punto de fluidez de las fracciones obtenidas

F.A.S. Mota[1]*, A.S.S. Furtado[2], A.B.V. Leitao[2], N.C. Medeiros[1], G.S. Pereira[1], M.N. Almeida[1], A. Oliveira[3], M.M. Oliveira[3], F.T.R. Caselli[1]
[1]Federal University of Piaui -Technology Center – Department of Production Engineering
Teresina-PI
[2]Federal University of Piaui -Technology Center – Department of Mechanical Engineering
Teresina-PI
[3]State University of Ceará, Science and Technology Center – Department of Physics
Fortaleza-CE

Received: May 21, 2023; Accepted: September 30, 2024

Abstract

The study aimed to obtain distilled fractions from babassu oil esters. A simulation of ester distillation was performed and compared with the results obtained from an actual distillation unit. Simulations were evaluated for both batch and continuous operations. However, the results from the continuous simulation showed a smaller percentage variation compared to the fractions obtained from the developed system. It was observed that the product from batch distillation contained higher fractions of constituents that could affect its flow properties. One such constituent, Methyl Esters (C18), had a pour point of 39.30°C. The continuous system operated with a reflux ratio (RR) of one. The product sample BK011107 had a pour point of -21.00°C, while samples from the batch system (BK0507F1) had a pour point of -18.00°C. A NRTL model was used in the simulation. The continuous process in the real distillation system yielded better compositional results.

Keywords: Methyl Esters, Distillation, Freezing Point.

Resumen

La obtención de fracciones destiladas de los ésteres del aceite de babassu se realizó en este trabajo. Así, se realizó una simulación de la destilación del éster y se comparó con el resultado obtenido en una unidad real. Por lo tanto, las simulaciones del sistema se evaluaron cuando está trabajando por lotes y continuamente. Sin embargo, los resultados de las muestras obtenidas por simulación continua trajeron un porcentaje de variación más pequeño con los valores de fracciones obtenidos en el sistema desarrollado. De la observación, se concluye que el producto obtenido de la destilación por lotes mostró altas fracciones de constituyentes que pueden afectar sus propiedades de flujo. Entre estos elementos, se encuentran los ésteres metílicos (C_{18}) que muestran un punto de fluidez de 39,30°C. Entre las porciones obtenidas, el sistema que trabaja continuamente con una relación de reflujo (RR) igual a uno. El producto de la muestra BK011107 indicó un punto de flujo igual a -21,00°C. Las muestras del sistema que operan en lote (BK0507F1) presentaron un punto de flujo igual a -18,00°C. Se ha utilizado un modelo NRTL en el simulador. El proceso continuo en un sistema de destilación real funcionó mejor en términos de composición.

Palabras clave: Ésteres metílicos, Destilación, Punto de congelación.

---

*Corresponding author. E-mail: assismota@ufpi.edu.br;
https://doi.org/10.24275/rmiq/IE244
ISSN:1665-2738, *issn-e*: 2395-8472

1 Introduction

The increasing global population, the need for new energy sources, and public awareness of the importance of cleaner fuels have made biodiesel a promising product. Studies and the development of new technologies are proving to be more efficient compared to fossil fuels and have less impact on nature (Araújo *et al.*, 2010; Atadashi *et al.*, 2011; Wang et al., 2014; Sánchez-Cárdenas *et al.*, 2021; Aldana-González *et al.*, 2022). As a result of this scenario, there has been an increase in demand for materials that can be used for biodiesel production. Raw materials of vegetable or animal origin have been widely sought after because they contain triglycerides, which can be converted into methyl or ethyl esters. These materials are easily accessible and assist in the separation of glycerine (Dunn *et al.*, 1996; Glisic *et al.*, 2007; Han et al., 2017; Sotoft *et al.*, 2007; Torres *et al.*, 2011; Okolie *et al.*, 2023; Yusuff *et al.*, 2023).

The primary method of biodiesel production is through a chemical process called transesterification. This process involves the use of an alcohol, typically methanol or ethanol, a catalyst (either basic or acid), and an ester derived from animal or vegetable sources. The molar fraction of alcohol to ester is typically 3:1. The ester itself is derived from carboxylic acids, specifically triglycerides found in long-chain form in oils (Panchal *et al.*, 2020; Soares *et al.*, 2020; Pandit *et al.*, 2023). Several factors can affect this chemical process, including the type and purity of the reactants and catalyst, the molar ratio, stirring of the mixture, temperature, and reaction time (Kumbhar *et al.*, 2022).

The boiling, freezing, and pour points of fatty acids are determined by factors such as the length of the carbon chain, the presence or absence of double bonds, and chemical interactions. These factors directly affect the choice between fatty acid methyl esters or fatty acid ethyl esters (Imahara *et al.*, 2006; Wes *et al.*, 2008; Mota *et al.*, 2010; Liston *et al.*, 2016; Miller *et al.*, 2022; Malode *et al.*, 2022). Triacylglycerols primarily composed of saturated fatty acids have high melting points, meaning they remain in a solid state at room temperature. On the other hand, triglycerides composed of unsaturated and polyunsaturated fatty acids have lower melting points and remain in a liquid state at room temperature (Yeong *et al.*, 2022; Carsten, 2023).

Oleaginous plants are natural sources of esters, and the choice of these plants directly impacts the quality of the oil and, consequently, the biofuel. One major drawback of using feedstock derived from plants with saturated constituents is the potential for freezing or reduced flow at low temperatures, which is currently one of the main problems in the marketing and industrialization of biofuel (May *et al.*, 2006; Troy; Chen *et al.*, 2017; Xue *et al.*, 2016; Macmillan, 1952; Mujtaba *et al.*, 2020; and Babinszki *et al.*, 2022). The Fog Point (FP) refers to the formation of paraffinic crystals at low temperatures. These crystals can agglomerate and restrict or block the flow of fuel in pipes and filters, leading to engine problems and reduced performance (Kumbhar *et al.*, 2022; Marques *et al.*, 2021).

Table 1 - Freezing points and fluidity of methyl esters.

Methyl Esters	Pour Point (°C)	Freezing Point (°C)
M- Caproate – C_6	-	-38.00
M-Caprylate - C_8	-	-35.37
M-Caprice - C_{10}	-	-13.00
M-Laureate - C_{12}	5.00	4.90
M-Myristate - C_{14}	18.50	18.00
M-Palmitate - C_{16}	30.50	29.50
M-Stearate - C_{18}	39.30	37.00
M-Oleate - $C_{18:1}$	-20.00	-21.00
M-Linoleate - $C_{18:2}$	-35.00	-36.00

Source: (May *et al.*, 2006; Suppes *et al.*, 2005, Troy and Macmillan, 1952).

An example of this issue can be seen in the use of biodiesel produced from oilseeds, such as babassu. Raw materials with a high percentage of saturated constituents can pose challenges in cold regions. Table 1 displays the constituents found in the composition of methyl biodiesel from babassu, along with their freezing points and fluidity.

When used as additives for biofuels, these compounds can help achieve a balance between saturated and unsaturated esters in the composition. Unsaturated esters contribute to the fluidity of the biofuel, while saturated esters can enhance its oxidative stability (Zarrinmehr *et al.*, 2021). Oxidation is a chemical process that involves the loss of electrons, often triggered by the presence of oxygen (O_2). Biodiesel is susceptible to oxidation due to the presence of double bonds, which are more reactive and can be easily broken by free radicals. These double bonds are primarily found in unsaturated fatty esters, and they can undergo unfavorable changes in their energy value and may generate elements harmful to human health (Lau *et al.*, 2022; Zarrinmehr *et al.*, 2021; Mantovani *et al.*, 2020; Lužaić *et al.*, 2023).

The objective of this study is to assess the composition variations of methyl esters obtained through continuous and batch distillation processes. Additionally, the study aims to differentiate the top products and evaluate the flow properties of the obtained phases.

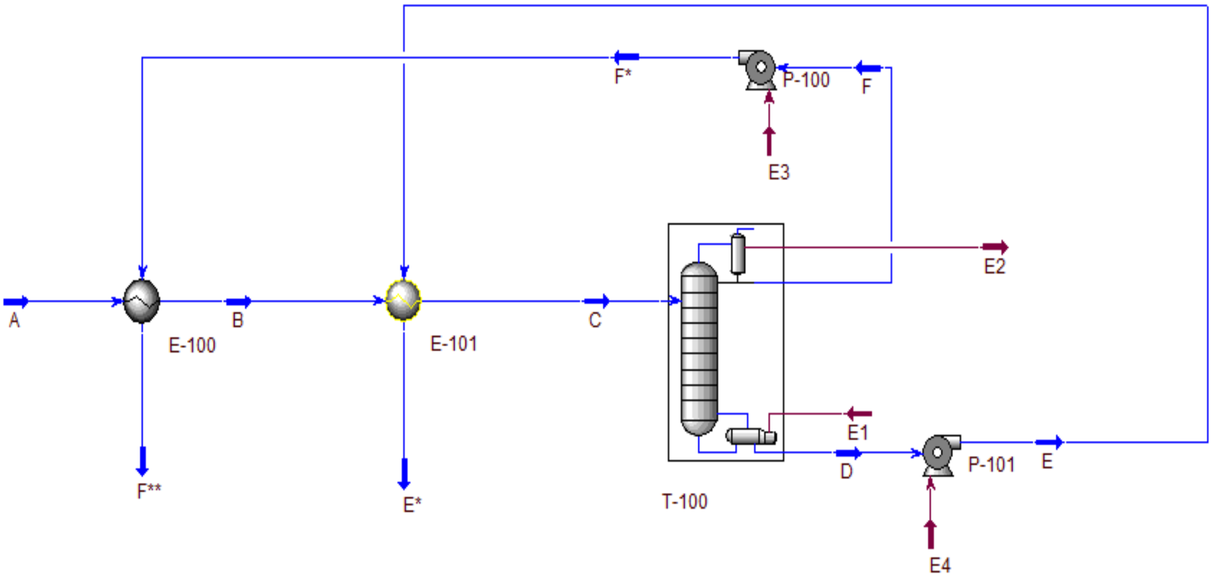


Figure 1 - The flowchart of the transesterification process.

Table 2 - Constituents and their respective mass flows.

Methyl Esters	Mass Flows (kg/h)
M- Caproate – C_6	0.18402
M-Caprylate - C_8	5.9473
M-Caprice - C_{10}	9.1548
M-Laureate - C_{12}	62.381
M-Myristate - C_{14}	34.184
M-Palmitate - C_{16}	25.299
M-Stearate - C_{18}	14.247
M-Oleate - $C_{18:1}$	39.323
M-Linoleate - $C_{18:2}$	9.2796

Source: (May *et al.*, 2006; Suppes *et al.*, 2005, Troy and Macmillan, 1952).

The simplified flowchart of the transesterification of the babassu oil process and its components of the pilot plant is shown in Figure 1.

2 Methods

2.1 Simulation in Aspen Hysys®

In the simulation, a distillation tower was implemented to determine the optimal number of stages for achieving the desired top composition. The feed composition consisted of babassu biodiesel, which includes methyl stearate. The NRTL thermodynamic model was used, which allowed for the calculation of activity coefficients for the components. The tower was operated under a vacuum of 10 mmHg. The reflux ratio (RR), the number of theoretical stages evaluated, and the results were presented to gain insights into the operation of the unit. The simulation parameters related to the mass flows of the components used in *Aspen Hysys*® are presented in Table 2.

2.2 Transesterifications of Babassu Oil

The transesterification of babassu oil was conducted in a laboratory experiment using homogeneous catalysis. The process involved two stages and two reactions. In the first reaction, 220.85g of babassu oil was mixed with 37.94g of methanol and 8.42g of catalyst solution (NaOH dissolved in alcohol). After the first reaction, the resulting products (esters, alcohol, and glycerol) were left undisturbed in a decantation flask for 45 minutes to allow for the separation of glycerin. In the second reaction, 191.47g of esters from the first reaction were combined with 8.11g of catalyst solution and 37.05g of methanol. These steps were performed to achieve a higher conversion of babassu oil into methyl esters.

2.3 Analysis of the Produced esters and Distillates

2.3.1 Gas Chromatography (CG)

The chemical composition of the fatty acids in the oil was determined using gas chromatography (GC) with a flame ionization detector (FID). The compounds were identified by comparing the retention time of the sample with the standard retention times of fatty acids in the chromatogram. Quantification was achieved by converting the peak areas to concentrations using calibration curves of the standard patterns.

The analyses were conducted using a Shimadzu Model 17 instrument equipped with a Supelco capillary column containing 5% phenyl and 95% dimethylpolysiloxane. The column had a length of 100m, an internal diameter of 0.25mm, and a stationary phase with a thickness of 0.25μm. Nitrogen was used as the carrier gas. The operating conditions were as follows: an initial column temperature of 150°C, a detector temperature of 280°C, and a column temperature program with a ramp rate of 15°C/min up to 240°C, held for 2 minutes, followed by a ramp rate of 20°C/min up to 260°C, maintained for 21 minutes. Other chromatographic parameters included a split mode of 1:30, a pressure of 206 atm, a gas flow rate of 1.5 mL/min, a linear velocity of 32.6 ml/min, and a total flow rate of 55 ml/min.

2.3.2 *Analysis of Pour Point*

The freezing point of the distilled ester fraction was determined using the ASTM D7154/IP528 method. In this method, a sample of the ester fraction was placed in a container and the container was then agitated to observe the point at which the ester fraction stopped flowing, indicating its freezing point.

2.3.3 *Developing a Pilot Unit*

The unit is designed to operate with a flow rate of 10 L/h and a reflux ratio of one. These specifications were determined based on data obtained from the system simulation.

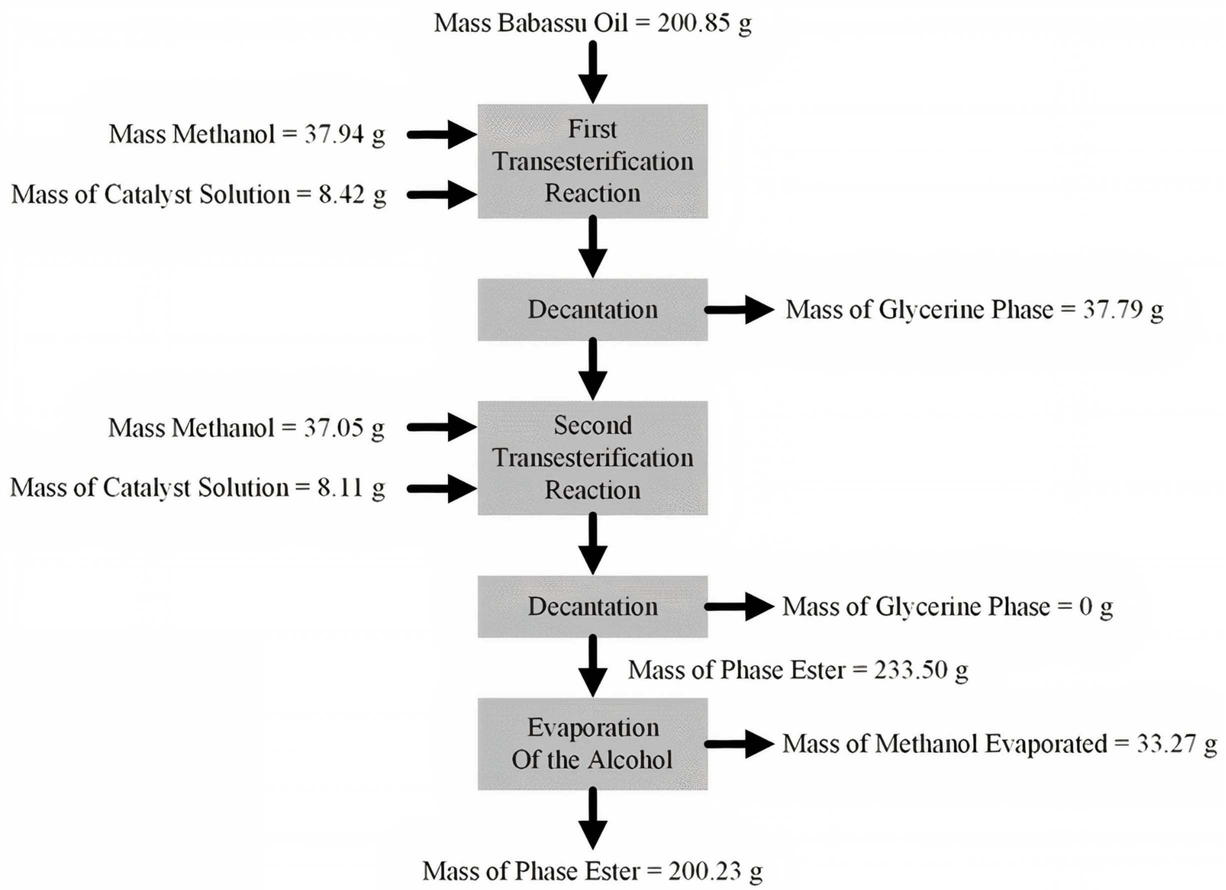


Figure 2 - Mass balance obtained in the production of phase ester of babassu.

Table 3 - Constituents and their respective residence times.

Constituents	Residence Time (min)
M- Caproate – C_6	3.06
M-Caprylate – C_8	6.24
M-Caprice – C_{10}	10.95
M-Laureate – C_{12}	15.95
M-Myristate – C_{14}	20.64
M-Palmitate – C_{16}	24.02
M-Stearate – C_{18}	26.43

3 Results and discussion

3.1 *Mass Balance in Stage of Transesterification*

A clear understanding of the necessary steps to obtain phases with desired flow properties is to achieve producing methyl esters in stoichiometric terms. Figure 2 illustrates the flowchart of the ester

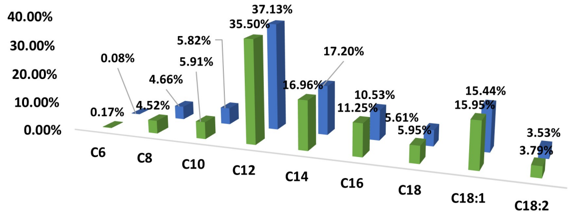


Figure 3 - Analysis of Conversion.

blocks in the production laboratory workbench. Once the balance is established, any increase in quantity should follow the proportions outlined in this step.

3.2 *Chromatographic Analysis of Biodiesel Obtained*

Tests were conducted to analyze the impact of the ester conversion phase on the components of the babassu. The production conditions and workbench tests for both phases were as follows. Chromatography analyses were performed and are presented in Table 3. The results are displayed based on the retention time of the constituents in the chromatographic column.

The biodiesel being monitored was classified as BD014 and BD017. By analyzing the retention time on the column and calculating the area in terms of concentration, values were obtained for the composition of each methyl ester produced. The comparison between the samples is depicted in Figure 3. Based on the analysis of these results, it can be observed that both tests had the same composition in terms of percentage. The only methyl ester that had a proportion higher than 2% in terms of percentage was Methyl Laureate C_{12}.

3.3 *The unit is designed for distillation with partial condensation phases*

The composition of esters in the fractions obtained after the transesterification step has been assessed and these data have been incorporated into the simulator for which the unit was designed. The general configuration of the unit is showed in Figure 4.

The designed system can perform batch or continuous distillation. During the distillation process, the separation of phases was observed. The unit is configured for partial condensation. Due to the close boiling points of the base compounds, it is challenging to fractionally distill and isolate each ester in a distillation unit. Similar to the separation of oil fractions, the unit is designed to separate ester fractions with similar boiling points. Since one of the specified properties of biodiesel is its oxidative stability, the system operates under a vacuum of 10 mmHg. This vacuum reduces the boiling points of the phases to be separated. As a result, the developed system separates the phases in collection tanks.

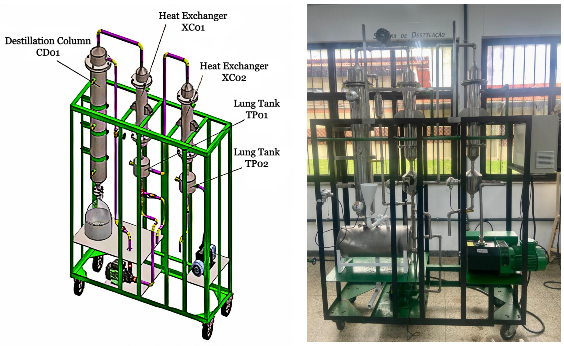


Figure 4 – Pilot plant for distillation of methyl esters of babassu.

Table 4 - List of equipment on the unit.

TAG	Equipment	Function
CD01	Distillation Column	Distill Light Fractions of Esters
XC01	Condenser 1- Middle Phase	Condense Distillates
XC02	Condenser 2 – Light Phase	Condense Distillates
TP01	Lung Tank to Collect Condensates	Collect Condensates
TP02	Lung Tank to Collect Condensates	Collect Condensates

The list of equipments that compounds the unit is presented in Table 4.

3.4 *Distillation Process*

The distillation process was evaluated for both batch and continuous distillation methods. Samples were collected from the distillates, specifically from the lighter fractions of the phases. Samples were obtained after both batch and continuous distillation processes. Table 5 presents the samples obtained from the distillation process, along with the temperature ranges observed in the reboiler and the top of the column. The table also includes the phase code for each sample and the distillation process used.

3.5 *Monitoring of the Distillation Process*

This topic will be divided into two sections: the monitoring of the batch process and the monitoring of the continuous process. These two processes not only have different monitoring points but also yield different compositions of distillates.

Table 5 - Operating conditions in the prototype used.

Distillation Type	Code Samples	Operating Conditions Temperature of the Reboiler/top	
Batch	BK0507F1	154°C	164°C
Continuous	BK011107	210°C	180°C

Table 6 - Simulation of the top composition.

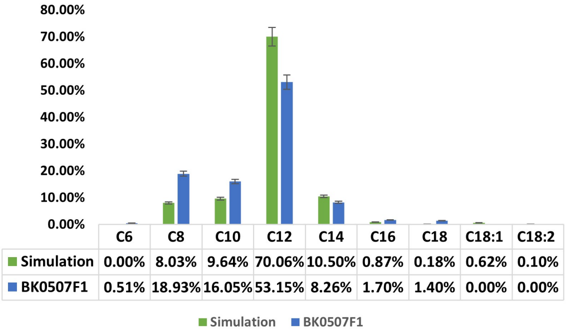
Constituents	Top Composition (%)
C_6	0.0
C_8	8.03
C_{10}	9.64
C_{12}	70.06
C_{14}	10.50
C_{16}	0.866
C_{18}	0.179
$C_{18:1}$	0. 633
$C_{18:2}$	0.097

3.5.1 *Monitoring of the top product obtained - Batch Process*

The most effective method to evaluate the distillation process is by comparing the simulation results with the chromatographic data and analyzing the efficiency of the simulation. Table 6 presents the results of the top composition of the distillate in the tower operating with differential distillation (batch). It can be observed from the table that methyl caproate (C_6) is not present as a top product in this simulation when considering two decimal places. Additionally, in this analysis, it is evident that at 10 mmHg, methyl laurate (C_{12}) has the highest percentage.

The comparison between the two is shown in Figure 5. The data obtained from the simulation differ from those obtained in the pilot system. The percentage of methyl caprylate (C_8) as a product was above 10%, whereas products like methyl laurate (C_{12}) showed values below 70% by weight. In the same simulation, under the same controlled conditions, the presence of $C_{18:2}$ (linoleic methyl) was observed, while it was not observed in the actual equipment. It is important to note that the simulation results diverged from the pilot unit. This discrepancy may be because the thermodynamic model used is not suitable for accurately representing the intermolecular behavior of the assessed phases.

Another parameter that needs to be analyzed is the hydrodynamics of the designed tower, as it may not be conducive to the mass exchange process of the mixture. While phase separation has been observed, the drag of constituents C_{14} to C_{18} (methyl myristate to methyl stearate) can potentially compromise the flow properties of the phase. This is because these constituents have pour points ranging from 18.00°C to 39.00°C.



	C6	C8	C10	C12	C14	C16	C18	C18:1	C18:2
Simulation	0.00%	8.03%	9.64%	70.06%	10.50%	0.87%	0.18%	0.62%	0.10%
BK0507F1	0.51%	18.93%	16.05%	53.15%	8.26%	1.70%	1.40%	0.00%	0.00%

Figure 5 - Simulation Analysis versus BK0507F1.

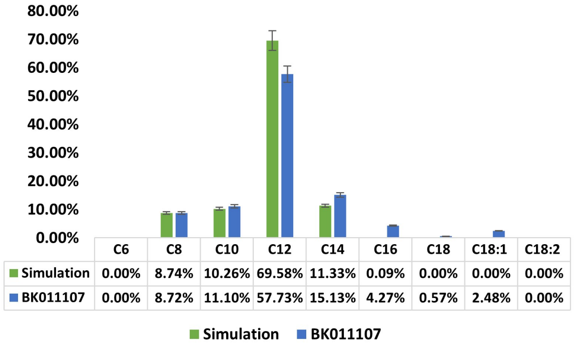
The results of batch distillation indicate that the simulated fractions differ from the actual product obtained from the equipment. Therefore, during batch operation, it is crucial to ensure that the mechanisms of heat and mass transfer are properly observed. The hydrodynamics of the tower must be designed in a way that facilitates the transfer of mass within its filling.

3.5.2 *Monitoring of the top product obtained - Continuous Process*

The evaluation of heat transfer mechanisms and mass transfer that could affect the top product was conducted, focusing on the study of the continuous feeding process into the distillation tower. In this evaluation, the feeding condition (stage/dish feed) and the reflux ratio (RR) were set. The top product conditions included a vacuum of 10 mmHg and a reflux ratio equal to one. In this simulation, the component with the highest concentration at the top of the column was methyl laurate (C_{12}), which accounted for 69.58% of the total composition.

In this simulation, elements with flow properties that could potentially impact the final product have low percentage concentrations. These elements include Methyl Palmitate (C_{16}) and Methyl Stearate (C_{18}). However, if present in high concentrations, these two elements can significantly affect the ester mixture due to their pour points of 30.50°C and 39.30°C, respectively. On the other hand, the top fraction also contains elements with low freezing points, such as Methyl Caprylate and Methyl Caprice, which together account for approximately 19.00% of the mixture.

The sample obtained from the continuous distillation system was labeled as BK011107. In this test, the percentage of C_{12} obtained was 57.73%, whereas the simulation result was approximately



	C6	C8	C10	C12	C14	C16	C18	C18:1	C18:2
🟩 Simulation	0.00%	8.74%	10.26%	69.58%	11.33%	0.09%	0.00%	0.00%	0.00%
🟦 BK011107	0.00%	8.72%	11.10%	57.73%	15.13%	4.27%	0.57%	2.48%	0.00%

Figure 6 - Simulation Analysis versus BK01107.

69.58% (a reduction of about 12.00%). The elements that make up the C_8 and C_{10} fractions were obtained in percentages of 8.72% and 11.10%, respectively.

The values obtained in this test were very close to those evaluated in the simulation. These data suggest that the designed system has effective mass transfer and heat exchange mechanisms. Factors that may contribute to the agreement between the simulated and obtained compositions in the system tests include the maintenance of equilibrium points, flood factor, tower hydrodynamics, and efficient mass transfer and heat exchange. Unlike batch distillation (differential), in continuous distillation, the phases are continuously kept in equilibrium, which helps to maintain consistency between the simulated and obtained compositions.

Based on Figure 6, it can be concluded that in all tests, the value of C_{12} obtained was approximately 57.00% of the total composition. Among the tests, the BK011107 (continuous process) showed a higher proportion of C_{12}. In terms of obtaining components in the C_6-C_{10} range, the test conducted with sample BK0507F2 yielded a better result, with approximately 20%. However, this sample also had a higher percentage of C_{18} (Methyl Stearate).

The comparison of flow points between the samples obtained from the batch and continuous systems is presented in Table 7. Based on the results, it can be concluded that the continuous system generated samples of methyl esters with a lower freezing point (-21.00°C). Although sample BK0507F1 showed larger portions in the C_6-C_{10} range, it had a higher freezing point compared to BK11107. This is because BK0507F1 has a higher percentage of C_{18} (Methyl Stearate), which contributes to the higher freezing point. The selection of the batch and continuous distillation process is based on verifying and comparing the mass transfer regime. In the continuous regime, a higher percentage of the C18:1 component, around 2.48%, can be observed. However, in the batch process, the percentage is almost zero, as shown in Figure 5 and Figure 6.

Table 7 - Flow Properties of the Distilled Fractions.

Sample	Density (Kg/m^3)	Freezing Point (°C)
BK0507F1	878.80	-18.00
BK011107	871.80	-21.00

The estimated confidence in the study was 95%, and the p value in the variance test was equal to one. This indicates that the samples are similar, suggesting that there is no significant variation in the test compositions.

Conclusion

In this study, the continuous distillation in differential mode (batch) of babassu oil's esters was evaluated. Babassu biodiesel was chosen for this evaluation due to its ester fractions that have low freezing points. The esters present in babassu biodiesel range from C_6 to $C_{18:2}$. When these esters are isolated, they can have a freezing point as low as -38.00°C (Methyl Caproate - C_6), while others, such as Methyl Stearate (C_{18}), can be solid under normal temperature and pressure conditions. The results obtained from the two distillation processes revealed differences between the top samples and the simulation using *Hysys*®. However, the products obtained from continuous distillation showed good agreement with the distillation results. In this case, the continuous feed and the maintenance of phase balance can contribute to the consistency between the simulation and the distillation system. Therefore, the effective separation of different methyl ester fractions can contribute to the desired flow properties of the final product.

The purpose of this research is to obtain esters with low freezing points and fractions of esters from different chains. This research will serve as a technological foundation for future studies that aim to use these distillation products as mixtures in fuels that require fractions with low freezing points. One example of such application is the production of blends with aviation fuels. This research opens new possibilities for the production of Sustainable Aviation Fuels (SAFs) using various raw materials.

References

Aldana-González, M.G., Gómez-Castro, F.I., Romero-Izquierdo, A.G., Conde-Mejía, C., Gutiérrez-Antonio, C., Morales-Rodríguez, R. Supercritical biodiesel production: Feasibility of energy integration with a bioethanol production process. *Revista Mexicana de Ingeniería Química*, v. 21, n. 1 (2022). DOI: https://doi.org/10.24275/rmiq/Proc2534.

Araújo, V. K. W. S., Hamacher, S and Scavarda, L. F. "Economic assessment of biodiesel production from waste frying oils". Bioresource Technology, 101, 4415–4422 (2010).

Atadashi, I. M., Aroua, M. K. and Aziz, A. A. "Biodiesel separation and purification": *A review. Renewable Energy*, 36, 437- 44 (2011).

Babinszki, B., Jakab, E., Terjék, V., Sebestyén, Z. Czirok, I. S., Bozi, J., Attanatho, L., Thanmongkhon, Y., Czégény, Z. In situ formation of fatty acid methyl esters via thermally assisted methylation by lignin during torrefaction of oil palm biomass. *Journal of Analytical and Applied Pyrolysis*, Volume 168, 2022, 105720, ISSN 0165-2370, https://doi.org/10.1016/j.jaap.2022.105720.

Bósquez-Molina, E. (2002). Water vapor permeability of edible films. Presentación 100B-34. 15-19 Junio. Anaheim, California: *Institute of Food Technologists Annual Meeting.*

Bourriot, S., Garnier, C. y Doublier, J.L. (1999). Phase separation, rheology, and microstructure of micellar casein-guar gum mixtures. *Food Hydrocolloids 7*, 90-95.

Carsten Wedler, C., J.P. Martin Trusler, J. P. M. Review of density and viscosity data of pure fatty acid methyl ester, ethyl ester and butyl ester. *Fuel*, Volume 339, 2023, 127466, ISSN 0016-2361, https://doi.org/10.1016/j.fuel.2023.127466.

Carvajal, M. N. (2000). *Estudio del Sembrado en Procesos de Cristalización por Lotes*. Tesis de Maestría en Ciencias en Ingeniería Química, Instituto Tecnológico de Celaya, México.

Chen, W., Wang,Y., Ding, M.,Shi, S and Yang, Z. "Crystallization behaviors and rheological properties of biodiesel derived from methanol and ethanol". *Fuel*, 207, 503–509 (2017).

Dunn, R.O., Shockley, M.W and Bagby, M.O."Improving the low-temperature flow properties of alternative diesel fuels: vegetable oil-derived methyl esters". *J Am Oil Chem Soc.*, 73, 1719–1728 (1996).

Glisic, S., Montoya, O., Orlovic, A and Skala, D. "Vapor–liquid equilibria of triglycerides–methanol mixtures and their influence on the biodiesel synthesis under supercritical conditions of methanol". J. Serb. *Chem. Soc.*, 72, 13–27 (2007).

Grases, F. F., Costa, B. A. y Söhnel, O. (2000). *Cristalización en disolución, conceptos básicos*. Editorial Reverté, México.

Han, P., Genkuo Nie, G., Xie, J, Xiu-tian-feng, E., Pan, L., Zhang, X and Zou, J.J. "Synthesis of high-density biofuel with excellent low-temperature properties from lignocellulose-derived feedstock". *Fuel Processing Technology*,163, 45–50 (2017).

Imahara, H., Minami E and Saka. S. "Thermodynamic study on cloud point of biodiesel with its fatty acid composition". *Fuel*, 85,1666–1670 (2006).

Krochta, E.M. (1990). Emulsion films on food products to control mass transfer. En: *Food Emulsions and Foams*, (E.L. Gaden y E. Doi, eds.), Pp. 65-78. Plenum Press, Nueva York.

Kumbhar, V., Pandey, A., Sonawane, C. R., El-Shafay, A.S., Panchal, H., Chamkha, A. J. Statistical analysis on prediction of biodiesel properties from its fatty acid composition. *Case Studies in Thermal Engineering*, Volume 30, 2022, 101775, ISSN 2214-157X, https://doi.org/10.1016/j.csite.2022.101775.

Lau, C. H., Gan, S., Lau, H. L. N., Lee, L. Y., Thangalazhy-Gopakumar, S., Kiat Ng, H. Insights into the effectiveness of synthetic and natural additives in improving biodiesel oxidation stability. *Sustainable Energy Technologies and Assessments*, Volume 52, Part D, 2022, 102296, ISSN 2213-1388, `https://doi.org/10.1016/j.seta.2022.102296`.

Lužaić, T., Kravić, S., Stojanović, Z., Grahovac, N., Jocić, S., Cvejić, S., Pezo, L., Romanić, R. Investigation of oxidative characteristics, fatty acid composition and bioactive compounds content in cold pressed oils of sunflower grown in Serbia and Argentina. *Heliyon*, Volume 9, Issue 7, 2023, e18201, ISSN 2405-8440, https://doi.org/10.1016/j.heliyon.2023.e18201.

Mantovani, A. C. G., Chendynski, L. T., Galvan, D., Macedo, F. C. J., Borsato, D., Mauro, E. Thermal-oxidation study of biodiesel by proton nuclear magnetic Resonance (1H NMR). *Fuel*, Volume 274, 2020, 117833, ISSN 0016-2361, https://doi.org/10.1016/j.fuel.2020.117833.

Malode, S. J. Gaddi, S. A. M. Kamble, P. J. Nalwad, A. A. Muddapur, U. M. Shetti, N. P. Recent evolutionary trends in the production of biofuels. *Materials Science* *for Energy Technologies*, Volume 5, 2022, Pages 262-277, ISSN 2589-2991, DOI: https://doi.org/10.1016/j.mset.2022.04.001.

May, C.H., Dian, N.L.H.M., Liang, Y.C., Foon, C.S., Ngan, M.A., Hock, C.C. "Crystallization and Melting Behavior of Methyl of Palm Oil". *American Journal of Applied Science*, 1859 - 1863 (2006).

Miller, J. H. *et al*. Screening and evaluation of biomass upgrading strategies for sustainable transportation fuel production with biomass-derived volatile fatty acids. *iScience*, Volume 25, Issue 11, 2022, 105384, ISSN 2589-0042, https://doi.org/10.1016/j.isci.2022.105384.

Mota, C.J.A., Silva, P.H.R and Gonçalves, V.L.C. "Glycerol acetals as anti-freezing additives for biodiesel". *Bioresource Technology*, 101, 6225–6229 (2010).

Mujtaba, M.A., Haeng Muk Cho, Masjuki, H.H., Kalam, M.A., Ong, H.C., Gul, M., Harith, M.H., Yusoff, M.N.A.M. Critical review on sesame seed oil and its methyl ester on cold flow and oxidation stability. *Energy Reports*, Volume 6, 2020, Pages 40-54, ISSN 2352-4847, https://doi.org/10.1016/j.egyr.2019.11.160.

Okolie, J. A., Awotoye, D., Tabat, M. E., Okoye, P. U., Epelle, E. I., Ogbaga, C. C., Güleç, F., Oboirien, B. Multi-criteria decision analysis for the evaluation and screening of sustainable aviation fuel production pathways. *iScience*, Volume 26, Issue 6, 2023, 106944, ISSN 2589-0042, https://doi.org/10.1016/j.isci.2023.106944.

Panchal, B., Chang, T., Qin, S., Sun, Y., Wang, J., Bian, K. Optimization of soybean oil transesterification using an ionic liquid and methanol for biodiesel synthesis. *Energy Reports*, Volume 6, Supplement 7, 2020, Pages 20-27, ISSN 2352-4847, DOI: `https://doi.org/10.1016/j.egyr.2019.11.028`.

Pandit, C. Srijoni Banerjee, S., Pandit, S., Lahiri, D., Kumar, V., Chaubey. K. K., Al-Balushi, R., Al-Bahry, S., Joshi, S. J. Recent advances and challenges in the utilization of nanomaterials in transesterification for biodiesel production. *Heliyon*, Volume 9, Issue 4, 2023, e15475, ISSN 2405-8440, `https://doi.org/10.1016/j.heliyon.2023.e15475`.

Roger V. Marques, R. V., Guidoni, L. L. C., Araujo, T. R., Santos, M. A. Z., Pereira, C. M. P., Duval, E. H., Corrêa, L. B., Corrêa, E. K. Modification of bovine fatty waste with strains of Staphylococcus xylosus: Feedstock for biodiesel. *Environmental Challenges*, Volume 4, 2021, 100180, ISSN 2667-0100, https://doi.org/10.1016/j.envc.2021.100180.

Sánchez-Cárdenas *et al*. Esterification of oleic acid into biodiesel and use it as fuel in a diesel engine to determine its impact. *Revista Mexicana de Ingeniería Química* Vol. 21, No. 3(2022)., ISSN: 1665-2738. DOI: https://doi.org/10.24275/rmiq/Ener2969.

Saunders, L. (1994). Beverage creation. *Design elements*. Disponible en: www.foodproductdesign.com/archive

Soares, S. Rocha, F. R.P. Green volumetric procedure for determining biodiesel content in diesel blends or mixtures with vegetable oils exploiting solubility differences in ethanol: water medium. *Fuel*, Volume 276, 2020, 118042, ISSN 0016-2361, `https://doi.org/10.1016/j.fuel.2020.118042`.

Sotoft, L. F., Rong, B. G., Christensen, V. K. and Norddah L, B. "Process simulation and economical evaluation of enzymatic biodiesel production plant". *Bioresource Technology*, 101, 5266–5274 (2010).

Suppes, G.J., Goff, M.J and Dasari, M.A. "Interpreting freezing point depression of stearic acid and methyl stearate". *Fluid Phase Equilibria*, 238, 149–156 (2005).

Torres, M., Jiménez-Osés, G., Mayoral, J.A ans Pires, E. "Fatty acid derivatives and their use as CFPP additives in biodiesel". *Bioresource Technology*, 102, 2590–2594(2011).

Troy, A.S and Macmillan, D. "Vapor pressure and distillation of Methyl Esters of some Fatty Acids". *Ind. Eng. Chem*., 44, 172–175 (1952).

Xue,Y., Zhao,W., Ma,P.,Zhao, Z., Xu,G., Yang,C., Chen, H., Lin, H and Han, S. (2016). Ternary blends of biodiesel with petro-diesel and diesel from direct coal liquefaction for improving the cold flow properties of waste cooking oil biodiesel. *Fuel*, 177, 46-52.

Wang, M., Nie, K., Hao Cao, H., Deng, L., Fang Wang, F and Tan, T. "Biodiesel production by combined fatty acids separation and subsequently enzymatic esterification to improve the low-temperature properties". *Bioresource Technology*, 174, 302-305(2014).

West, A. H., Posarac, D. and Ellis, N. "Assessment of biodiesel production process using HYSYS". *Bioresource Technology*, 99, 6587–6601(2008).

Yeong, S. P., Chan, Y. S., Law, M. C., Ling, J. K. U. Improving cold flow properties of palm fatty acid distillate biodiesel through vacuum distillation. *Journal of Bioresources and Bioproducts*, Volume 7, Issue 1, 2022, Pages 43-51, ISSN 2369-9698, `https://doi.org/10.1016/j.jobab.2021.09.002`

Yusuff, A. S., Dada, T., Olateju, I. I., Azeez, T. M., Azeez, S. O. Experimental investigation of the influence of methyl, ethyl, and methyl-ethyl ester blends of used cooking oil on engine performances and emissions. *Energy Conversion and Management*: X, Volume 17, 2023, 100346, ISSN 2590-1745, `https://doi.org/10.1016/j.ecmx.2023.100346`

Zarrinmehr, M. J., Daneshvar, E., Nigam, S., Gopinath, K. P., Biswas, J. K., Kwon, E. E., Wang, H., Farhadian, O. Bhatnagar, A. The effect of solvent polarity and extraction conditions on the microalgal lipids yield, fatty acids profile, and biodiesel properties. *Bioresource Technology*, Volume 344, Part B, 2022, 126303, ISSN 0960-8524, `https://doi.org/10.1016/j.biortech.2021.126303`