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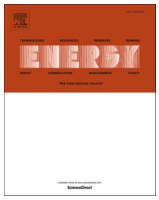

Techno-economic evaluation of transesterification processes for biodiesel production from low quality non-edible feedstocks: Process design and simulation

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ABSTRACT

The global demand for fossil fuels has led to increased pollutant emissions and depleted fossil fuel resources. Biodiesel, a fossil fuel alternative, is widely produced via transesterification. This study assesses the techno-economic performances of three transesterification processes (alkaline, acid, and CaO catalytic) for biodiesel production from low-quality non-edible feedstocks. The study explores effects of elevated free fatty acids (FFAs) and oil/ethanol flow rates on these processes, focusing on their impact on yield, purity, economics and energy aspects. Aspen Plus® V10 software was used for simulations. Despite meeting international biodiesel standards, significant technical and economic variations exist among the processes. The acid catalytic process exhibits energy requirements surpassing those of alkaline and CaO catalytic processes by over 29.58%, leading to operational costs exceeding those of CaO catalysis by 13.11%. The study establishes CaO catalysis as the most feasible option due to its simplicity, adaptability, and substantial energy and cost reductions. By introducing a closed-loop blending setup configuration, the study reveals that CaO catalysis outperforms alkaline and acid catalysis, achieving 11.59% cost reduction and 13.31% energy decrease in closed-loop configurations. The overall results highlight the potential of non-edible feedstocks in biodiesel production for a more environmentally friendly and sustainable energy future.

1. Introduction

The global energy sector has seen a growth in the last two decades [1], largely driven by an increasing demand for fossil fuels due to population growth [2]. However, this dominance of fossil fuels, projected to continue until 2050 [3], has led to various socio-economic challenges including supply-demand [4] and environmental challenges [5], prompting a need to transition to renewable energy sources. Researchers are increasingly exploring sustainable alternatives [6,7], and biodiesel is emerging as a promising option due to its renewability and potential to decrease reliance on fossil fuels while mitigating environmental impacts [8–10]. Despite its potential, the high production costs of biodiesel, particularly attributed to feedstocks and catalysts, pose a significant challenge [11–13]. To address this, there's a shift towards utilizing low quality non-edible feedstocks, offering both environmental sustainability and economic viability [14–17]. These low quality non-edible feedstocks, including Jatropha curcas [18–20] and various other tree species [21–26], present significant potential for biodiesel production. However, they come with challenges such as higher impurity levels, necessitating additional processing steps and leading to increased production costs [17,27–29]. This, in turn, affects the retail price per unit, potentially hindering widespread adoption of biodiesel. Thus, while biodiesel from low quality non-edible feedstocks holds potential for improving energy security, mitigating environmental challenges and reducing dependence on imported fossil fuels, overcoming production cost barriers is central for its widespread adoption in the market.

In relation to this barriers, the advancements in various technologies for the production of biodiesel have given rise to two primary methodologies: catalytic [30–32] and non-catalytic [33,34]. Both of these approaches aims to tackle challenges linked with biodiesel production, such as managing high levels of free fatty acids (FFA) and water content in non-edible feedstocks [35], increased production costs [36], and the

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release of nitrous oxide (NOx) emissions [37]. Catalytic and non-catalytic techniques serve different purposes in chemical reactions. Within catalytic processes, catalysts accelerate reactions by diminishing necessary energy without depletion [38,39]. Equally, in non-catalytic reactions, the reaction takes place because of the natural characteristics of the substances participating, like their chemical makeup, molecular arrangement, and how they react. Catalytic technology involves vital reactions - transesterification and esterification [35,40] offering flexibility in utilizing alcohols such as methanol, ethanol, propanol, and butanol, with methanol being preferred due to its affordability, accessibility, and higher reactivity [41]. Catalytic transesterification reactions can employ homogeneous or heterogeneous catalysts [30,31], occasionally aided by lipase enzymes [42,43]. In industrial biodiesel production, homogeneous alkali catalysis is widespread, with substances such as sodium methoxide, sodium hydroxide, and potassium hydroxide being commonly used [44–46]. This approach offers several advantages over acid catalysts [17,41]. These advantages include improved accessibility, cost-effectiveness, efficient conversion, and the use of mild reaction conditions. However, alkali catalysts also present drawbacks such as increased methanol requirements, extended neutralization intervals, and higher wastewater volumes, contributing to elevated processing costs [47–49]. In contrast, heterogeneous catalysts are employed due to their high catalytic efficiency, accelerated conversions, reduced soap formation, and lower effluent production [50,51], thus improving processing efficiency and reducing costs and environmental impact [52]. The advancements of these biodiesel production techniques hold significant position, envisioning a more economically viable and ecologically responsible biodiesel industry.

There have been several studies, reports and reviews on techno-economic analysis of biodiesel production from various feedstocks, spanning from edible to non-edible materials. Gebremariam and Marchetti [53] conducted a study to assess how changes in production capacity and fluctuations in biodiesel prices and oil costs impact the techno-economic performance of three distinct biodiesel production processes. The findings concluded the economic viability of CaO catalyzed biodiesel production as compared to supercritical ethanol and solid acid catalyzed alternatives. Further, it was found that the economic feasibility of the biodiesel production industry is predominantly influenced by oil prices, with higher production capacities favouring the profitability of the CaO catalyzed method. In another study, the discussion around using multifunctional catalysts to enhance biodiesel production with moderately high FFA feedstocks (ranging from 2.47% to 3.25%) was also noted [54]. The main focus in this study was on assessing the catalyst properties, increasing production yield, and meeting quality criteria. The study revealed the significance of having specialized multi-function catalysts with long-lasting qualities to simultaneously convert low cost feedstocks using esterification and transesterification. Aniokete and Aniaku [55] studied the economic and environmental aspects of converting animal fat oil (AFO) into biodiesel using a solid catalyst made from waste materials. The comparison between this waste-derived catalyst (HSOD) with a traditional acid catalyst (H_2SO_4) using ASPEN software in a techno-economic analysis was done. The study among others concluded that applications of waste-derived HSOD is economically viable in comparison with that of H_2SO_4 during transesterification of AFO to biodiesel.

However, it is clear that none of these researches and reports specifically addresses the impact of elevated FFA content on biodiesel production, which is a critical factor that can hinder the quality, efficiency, and energy consumption of the final product, especially when non-edible feedstocks are involved. It is also evident that biodiesel production challenges and opportunities vary significantly across different regions globally due to differences in feedstock availability, infrastructure, and market conditions. In addition, these reports and reviews focus point was hinged on issues like the cost of capital, the cost of production, the internal rate of return, the net present value, and the payback period. However, the specific economic influence of elevated FFA content on these metrics have not been given fully considerations. The knowledge of how elevated FFA content levels influence economic metrics is crucial for assessing the feasibility of any proposed biofuel project. However, the examined reports and reviews primarily emphasize evaluating biodiesel production technologies and feedstocks. Unfortunately, they do not directly address the impact of FFA content levels on economic aspects. This lack of connection highlights the absence of an in-depth analysis on how different catalytic and non-catalytic transesterification processes perform when faced with elevated FFA content. An in-depth analysis in this area holds significance because the choice of transesterification process significantly impact both the yield and quality of biodiesel under elevated levels of FFAs [56–58]. Moreover, the existing literature do not comprehensively addresses specifically how elevated FFA content influences energy consumption and thus efficiency in the production process. Additionally, there is a scarcity of literature that addresses the consequences of increased FFA levels and the associated cost implications when recovery of by-products options through looping are taken into account. Understanding the energy implications of high FFA content is vital for ensuring sustainable biodiesel production.

In that context, it is increasingly important to carefully examine techno-economic performance metrics of both catalytic and non-catalytic transesterification options for producing non-edible feedstocks biodiesel. In relation to these facets, this study intends to examine the techno-economic feasibility of producing biodiesel from non-edible feedstocks focusing on the effects of elevated free fatty acids (FFAs) and oil/ethanol flow rates on alkaline, acid, and CaO catalytic transesterification processes. The study employs Aspen Plus® V10 [59] which is an advanced simulation software to evaluate the three transesterification reactions. Namely: (1) Alkaline catalytic transesterification, (2) Acid catalytic transesterification, and (3) CaO catalytic transesterification. The study further investigates the performance of CaO catalysis by introducing a closed-loop blending setup. The setup is designed to ensure an uninterrupted and effective biodiesel production process by recycling ethanol and oil efficiently for reutilization while maintaining a continuous operation. The technical performance metrics investigated in this study includes the effects of elevated FFA molar content on product purity, process byproducts and energy usage. Further to that, the study investigates the effects of oil flow rate on product purity in CaO catalysis open loop blended and closed loop transesterification processes. This closed loop transesterification processes involves recycling ethanol and oil, establishing a continuous and efficient system for biodiesel production. The study further analyses other economic parameters such as capital expenditures (CAPEX), annual operating expenses (OPEX), annual raw material costs, annual product sales, and utility expenses.

2. Materials and methods

2.1. Biodiesel production model setup

Biodiesel production technology models including alkali, alkaline and CaO catalytic transesterification processes were developed by using Aspen Plus® V10 commercial simulation software. The procedures taken during biodiesel production models build-up comprised of: (a) components specification, (b) thermodynamic fluid package selection, (c) process flowsheet development and (d) process simulation, convergence and modelling. Component specification was the initial step in model build-up as the key components taking place in the transesterification reactions via ethanolysis method [60] were specified for the aim of determining the accurate thermodynamic model for property analysis and performance prediction of the designed process.

The setup of a biodiesel production model is crucial for process reliability and accuracy. It is dependent on selecting the suitable thermodynamic fluid package since these models are required for calculating various sorts of data, such as liquid-liquid, vapour-liquid, and

vapour-liquid-liquid data. Process flowsheet development was conducted block-wise by placing the required blocks or unit operations from the model pallete together with their corresponding processing streams. Thereafter, process simulation and convergence was conducted by specifying the processing and operating parameters for the input streams and unit operations, respectively. Modelling of the converged process was then conducted by varying the FFA content in the oil, oil and ethanol flow rates. The variation of this parameters were achieved under one-factor at time analysis aiming at determining their respective impact on product purity, economic parameters and energy requirements.

2.2. Raw materials description

The raw materials for the three technological options for biodiesel production via transesterification processes adopted in this study are shown in Fig. 1. The selection of non-edible feedstocks in this study was justified based on several factors related to their suitability for biodiesel production. Firstly, low quality non-edible feedstocks were chosen because they are economically viable and commonly associated with biodiesel production [61,62]. This choice aligns with the objective of exploring economically feasible options for biodiesel feedstock. In addition to that, the assumption of a 10% free fatty acid (FFA) content on a molar basis in the oil feedstock reflects a characteristic often found in low quality non-edible feedstocks, as established in previous literature. This assumption allowed for the evaluation of the impact of FFA content, within a relevant range of 10%–20%, on the techno-economic performance of biodiesel production.

The focus on triglycerides and FFAs as the main components in the oil feedstock further supports the selection of non-edible feedstocks. These components are predominant in non-edible oils, and by simulating them using symmetrical triglycerides (triolein) and oleic acid for triglycerides and FFAs respectively, the study represents the composition of non-edible feedstocks commonly used in biodiesel production processes. Furthermore, the compatibility of the chosen transesterification technology options with ethanol as the alcohol source reinforces the suitability of non-edible feedstocks. Ethanol is preferred for its non-toxic properties and renewable nature, making it a practical and environmentally friendly choice for biodiesel production [53]. Furthermore, the use of calcium oxide catalysts in some transesterification processes highlights the cost-effectiveness and sustainability of the chosen options, as these catalysts are known for their reusability and cost-reducing properties [63,64] with additions of a high level of basicity [65] and thus helps to reduce production costs. The selection of low quality non-edible feedstocks in this study was justified based on their economic viability, typical composition, and compatibility with the chosen biodiesel production technologies, highlighting the researchers' intention to explore sustainable and feasible options for biodiesel feedstock.

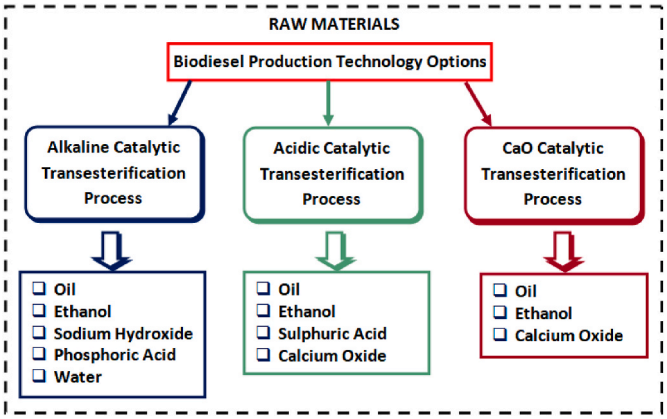

Fig. 1. Raw material for biodiesel production technological options.

2.3. Production technology options

In this study, biodiesel production technologies, including alkaline, acidic, and CaO catalytic transesterification processes, were designed. Various reaction conditions necessary to ensure forward transesterification reactions for the designed processes and favour higher biodiesel yield were compared based on previous studies. The optimum reaction conditions adopted in this study by taking into account designed processes and operational safety are presented in Table 1.

2.3.1. Alkaline catalytic transesterification process design description

The depiction in Fig. 2 illustrates the transesterification process utilizing alkaline catalysis. Further details on process specifications, operating conditions, and stream results are provided in supplementary materials. The process shown includes mixing sodium hydroxide (NaOH) with ethanol in a mixer. The resulting mixture is pumped to respective heat exchangers along with oil. Prior to entering the reactor, both the oil stream and the ethanol-sodium hydroxide solution are heated. Within the reactor, the transesterification process occurs under specific conditions. The outlet stream from the reactor, containing ethanol, undergoes further treatment in the ethanol recovery unit.

The ethanol recovery unit consists of twin RadFrac columns operating under vacuum. High purity ethanol is recovered and recycled back to the mixer, while additional recovered ethanol can be sold or stored for re-use. The bottom product from one of the columns, containing significant biodiesel, is directed to an extraction column for further processing. After liquid-liquid separation, biodiesel is obtained as a product. The bottom stream from the extraction column is sent to a neutralizing reactor, where phosphoric acid is added to ensure the complete conversion of sodium hydroxide. In the ethanol recovery unit, the outlet stream from the neutralizing reactor undergoes separation, yielding sodium phosphate as the bottom product. Another round of liquid-liquid separation results in streams containing glycerol and biodiesel. Glycerol is produced as a bottom product in a purification column, while biodiesel undergoes further purification in other columns to obtain pure biodiesel as the final product.

2.3.2. Acid catalytic transesterification process description

The process of transesterification with acidic catalysis is shown in Fig. 3, accompanied by additional information regarding process specifications, operating conditions, and stream results in supplementary materials. The process involves the combination of sulfuric acid with 35% purity and pure ethanol, then proceeding to preheat the mixture using heat exchangers. Oil is preheated separately and then combined with the ethanol-sulfuric acid solution in a reactor where transesterification occurs. The outlet from the reactor goes to the FFA-RX converter, converting oleic acid to ethyl oleate. The product, enriched with ethanol, undergoes further processing in an ethanol recovery unit consisting of twin RadFrac columns operating under vacuum conditions. The recovered ethanol, with high purity, is recycled back to the mixer, while another stream is stored and reused. The bottom product from the second column, containing biodiesel, is cooled and then neutralized in a reactor using calcium oxide. The produced biodiesel meets different criteria and generates valuable by-products like glycerol and sodium phosphate. After neutralization, the stream is separated in a separator, producing calcium sulfate as the bottom product. Glycerol is obtained from further liquid-liquid separation, and the remaining biodiesel undergoes purification in a column, resulting in a purified biodiesel product. This product undergoes another round of purification in a second column to achieve higher purity biodiesel, while the top product containing water and ethanol is considered waste due to separation challenges caused by their azeotropic behaviour.

Table 1
Optimum reaction conditions for the designed processes.

Production Technologies		Pressure [bar]	Temperature [°C]	Time [h]	Ethanol: Oil ratio	References
Acidic catalytic process		4	80	4	6:1	[66]
Alkaline catalytic process		4	80	4	6:1	[66]
CaO catalytic	CaO catalytic open-loop process	1	75	2	6:1	[53]
	CaO catalytic open-loop blended process	1	75	2	6:1	[53]
	CaO catalytic closed-loop blended process	1	75	2	6:1	[53]

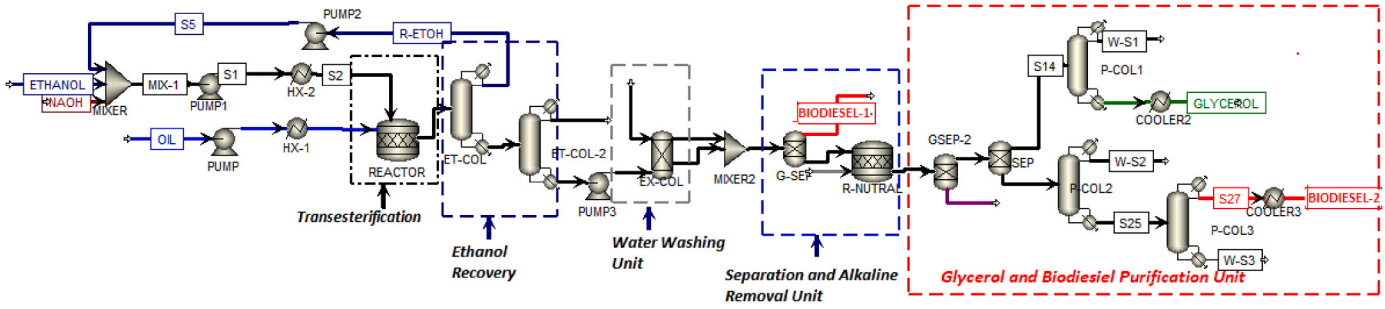

Fig. 2. Alkaline catalysis transesterification process flowsheet.

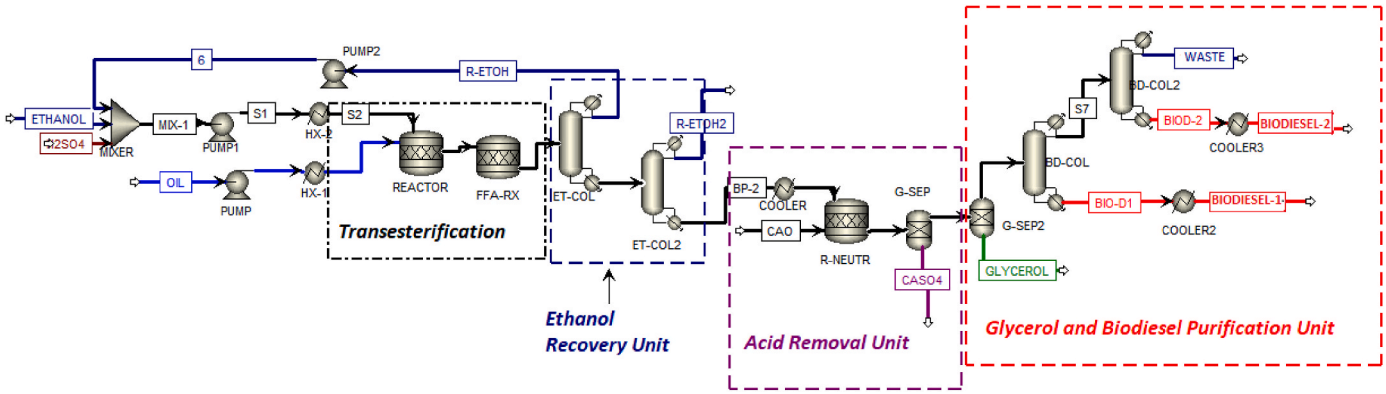

Fig. 3. Acidic catalysis transesterification process flowsheet.

2.3.3. CaO catalytic transesterification process description

Fig. 4 illustrates the process of transesterification using the CaO catalytic open-loop approach, while additional information on process specifications, operating conditions, and stream results are depicted in supplementary materials. Ethanol and oil are preheated separately before entering the reactor (RSTOIC) where the transesterification process takes place. The product stream from RSTOIC is directed to the ethanol recovery column (COL-1) for ethanol recovery. Ethanol is obtained as a distillate, while glycerol is produced as the bottom product. The top product from COL-1, containing biodiesel, is sent to the biodiesel purification unit.

The biodiesel purification unit consists of twin RadFrac columns (COL-2 and COL-3) with 4 actual stages, operating under specific conditions. In COL-2, biodiesel is recovered as a distillate and cooled. The bottom product stream undergoes further purification in COL-3, producing a purer biodiesel. The purified biodiesel is then cooled for storage purpose. The bottom stream from COL-3 is cooled before entering the component separator (C-SEP) where biodiesel and unreacted oil are separated. Biodiesel is extracted as the top stream, and unreacted oil is obtained as the bottom product.

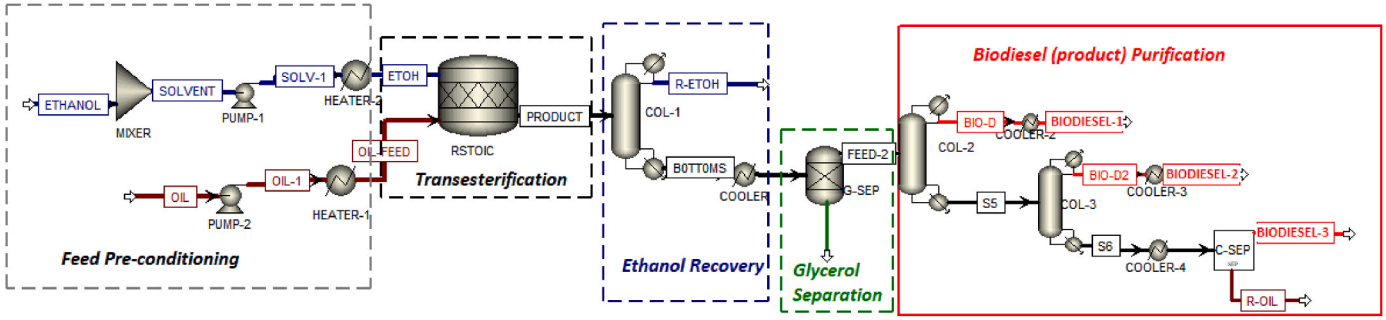

Fig. 4. CaO catalysis transesterification open loop process flowsheet.

The produced biodiesel from open loop process can also be blended for the aim of producing a uniform product as shown in Fig. 5. Additional information on process specifications, operating conditions, and stream results for CaO catalytic transesterification open-loop blending process are depicted in supplementary materials. In addition, the process shown in Figs. 4 and 5 can be modified into a closed-loop design by recycling ethanol and oil, resulting in a continuous system for biodiesel production, as depicted in Figure Additional details about the process specifications, operating conditions, and stream results for the closed-loop CaO catalytic transesterification are provided in supplementary materials. Within this closed-loop setup, a CaO catalyst-facilitated reaction generates biodiesel and glycerol as primary products. Subsequent purification steps enhance biodiesel purity, while glycerol and other byproducts are recycled back into the process. Through this recycling and refining process, the purity of biodiesel is notably increased, exceeding the quality of the setups shown in Figs. 4 and 5. The closed-loop arrangement optimizes resource utilization and minimizes waste, illustrating the potential for eco-friendly biodiesel production. The shift to this closed-loop setup hinges on the high purity of ethanol and oil, and this alteration substantially influences the purity of glycerol and biodiesel due to the composition of ethanol. To implement this change, an additional column (G-COL) with four stages, operating at 0.20 bar with a reflux ratio of 2 mol/mol, is introduced. This column recovers ethanol from the H-STREAM originating from the G-SEP unit (see Fig. 6).

To ensure that the blended technical grade biodiesel meets the requirements of EN14213, EN14214, ASTM D6751, ANP42, IS15607, and JASOM360 specifications [67,68], an extra purification column (COL-4) is added to the process. This column has four stages and operates at 0.10 bar with a reflux ratio of 2 mol/mol. Its purpose is to further purify the BIO-D stream, resulting in the production of biodiesel (stream S9 at 500 kg/h). Similarly, as shown in Figure, the process generates biodiesel (stream B-DIESEL at 3956.07 kg/h). The upper product stream from COL-4 contains 92.44% biodiesel, suggesting the potential inclusion of an extra purification step to achieve the production of technical-grade biodiesel.

2.4. Energy and economic analysis

The energy and economic analyses for adopted technological options in biodiesel production were conducted using Aspen Plus® V10 energy and economic analyser. The technical and economic assumptions adopted in this study include:

i). To represent the majority of non-edible feedstocks available in SSA, a molar percentage of free fatty acids (FFA) of roughly 10% was adopted. Further, the FFA molar content was adjusted by 2% increments from a base level of 10% to a maximum of 20%.
ii). Non-random two-liquid (NRTL) approach, as shown in Equation (1), is used for property analysis and performance prediction of the designed processes.
iii). Products, by-products, feedstocks, and other raw materials have no storage costs because they are assumed to be used/sold promptly [69,70].
iv). The number of 7920 annual operating hours, equivalent to 330 days, has been considered [71,72].
v). The total lifespan of the project(s), excluding loan considerations, is fixed at 15 years.
vi). The reusability of catalysts has been considered to lower production costs.
vii). Combined weighted cost method (Equation (2)) is applied to determine the price of products and raw materials.

The energy and economic analyses for the adopted technological options in biodiesel production were conducted using Aspen Plus® V10 energy and economic analyser [73–75].

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{ki}} \right) \quad (1)$$

where: $G_{ij} = \exp(\alpha_{ji}\tau_{ji})$

$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T$

$a_{ij} = c_{ij} + d_{ij}(T - 273.15K)$

$\tau_{ii} = 0$ and $G_{ii} = 1$

The parameter α_{ji} represents the non-random distribution tendency of components j and i. Binary parameters a_{ij}, b_{ij}, d_{ij}, e_{ij} and f_{ij} are unsymmetrical thus, $(a_{ij} = a_{ji})$ and can be determined through regression of VLE and LLE data. T denotes the temperature, and the recommended values of c_{ij} are as follows: 0.30 for non-polar substances, 0.20 for saturated hydrocarbons with polar-associated liquids, and 0.47 for strongly self-associated non-polar substances.

$$C_T = \sum_{i=1}^{n} x_i c_i \quad (2)$$

where:

C_T represents the total stream price, c_i is the price of component i in the stream, x_i is the mass fraction of the component i in the stream and n represents total number of component in the stream.

The procedures involved setting up costing options, specifying stream prices, mapping and sizing equipment, and evaluating the processes from an energy and economic perspective. Costing option setup was achieved by defining the Aspen Plus® V10 costing template, considering economic saving scenarios, and selecting investment options, such as plant-operating life, start-up length, and estimated commencement time for basic engineering works. The NRTL model and its corresponding equations, demonstrated in Equation (1), serve as mathematical tools harnessed by chemical engineers for the elucidation and prediction of liquid mixture behaviour [76,77]. The selection of the NRTL model in this particular study is rooted in its ability not only to accommodate reaction parameter interactions but also to attain liquid-liquid equilibrium [78].

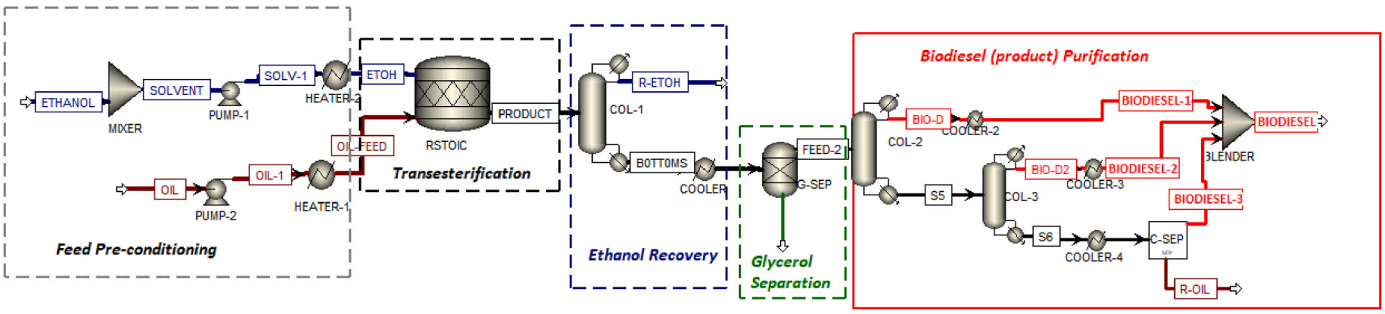

Fig. 5. CaO catalysis transesterification open loop blending process.

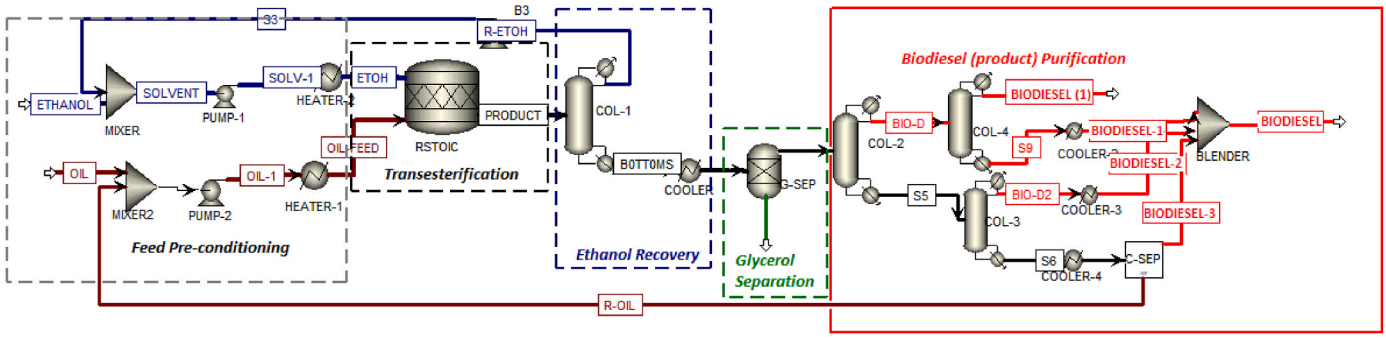

Fig. 6. CaO catalysis transesterification closed loop blending process.

Equation (2) forms the basis for utilizing these models in calculating comprehensive costs associated with both feed and product streams. These models hold immense significance in devising strategies and enhancing separation processes like distillation and extraction. The costs of components specified in the processes, as shown in Table 2, were based on global market prices as of the year 2023. Further, the produced main product, i.e., biodiesel, and valuable by-products such as glycerol, recovered ethanol, sodium phosphate, and calcium sulfate (that depend on the process employed) were assumed to be sold. The annual operating hours, were assumed to be 7920 in order to account for process downtime and maintenance operations. Additionally, depending on material selections, the designed plant can be operated effectively for up to 10–20 years [73]. In this study, an average of 15 years as an operating lifespan was used during economic analysis.

Equipment mapping was performed to allocate and select the appropriate operational blocks of the processes, ensuring higher energy efficiency, production yield, and quality. Equipment sizing based on production capacity was conducted to determine the physical parameters of the unit operations and the amount of process utilities required for desired process reactions and purification efficiencies. Following equipment mapping and sizing, the energy and economic analysis for the technological options was evaluated, and the results obtained were collected and analyzed in Ms Excel 2007.

2.5. Modelling and simulation

The modelling and simulation of the biodiesel production technologies were carried out to analyze how variations in FFA molar content, oil, and ethanol flow rates impact the overall process performance concerning product purity, economic parameters, and energy needs. FFA molar content with values of 10%, 12%, 14%, 16%, 18%, and 20% were each varied and tested in all the designed biodiesel production technologies. The testing involved monitoring the purity of produced products, energy usage, and economic parameters. The economic parameters included CAPEX, OPEX, raw materials expenses, revenues, and utilities costs.

Table 2
Component prices for biodiesel production process.

Components	Price	Unit	Source and Year
Triglycerides	1.83	$/kg	Made-in-China (2023)
Oleic Acid	1.49		indiaMART (2023)
Ethanol	0.74		ChemAnalyst (2023)
Water	0.00072	$/l	DAWASCO (2023)
Sodium Hydroxide	0.3	$/kg	Alibaba (2023) and ECHEMI (2023)
Phosporic Acid	0.71		indiaMART (2023)
Sulfuric Acid	0.65		
Calcium Oxide	0.36		indiaMART (2023)
Biodiesel	1378.98	$/m^3	Neste (2023) and Statista (2023)
Glycerol	2.8	$/kg	ChemAnalyst (2023)
Calcium Sulfate	0.36		Amazon (2023)
Sodium Phosphate	2.31		indiaMART (2023)

In this study, the 'one factor at a time analysis' method was utilized, which involves altering a single factor or variable while holding all other factors constant. This approach allows for the examination of the individual impact of the variable in isolation. This was achieved by creating a new sensitivity identification (ID), i.e., labelled as S-1 and specifying manipulated variable 1 of type mass-flow for an oil and ethanol streams. Oil flow rate was varied from 2000 to 12,000 kg/h and ethanol flow rate was varied from 1000 to 5000 kg/h. Further, during this study analysis, the molar purity of the main and by-products were defined and specified. The analysis was conducted only for the main component, which is ethyl oleate for biodiesel streams (BIODIESEL-1, BIODIESEL-2, BIODIESEL-3, BIODIESEL (1), and BIODIESEL) and waste product streams (W–S1, W–S2, and W–S3). Additionally, molar purity was determined for glycerol in the GLYCEROL stream, ethanol in the recovered ethanol streams (R-ETOH, R-ETOH2, WASTE), calcium sulfate in $CaSO_4$, sodium phosphate in Na_3PO_4, and triglyceride in the recovered oil stream (R-OIL).

3. Results and discussion

3.1. Product purity

The fractional conversion of triglyceride and oleic acid to ethyl oleate was investigated using process options as indicated in Table 3. These options included acidic catalytic, alkaline catalytic, and CaO catalytic processes. In the designed biodiesel production processes, triglyceride was converted into ethyl oleate or biodiesel. In these processes, oleic acid in the oil was also converted into ethyl oleate or biodiesel. The percentage conversion of triglyceride and oleic acid to biodiesel is presented for acidic, alkaline, and CaO catalytic transesterification processes. Slight changes in percentage conversion is attributed mainly due to difference in catalysts used and reaction conditions. Changes in catalysts and reaction condition used affects the chemical reaction kinetics, this consequently results into changes in percentage conversion. For instance, the use of acidic catalyst, i.e., sulfuric acid and alkaline catalysts, i.e., sodium hydroxide at 80 °C and 4 bar resulted into 98% conversion of triglyceride into biodiesel. On the other hand, the use of CaO catalysts at 75 °C and 1 bar resulted into 97.58% conversion of triglyceride into biodiesel. Similarly, oleic acid

Table 3
Triglyceride and FFA conversion to ethyl oleate.

Process Option	Acidic catalytic process	Alkaline catalytic process	CaO catalytic process		
			Open-loop process	Open-loop blended process	Closed-loop process
Operating Parameters	Temperature = 80 °C, Pressure = 4 bar		Temperature = 75 °C, Pressure = 1 bar		
Triglyceride	98%	98%	97.58%	97.58%	97.58%
Oleic Acid	99%	98%	95%	95%	95%

was converted also into biodiesel, with 99% conversion achieved when acidic catalyst was employed. The 99% conversion is due to the fact that the use of acidic catalysts results into simultaneously esterification and transesterification process which attributes to the reduction of FFA content in oil [79,80]. These product purity findings in this study demonstrate the effectiveness of the different catalytic processes and thus provide understandings for optimizing biodiesel production.

The significance of biodiesel quality produced through the transesterification process is pivotal for its efficiency and environmental implications. An in-depth analysis in Table 4 reveals the molar purity of biodiesel extracted from various catalytic processes. Despite the higher conversions of triglycerides and oleic acid to biodiesel noted in methods like the CaO open-loop and CaO open-loop blended, the overall molar purity remains relatively insufficient, particularly falling below 40%. This discrepancy mainly arises from the excess presence of ethanol and the formation of glycerol as a by-product Pirzadi and Meshkani [81]. In comparing different catalytic processes, it becomes evident that the molar purity of biodiesel in both the CaO open-loop and CaO open-loop blended processes surpasses that of the acidic, alkaline, and CaO closed-loop processes by approximately 58.81%. This indicates the superiority of CaO-based techniques in maintaining the purity of the biodiesel product. This correlation aligns with prior studies by Gebremariam and Marchetti [53] and Nasreen, Nafees [82], which exhibited the effectiveness of CaO-based catalysts in improving biodiesel purity and yield. The reduced molar purity observed in acidic and alkaline procedures can be attributed to the additional introduction of acid and alkaline solutions Salehi, Karbassi [66], unintentionally leading to an excess of ethanol that favours the forward reaction. This surplus of ethanol not only impacts purity levels but also raises concerns about process efficiency and environmental sustainability.

Similar findings were highlighted by Hossain, Boyce [88], emphasizing the negative impacts of excessive ethanol in transesterification on biodiesel quality and process efficiency. In the case of CaO closed-loop processes, the decreased molar purity is linked to recycling impure cuts back into the process, resulting in higher ethanol concentrations in processing streams. This recycling method introduces impurities into the system, jeopardizing the purity of the biodiesel end product. This issue has been explained in previous studies by Refs. [89,90], underlining the significance of managing process streams to uphold biodiesel product purity. Based on these results, optimizing transesterification processes by utilizing CaO-based catalysts and implementing effective recycling strategies is crucial for boosting the molar purity of biodiesel, ensuring its efficiency, and maintaining environmental sustainability.

In this study, the optimization of biodiesel production through transesterification processes as depicted in Figure(s) 2–6, was reached through a variety achieved via diverse purification processes, including ethanol recovery, glycerol separation, and multistage biodiesel purification. The resulting technical-grade biodiesel underwent quality assessment, showing promising results compared to existing literature. Table 4 offers a comprehensive comparison between the quality of biodiesel produced in this study and that documented in selected studies. The results indicate that the biodiesel produced through the process configurations adopted in this study displayed slightly higher purity levels than alternative production techniques. Particularly, the purity of the produced biodiesel surpassed that of Gebremariam and Marchetti [53] and Chai, Tu [91], across various production methods. For instance, in acidic catalytic processes, the purity of the biodiesel produced in this study reached 99.99997%, outperforming the purity reported by Chai, Tu [91], which was at 98.88%.

Similarly, in alkaline catalytic processes, the produced biodiesel attained a purity of 99.99999%, exceeding the reported 99.7% purity in a study by Salehi, Karbassi [66]. Furthermore, variations in purity were observed when using CaO catalytic processes across different configurations. In the CaO catalytic open-loop process, the purity of the biodiesel achieved in this study was noticeably higher at 99.97523% compared to study by Gebremariam and Marchetti [53] which reported a purity of 99.9%. Similar trends were observed in the CaO catalytic open-loop blended and closed-loop blended processes, where the purity of the produced biodiesel surpassed the reported levels in existing literature.

The purity of glycerol, an essential by-product of biodiesel production, also showed favourable outcomes in this study. Across various catalytic processes, the glycerol purity obtained from the purification methods employed consistently outperformed or nearly matched the purity levels documented in comparative studies as demonstrated in Table 5. These results highlight the effectiveness of the purification processes integrated into the biodiesel production framework presented in this study. The observed elevated purity levels suggest improved efficiency and quality control in biodiesel production, which could possess significant implications for its commercial viability and environmental footprint.

The quality of the produced biodiesel after purification process was evaluated and compared against various technical grade specifications as depicted in Table 6. These specifications set the standards for molar purity (%) of biodiesel, ethanol, glycerol, water, triglyceride and FFA. The biodiesel technical grade specifications from EN14213, EN14214, ASTM D6751, ANP42, ISI5607, and JASOM360 require a minimum molar purity of $\geq$96.5% for biodiesel, with specific limits for other components. In the acidic catalytic process, the produced biodiesel (Biodiesel-1and Biodiesel-2) exhibits remarkably high molar purity for biodiesel itself, with 99.97546% and 99.99997%, well above the specified standard thresholds. The presence of other impurities like water and triglyceride is negligible. Similarly, in the alkaline catalytic process, the produced biodiesel (Biodiesel-1and Biodiesel-2) meets or exceeds the required molar purity levels set by these standards, highlighting excellent quality.

The alkaline catalytic process yielded biodiesel with molar purities of 99.97791% for Biodiesel-1 and 99.99999% for Biodiesel-2. For the CaO catalytic open-loop and blended processes, although the molar purity of biodiesel remains high in Biodiesel-1and Biodiesel-2. The CaO catalytic open-loop process produced biodiesel with varying molar purities, with Biodiesel-1 at 99.20574%, Biodiesel-2 at 99.92742%, and Biodiesel-3 at 99.97523%. The CaO catalytic open-loop blended process showed similar results, while the CaO catalytic closed-loop blended process exhibited biodiesel molar purities ranging from 99.87578% to 99.97632%. The CaO catalytic closed-loop blended process, Biodiesel-1 and Biodiesel-2 maintain high biodiesel molar purity but exhibit slightly elevated FFA levels. However, the designed processes produces and yield a technical-grade biodiesel that meets EN14213, EN14214, ASTM D6751, ANP42, IS15607, and JASOM360 specifications.

In addition to the production of the main product (biodiesel) from the designed processes, valuable by-products that can be promptly sold to generate more revenues were also produced. The produced by-products, as shown in Table 7, depend on the designed process and include glycerol, recovered ethanol, recovered oil, calcium sulfate, and sodium phosphate. From Tables 7 and it can be seen that the molar purity of glycerol is approximately greater than 99%, satisfying the

Table 4
Biodiesel molar purity after transesterification process.

Components	Acidic catalytic process	Alkaline catalytic process	CaO catalytic process		
			Open-loop process	Open-loop blended process	Closed-loop process
Triglyceride	0.11%	0.11%	0.24%	0.24%	0.15%
Oleic acid	0.01%	0.02%	0.05%	0.05%	0.04%
Ethanol	74.17%	73.15%	59.02%	59.02%	73.77%
Ethyl oleate	16.43%	16.21%	30.00%	30.00%	18.89%
Water	3.27%	3.68%	1.04%	1.04%	1.08%
Glycerol	5.28%	5.21%	9.65%	9.65%	6.07%
H_2SO_4	0.73%	–	–	–	–
NaOH	–	1.62%	–	–	–

Table 5
Comparison between produced biodiesel quality (%) and other literature.

Production Technologies		Products	This study	[53]	[66]	[83]	[84]	[85]	[86]	[63]	[87]
Acidic catalytic process		Biodiesel	99.99997	–	98.88	92	–	–	–	–	–
		Glycerol	99.97	–	96	60	–	–	–	–	–
Alkaline catalytic process		Biodiesel	99.99999	–	99.7	–	76.65	–	–	–	–
		Glycerol	99.82	–	92	–	–	–	–	–	–
CaO catalytic	CaO catalytic open-loop process	Biodiesel	99.97523	99.9	–	–	–	98.7	90	92.5	91.5
		Glycerol	99.30	99	–	–	–	–	–	–	–
	CaO catalytic open-loop blended process	Biodiesel	99.6714	99.9	–	–	–	98.7	–	–	–
		Glycerol	99.30	97.6	–	–	–	–	–	–	–
	CaO catalytic closed-loop blended process	Biodiesel	99.94459	99.9	–	–	–	98.7	–	–	
		Glycerol	99.08	97.6	–	–	–	–	–	–	–

Table 6
Comparison between produced biodiesel quality and technical grade specifications.

Molar purity (%)								References
		Biodiesel	Ethanol	Glycerol	Water	Triglyceride	FFA	
Biodiesel technical grade specifications	EN14213	≥96.5	–	<1	<0.5	<1	<1	[67,68,92,93]
	EN14214	≥96.5	<0.20	<1	<0.5	<1	<12	
	ASTM D6751	≥96.5	<0.20	<1	<0.5	–	–	
	ANP42	≥96.5	–	<1	<0.5	<1	<1	
	ISI5607	≥96.5	<0.2	<1	<0.5	–	–	
	JASOM360	≥96.5	<0.2	<1	<0.5	<1	<1	
Simulation Results from this Study								
Acidic catalytic process	Biodiesel-1	99.97546	–	–	–	0.02454	–	–
	Biodiesel-2	99.99997	–	–	0.00003	–	–	–
Alkaline catalytic process	Biodiesel-1	99.97791	–	–	0.02209	–	–	–
	Biodiesel-2	99.99999	–	–	0.00001	–	–	–
CaO catalytic process	CaO catalytic open-loop process	Biodiesel-1	99.20574	–	0.75091	–	–	–	–
		Biodiesel-2	99.92742	–	–	–	–	–	–
		Biodiesel-3	99.97523	–	–	–	0.02477	–	–
	CaO catalytic open-loop blended process	Biodiesel-1	99.20574	–	0.75091	–	–	–	–
		Biodiesel-2	99.92742	–	–	–	–	–	–
		Biodiesel-3	99.97523	–	–	–	0.02477	–	–
		Biodiesel	99.67140	–	0.28377	–	0.00717	–	–
	CaO catalytic closed-loop blended process	Biodiesel-1	99.87578	–	–	–	–	–	–
		Biodiesel-2	99.92617	–	–	–	–	–	–
		Biodiesel-3	99.97632	–	–	–	0.02368	–	–
		Biodiesel	99.94459	–	–	–	0.01058	–	–

glycerol specifications [94–96]. Furthermore, the molar purity of recovered ethanol was observed to be greater than 93%, indicating the economic potential of ethanol to be re-used in the process. For the acidic catalytic process, the molar purity of produced by-products from biodiesel production technological options is as follows: Glycerol is obtained with an impressive purity of 99.97%, while ethanol (EtOH) purity reaches 96.44%. Calcium sulfate ($CaSO_4$) is produced with a purity of 86.54%.

In the case of the alkaline catalytic process, the molar purity of by-products is noteworthy: Glycerol attains a high purity of 99.82%, while ethanol (EtOH) achieves 96.01% purity. Sodium phosphate (Na_3PO_4) is produced with a remarkable purity of 99.83%. In the CaO catalytic processes, glycerol is produced with varying purities depending on the specific process used. In the CaO catalytic open-loop process, glycerol has a purity of 99.30%. In the CaO catalytic open-loop blended process, glycerol purity remains the same at 99.30%. To end with, in the CaO catalytic closed-loop blended process, glycerol is produced with a purity of 99.08%.

3.2. Effect of FFA molar content on product purity

The molar content of FFA has been shown to significantly affect biodiesel production, and thus they influence efficiency and product purity in transesterification process. Higher molar content of FFA levels lead to reduced catalyst effectiveness, lower yields, and compromised purity in both acidic and alkaline catalytic processes [52,97–99]. In this section, a discussion on the impact of FFA on the purity of biodiesel, glycerol, and by-products and process efficiency is presented. The section also discusses downstream processing-related issues that may arise as a result of the formation of salt and soap compounds. Fig. 7 offers valuable insights into how the molar purities of biodiesel-1 and biodiesel-2, recovered ethanol (R-EtOH2), glycerol, calcium sulfate ($CaSO_4$), and waste product are impacted by increasing FFA molar content in the oil feedstock, ranging from 10% to 20%.

The results from Fig. 7 provide the relationship among glycerol's molecular purity, R-EtOH2, ethanol concentration in waste byproduct, and the free fatty acids (FFA) molecular content. As shown, there is a distinct inverse correlation between glycerol's molecular purity and R-EtOH2, as well as the ethanol concentration in waste byproduct, regarding the FFA molecular content. Previous studies such as that by Anisah and Agustian [100] and that of Mandari and Devarai [101], have noted similar trends, emphasizing the impact of FFA content on various parameters within the transesterification process. For instance, as the FFA molecular content increases, glycerol's molecular purity slightly decreases from 99.971% to 99.963%, while R-EtOH2 drops from 96.44% to 95.33%. The reduction in ethanol concentration in waste byproduct, from 59.50% to 56.40%, branches from the higher ethanol quantity required for effective transesterification and FFA conversion as highlighted by Chanakaewsomboon, Phoungthong [102]. The slight decline in glycerol purity is connected to the growth in water molecular content due to FFA conversion reaction.

It is important to note that the decline in biodiesel-2 molecular purity with an escalation in FFA molecular content is insignificant, mainly because of the subsequent purification processes it undergoes,

Table 7
Molar purity of produced by-products from biodiesel production technological options.

Molar composition (%)													
Production Processes	By-Products	Bio-diesel	Glycerol	EtOH	$CaSO_4$	Na_3PO_4	H_2O	FFA	Triglyceride	NaOH	H_3PO_4	H_2SO_4	CaO
Acidic catalytic process	Glycerol	–	99.97	–	–	–	0.03	–	–	–	–	–	–
	R-EtOH2	–	–	96.44	–	–	3.56	–	–	–	–	–	–
	$CaSO_4$	–	–	–	86.54	–	–	–	12.73	–	–	–	0.73
Alkaline catalytic process	Glycerol	–	99.82	–	–	–	–	0.18	–	–	–	–	–
	R-EtOH2	–	–	96.01	–	–	3.99	–	–	–	–	–	–
	Na_3PO_4	–	–	–	–	99.83	0.10	–	–	0.07	–	–	–
CaO catalytic	CaO catalytic open-loop process	Glycerol	0.35	99.30	–	–	–	–	0.07	0.28	–	–	–	–
		R-EtOH	0.02	1.83	96.44	–	–	1.71	–	–	–	–	–	–
	CaO catalytic open-loop blended process	Glycerol	0.35	99.30	–	–	–	–	0.07	0.28	–	–	–	–
		R-EtOH	0.02	1.83	96.44	–	–	1.71	–	–	–	–	–	–
	CaO catalytic closed-loop blended process	Glycerol	0.46	99.08	–	–	–	–	0.09	0.37	–	–	–	–
		R-EtOH2	–	5.20	93.06	–	–	1.74	–	–	–	–	–	–

ultimately reaching around 100% purity. This describes the central role of post-transesterification purification steps in ensuring high-quality biodiesel production. Moreover, a direct correlation is apparent between CaSO4's molecular purity and biodiesel-1 with an increase in FFA content. When the FFA molecular content in the oil increases, there is a small improvement in the molecular purity of CaSO4 and biodiesel-1. This increase in $CaSO_4$ molecular purity can be attributed to the drop in sulfuric acid's molecular concentration due to the increase in water content. Furthermore, the heightened acidity of the oil resulting from an increase in FFA molecular content contributes to an improved yield and purity of biodiesel in the acidic catalytic transesterification process [103]. These findings emphasize the complex interplay among FFA content, catalyst performance, and the overall quality of biodiesel production.

From the data shown in Fig. 7, it is clear that the molar purity of different products in the process of acid-catalyzed transesterification is affected by the FFA molar content. This also describes the considerable impact of FFA molar content on the molar purity of different results throughout the process of acid-catalyzed transesterification. The trends observed in the data indicate a decrease in the molar purity of glycerol, R-EtOH2, and ethanol concentration in the waste product as the FFA content increases. Equally, there is an increase in the molar purity of $CaSO_4$ and biodiesel-1. In the context of acidic catalytic transesterification, these findings emphasize the importance of effectively managing FFA content to optimize biodiesel production and achieve the desired product purity.

Fig. 8 illustrates how the FFA level in the oil affects the quality of different products in an alkaline catalyzed transesterification process. The graph shows changes in the purity of biodiesel (Biodiesel-1and Biodiesel-2), recovered ethanol (R-EtOH2), glycerol, sodium phosphate (Na_3PO_4), and waste (W–S1, W–S2, and W–S3) as the FFA content in the oil increases from 10% to 20%. When the FFA content in the oil goes up, the purity of these products changes noticeably. For example, the purity of biodiesel-1 varies between 99.979% and 99.976%. Similarly, the purity of R-EtOH2 ranges from 96.2% to 94.8%. Glycerol purity fluctuates between 99.85% and 99.55%, and Na_3PO_4 purity shifts from 99.90% to 99.55%.The molar content of biodiesel in the waste products (W–S1, W–S2, and W–S3) increases from 0.00% to 0.40% as the FFA content rises. Alkaline catalyzed transesterification results in Fig. 8 suggest a correlation between initial FFA content and product quality. In addition, they emphasize that FFA levels must be carefully managed so that the various products produced during this process are consistent and pure.

When the level of FFA in the oil in Fig. 8 is raised from 10% to 12%, there is a consistent molar purity observed in the products. This indicates the effectiveness and efficiency of alkaline catalysts. However, when the FFA content exceeds 12%, there is a notable decrease in the molar purity of the products. This decline is particularly evident in biodiesel (Biodiesel-1 and Biodiesel-2), recovered ethanol (R-ETOH2), glycerol, and sodium phosphate (Na_3PO_4). The primary reason for this decrease is the diminishing effectiveness and efficiency of the alkaline catalysts. At this point, a portion of the catalysts is utilized to neutralize the acidic nature of the oil. Furthermore, when the FFA molar content surpasses 14%, a slight alteration is observed in the molar purity of Na_3PO_4. This shift is primarily due to the consistent production of water and un-reacted sodium hydroxide. In addition, Fig. 8 demonstrates that the molar content of biodiesel in waste streams (namely, W–S1, W–S2, and W–S3) remains relatively stable as the FFA molar content in the oil increases from 10% to 20%. This observation suggests that the efficiency of biodiesel purification is upheld during operational processes.

Generally, technical grade biodiesel witch satisfies EN14213, EN14214, ASTM D6751, ANP42, IS15607 and JASOM360 specifications is produced from the designed process regardless of increase in FFA molar content. As established in both Figs. 7 and 8, a slightly elevated molar purity of biodiesel products (approximately exceeding 0.0002%) is achieved through the utilization of an acidic catalytic

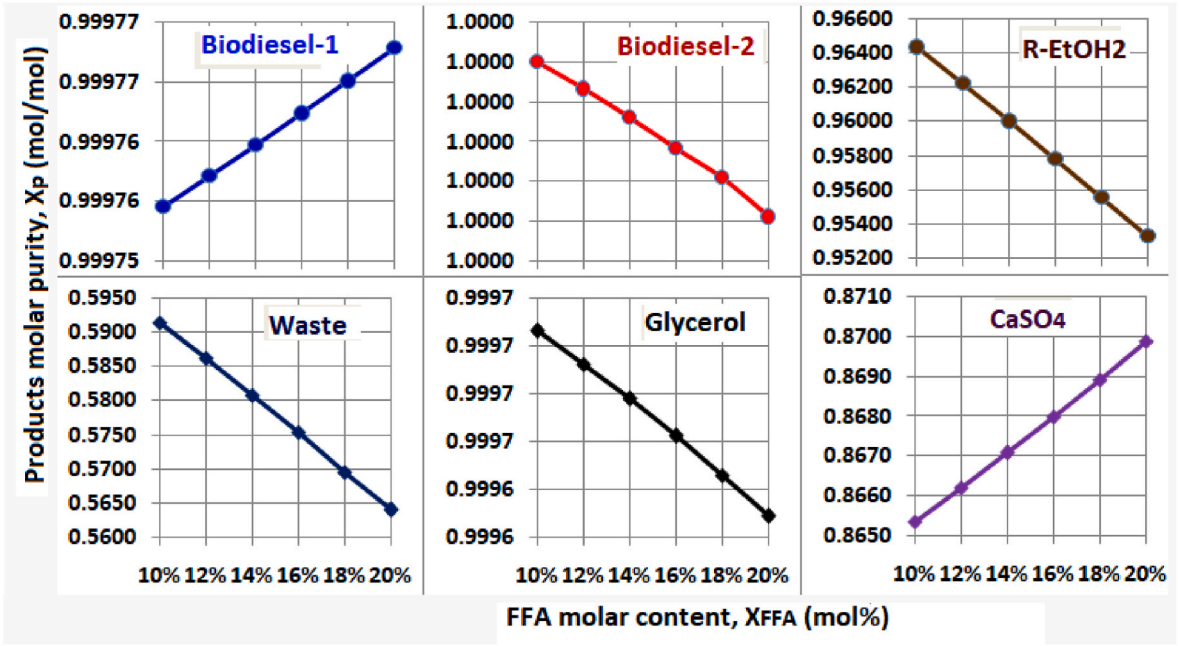

Fig. 7. Effect of FFA molar content on product purity in acidic catalytic transesterification process.

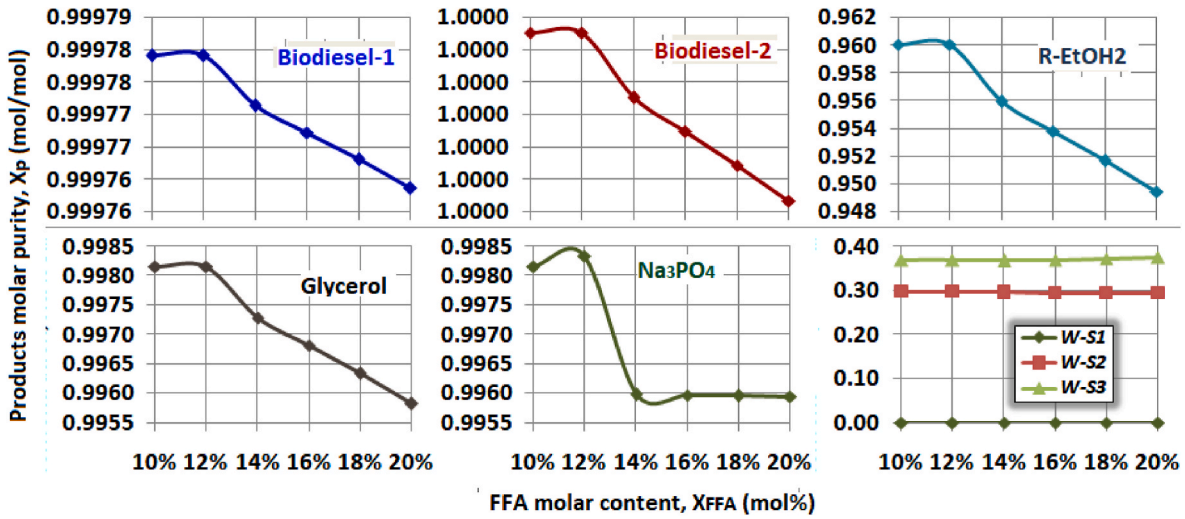

Fig. 8. Effect of FFA molar content on product purity in alkaline catalytic transesterification process (Key: R-ETOH2 = recovered ethanol and W–S1=W–S2 = W–S3 = waste product).

transesterification process. As a result of this observation, it appears that the transesterification process can be improved by employing acid catalysis with increased FFA content. This improvement is attributed to the capability of acid catalysts to withstand the presence of FFA molar content and water in the oil during the transesterification reaction [104, 105]. The unique ability of acid catalysts to endure and promote reactions in the presence of such demanding elements has been supported by previous research [105–107]. In these studies, it was shown that acid catalysis is highly efficient under a range of reaction conditions and therefore highly beneficial in improving biodiesel production. When dealing with non-edible feedstocks well known for their high FFA content, the applicability is particularly obvious.

Fig. 9 presents the effect of increasing FFA molar content in oil from 10 to 20% on molar purity of products including biodiesel (Biodiesel-1, Biodiesel-2 and Biodiesel-3), recovered ethanol (R-EtOH), glycerol and recovered oil (R-oil) produced in CaO catalyzed open loop transesterification process. Increase in FFA molar content from 10 to 20% results into an inverse relationship with the molar purity of the produced products. As the molar content of Free Fatty Acids (FFA) increases from 10% to 20%, there is a proportional decrease in molar purity observed in the products: biodiesel-1 decreases from 99.21% to 99.16%, biodiesel-2 decreases from 99.94% to 99.84%, biodiesel-3 decreases from 99.976% to 99.971%, R-EtOH decreases from 96.60% to 95%, glycerol decreases from 99.32% to 99.22%, and R-oil decreases from 0.85% to 0.70%. The decrease in molar purity of the produced products with increase in FFA molar content (as illustrated in Fig. 9) is mainly due to the fact increase in FFA molar content in oil results into proportional decrease in molar content of triglyceride. This consequently leads to decrease in the molar purity of the produced products due to increase in the amount of unreacted oleic acid.

Further the effect of increasing FFA molar content in oil from 10 to 20% on molar purity of products including biodiesel, recovered ethanol (R-EtOH), glycerol and recovered oil (R-oil) produced in CaO catalyzed open blended and closed loop transesterification process is presented in

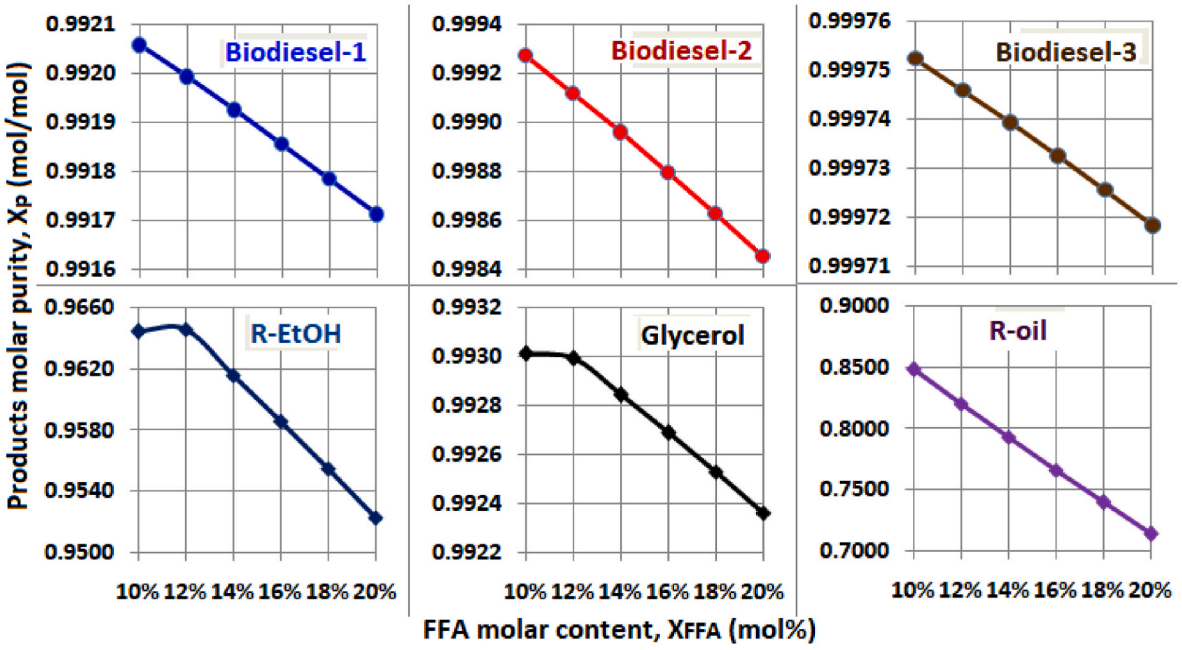

Fig. 9. Effect of FFA molar content on product purity in CaO catalysis open loop transesterification process (Key: R-ETOH = recovered ethanol, R-oil = recovered oil).

Table 8
Effect of FFA molar content on product purity in CaO catalysis open loop blended and closed loop transesterification process.

	CaO Open-loop blended process				CaO Closed-loop blended process			
FFA	Biodiesel	R-EtOH	Glycerol	R-oil	Biodiesel	R-EtOH2	Glycerol	R-oil
0.10	0.9967	0.9644	0.99301	0.8483	0.9994	0.9306	0.99081	0.8483
0.12	0.9966	0.9615	0.99287	0.8200	0.9993	0.9277	0.99061	0.8200
0.14	0.9966	0.9585	0.99271	0.7924	0.9993	0.9247	0.99040	0.7924
0.16	0.9965	0.9554	0.99256	0.7654	0.9991	0.9217	0.99017	0.7654
0.18	0.9964	0.9523	0.99239	0.7389	0.9990	0.9186	0.98994	0.7389
0.20	0.9963	0.9491	0.99222	0.7130	0.9989	0.9154	0.98970	0.7130

Table 8. Increase in FFA molar content from 10 to 20% results into decrease in molar purity of open-loop blended process from 99.95 to 99.89% for biodiesel, 96.5 to 94.5% for R-EtOH, 99.1 to 98.96% for glycerol and 0.85 to 0.70% for R-oil. Moreover increase in FFA molar content from 10 to 20% results into decrease in molar purity of closed loop process from 99.68 to 99.63% for biodiesel, 96.5 to 94.5% for R-EtOH, 99.32 to 99.20% for glycerol and 0.85 to 0.70% R-oil.

Similarly, the decrease in molar purity of the produced products with increase in FFA molar content as shown in Table 8 is attributed by decrease in molar content of triglyceride necessary for transesterification process. A closed loop process produces biodiesel with a molar purity approximately 0.26% greater than an open loop process produces biodiesel. The reason for this as highlighted by a number of literatures is that recycling of recovered ethanol and oil results into addition of impure cuts in the process [108–110]. This consequently leads to decrease in the molar purity of the produced products attributed by the increase in un-reacted oil acid in the process. Moreover, the molar purity of glycerol in open-loop blended process is approximately 0.221% times less than the molar purity of glycerol in closed loop process. The reason for this is because of additional glycerol purification unit in closed loop process consequently leading to increase in product quality. The increase in FFA molar content within the oil, as depicted in Figs. 9 and 10, leads to a decrease in the molar purity of the produced products during the CaO catalyzed transesterification process. This decrease is attributed to the reduction in triglyceride molar content within the oil [100].

The results depicted in Figs. 8 and 9 and Table 8 suggest that when

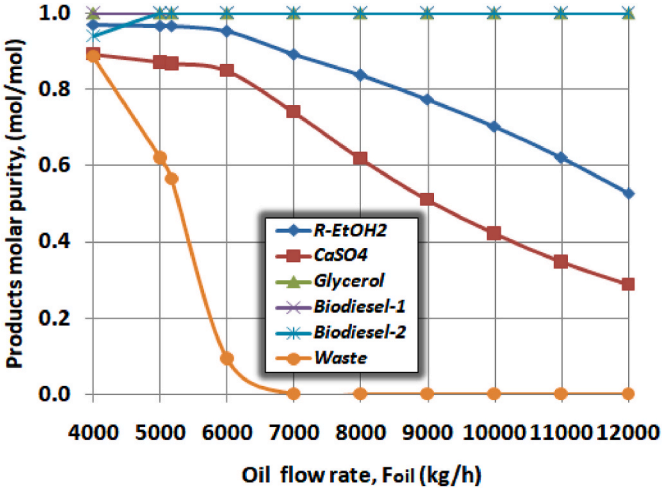

Fig. 10. Effect of oil flow rate on product purity in Acidic catalytic transesterification process.

dealing with non-edible feedstocks characterized with increased levels of FFA, both acid and CaO catalyses in transesterification processes offer superior advantages compared to alkaline catalysis. The interplay between FFA and water in the presence of an alkaline catalyst stands as the primary factor restricting the extensive utilization of non-edible

feedstocks [111]. Consequently, this presents a significant limitation to the most important attempt to lower overall production costs. The outcomes of this study align with the conclusions drawn by Demirbas, Bafail [112], who suggested that alkaline catalysts might not be suitable for producing biodiesel from non-edible oils. As a practical solution to this challenge, the study demonstrates the efficiency of acid catalysis for transforming FFAs into esters. Moreover, the utilization of CaO catalysis offers a dual advantage, encompassing the neutralization of FFAs and the facilitation of the transesterification reaction. The effectiveness of CaO catalysis in controlling non-edible feedstocks with high FFA content throughout the whole biodiesel production process is greatly improved by this multifaceted approach. It should be noted that an increase in the molar content of FFA, as indicated by various literature sources such as Anisah and Agustian [100], Handojo, Indarto [113] and Moradi, Saidi and Najafabadi [114], has the potential to result in a saponification reaction between FFAs and CaO. This interaction can potentially impact the overall performance of the plant in terms of biodiesel molar purity. Therefore a careful analysis based on reaction kinetics and real plant monitoring must be conducted to determine the trade-off between FFA molar content and biodiesel molar purity.

3.3. Effect of FFA molar content on energy analysis and usage

The efficiency of transesterification process in production of biodiesel depends on subsequent energy added and removed during the processing operation. The amount of energy required depends on several factors such as feed flowrate, feed conditions, catalysts used, reaction conditions and desired products purity [115,116]. Disturbances in oil FFA molar content may results into variation in energy requirements of the plant. This section provides more information on the impact of raising FFA molar content from 10 to 20% on energy requirements and potential energy savings based on pinch analyses on acidic, alkaline, and CaO catalyzed transesterification process. Qiao, Cui [117] point out pinch analysis as one of the most important methodologies for energy integration. The Pinch analysis's value for the biorefining process has recently been demonstrated by its successful use in the production of biodiesel [118] and biomethane [119].

Table 9 depicts the variations in actual, target, available energy savings, and percentage energy savings with the molar content of FFA in oil, particularly in the context of the acidic, alkaline, and CaO catalyzed transesterification processes. The transition from a 10% to a 20% FFA molar content in the oil feedstock leads to notable fluctuations in overall energy demands across all stages of biodiesel production. Specifically, these fluctuations encompass a range of 6.0–13.5 MW for actual process energy, 5.0–7.0 MW for target process energy, 0.44–7.44 MW for available energy savings, and a potential for energy savings spanning from 10% to 60%.

The total energy utilized by the plant's operational units is referred to as the actual process energy. A decrease in the actual energy usage is witnessed as the molar percentage of free fatty acids (FFA) rises from 10% to 20%, as indicated in Table 9. This shift signifies a reduction in the actual energy necessity across the various transesterification processes: acidic (from about 12 to 13.5 MW), CaO closed loop (from approximately 10.5 to 12 MW), alkaline (from around 9 to 10.5 MW), CaO open blended loop (from about 7.5 to 9 MW), and CaO open loop (from roughly 6–7.5 MW). The disparity in energy requirements among the different process technologies is mainly due to the number of operational components in each process, leading to an escalation in the demand for process utilities and subsequently raising the overall energy consumption. Moreover, the higher energy consumption observed in acidic catalyzed transesterification processes, in comparison to other methods, is attributed to the catalytic conversion of FFA found in the oil, resulting in increased energy needs with the rise in FFA molar content within the oil feedstock.

A slight rise in the actual energy needed occurs when the FFA content in the oil shifts from 10% to 20% due to slight changes in the purity of the final products. Similarly, the variations in the desired energy for the process, shown in Table 9, when the FFA content in the oil changes from 10% to 20%, stem from process pinch analysis that relies on the thermodynamics of the process and an examination of heat flow. The target process energy reflects the optimized energy requirements of the process, which are directly proportional to the actual energy. The higher the actual process energy, the greater the optimized target energy will be. The available energy saving requirement for the processing operations remains relatively steady with an increase in FFA molar content because available energy is calculated based on the difference between the actual and target process energy. Additionally, a higher level of available energy savings leads to a greater potential percentage of energy savings.

In comparison to alkaline, CaO closed-loop, and both CaO (open loop along with open blended loop) catalyzed processes, the actual energy requirements for an acidic catalyzed process are roughly more than 29.58%, 15.35%, and 71.75% higher, respectively. The reactions that convert FFA and increase the amount of biodiesel produced by the acidic catalyzed process have more energy. Additionally, the energy requirements that are optimized or targeted are roughly 3.04%, 15.62%, and 13.89% of the target energy needs for the alkaline, CaO closed-loop, and both CaO catalyzed processes, respectively, according to pinch analysis.

Table 9
Effect of FFA molar content on energy analysis and usage.

	FFA [mol/mol]	Actual [MW]	Target [MW]	Available savings [MW]	% of Actual
CaO Closed loop Process	0.10	11.31	6.60	4.72	41.66
	0.12	11.31	6.60	4.72	41.66
	0.14	11.41	6.69	4.72	41.37
	0.16	11.41	6.69	4.72	41.37
	0.18	11.41	6.69	4.72	41.37
	0.20	11.41	6.69	4.72	41.37
CaO Open Blended Process	0.10	7.60	6.72	0.87	11.49
	0.12	7.57	6.72	0.86	11.36
	0.14	7.59	6.74	0.85	11.16
	0.16	7.59	6.74	0.85	11.16
	0.18	7.59	6.74	0.85	11.16
	0.20	7.59	6.74	0.85	11.16
CaO Open loop Process	0.10	7.60	6.72	0.87	11.49
	0.12	6.10	5.14	0.95	15.65
	0.14	6.10	5.14	0.95	15.65
	0.16	6.10	5.14	0.95	15.65
	0.18	6.10	5.14	0.95	15.65
	0.20	7.55	6.69	0.86	11.42
Alkaline Process	0.10	10.07	5.51	4.56	45.32
	0.12	10.07	5.51	4.56	45.32
	0.14	10.10	5.55	4.55	45.04
	0.16	10.10	5.55	4.55	45.04
	0.18	10.10	5.55	4.55	45.04
	0.20	10.10	5.55	4.55	45.04
Acidic Process	0.10	13.05	5.67	7.38	56.52
	0.12	13.07	5.68	7.39	56.52
	0.14	13.10	5.70	7.40	56.49
	0.16	13.13	5.72	7.41	56.45
	0.18	13.15	5.73	7.42	56.41
	0.20	13.18	5.75	7.43	56.37

3.4. Effect of FFA molar content on economic parameters

The effect of FFA molar content in oil on various aspects such as total capital expenditures (CAPEX), yearly operating expenses (OPEX), raw material annual costs, yearly product sales, and utilities costs is analyzed in the context of the acidic, alkaline, and CaO catalyzed transesterification process. This analysis is detailed in Table 10. An increase in FFA molar concentration in oil from 10% to 20% results in modest variations in overall plant expenses. These variations are mainly due to a slight decrease in the molar purity of the produced products. As a consequence, there is a minor alteration in overall energy

Table 10
Effect of FFA molar content on economic parameters.

	FFA [mol/mol]	CAPEX [USD]	OPEX [USD/Year]	Raw Materials [USD/Year]	Sales [USD/Year]	Utilities [USD/Year]
CaO Closed loop Process	0.10	11.2400	96.5550	87.5120	86.1000	0.4883
	0.12	11.2400	96.5560	87.5120	86.0840	0.4889
	0.14	11.2400	96.5560	87.5120	86.0690	0.4894
	0.16	11.2400	96.5570	87.5120	86.0520	0.4900
	0.18	11.2760	96.5580	87.5120	86.0350	0.4905
	0.20	11.2770	96.5590	87.5120	86.0170	0.4911
CaO Open Blended Process	0.10	14.0960	96.1950	87.5120	87.9000	0.1719
	0.12	14.0970	96.1950	87.5120	87.8840	0.1720
	0.14	14.0970	96.1960	87.5120	87.8670	0.1721
	0.16	14.0980	96.1960	87.5120	87.8500	0.1721
	0.18	14.0980	96.1960	87.5120	87.8330	0.1722
	0.20	14.1250	96.1970	87.5120	87.8140	0.1723
CaO Open loop Process	0.10	14.0960	96.1950	87.5120	58094.0000	0.1719
	0.12	14.0970	95.2710	86.6570	57437.0000	0.1711
	0.14	14.0970	95.2710	86.6570	57450.0000	0.1712
	0.16	14.0970	95.2710	86.6570	57463.0000	0.1713
	0.18	14.0980	95.2710	86.6570	57476.0000	0.1713
	0.20	14.1250	95.2730	86.6570	57490.0000	0.1714
Alkaline Process	0.10	20.3480	109.0100	97.8650	94.1470	1.1821
	0.12	20.3480	109.0100	97.8650	94.1470	1.1821
	0.14	20.3570	109.0100	97.8650	94.0540	1.1845
	0.16	20.3520	109.0100	97.8650	94.0090	1.1861
	0.18	20.3510	109.0100	97.8650	93.9610	1.1874
	0.20	20.3380	109.0100	97.8650	93.9140	1.1889
Acidic Process	0.10	18.7190	108.8300	97.8560	96.9100	1.0090
	0.12	18.7190	108.8300	97.8560	96.8770	1.0098
	0.14	18.7200	108.8300	97.8560	96.8430	1.0107
	0.16	18.7210	108.8300	97.8560	96.8080	1.0115
	0.18	18.7210	108.8300	97.8560	96.7710	1.0125
	0.20	18.7210	108.8300	97.8560	96.7340	1.0134

responsibilities, as discussed in preceding sections. Moreover, the increase in FFA molar content in the oil from 10% to 20% affects the processes of acidic, alkaline, and CaO catalyzed transesterification. Consequently, this leads to changes in the overall expenses of the plant. These changes encompass a range of 11.0–20.5 million USD for CAPEX, 95 to 111 million USD per year for OPEX, 80 to 110 million USD per year for raw material costs, 86 to 97 million USD per year for product sales, and 0.17 to 1.19 million USD per year for utilities costs.

The total capital expenditures (CAPEX) for the alkaline catalyzed transesterification process are roughly more than 8.64% higher than those for the acidic catalyzed process. This increase is because the alkaline process involves additional operational blocks, such as an extraction column for water washing, a decantation unit for separation, and an alkaline removal unit, along with a third biodiesel purification column. Likewise, the capital expenditures (CAPEX) for both the alkaline and acidic catalyzed transesterification processes are approximately more than 39.19% and 27.64% higher, respectively, than the CAPEX for CaO catalyzed processes. These CaO processes encompass open loop, open blended loop, and closed loop configurations. This difference is mainly due to the simplicity of the CaO catalyzed transesterification process, which requires fewer operational blocks. Moreover, the yearly operating expenses (OPEX) for both the alkaline and acidic catalyzed transesterification processes are approximately over 13.11% greater than the OPEX for CaO catalyzed processes. These CaO processes include various configurations like open loop, open blended loop, and closed loop. This difference is also attributed to the streamlined nature of the CaO catalyzed process, resulting in a decrease in the number of operational blocks. Similar findings in economic analysis were also reported by Nasreen, Nafees [82].

In addition, the yearly costs for raw materials in both the alkaline and acidic catalyzed transesterification processes are roughly more than 11.8% higher than the costs for raw materials in CaO catalyzed processes. These CaO processes include various configurations such as open loop, open blended loop, and closed loop. The increased raw material costs in the alkaline and acidic catalyzed transesterification processes stem mainly from the requirement of neutralization reagents. These reagents are essential for eliminating the acidic and alkaline components in the end products. The decrease in annual product sales as FFA molar content increases from 10% to 20%, as indicated in Tables 10 and is mainly due to the decrease in molar purity of the products. The additional production of valuable products in alkaline removal units (such as Na_3PO_4) and acidic removal units (such as CaSO4) leads to increased production sales in both alkaline and acidic catalyzed transesterification processes. This increase is approximately more than 6.95% for the alkaline process and about 10.16 times for the acidic process compared to the annual raw materials expenses for CaO catalyzed processes. Moreover, the CaO catalyzed closed loop transesterification process yields a lower annual product sales of around 86 million USD per year compared to the open and open blended loop process configurations. The reason for this difference lies in the fact that the valuable products recovered in the open and open blended loop processes are reintroduced into the closed loop process through recycling. Consequently, this recycling approach eliminates their economic potential during the analysis.

The annual utilities costs of the process are directly influenced by the process's energy requirements, resulting in higher utilities consumption to ensure stable operation as energy demands increase. Table 10 displays a decreasing trend in annual utilities costs as FFA molar content rises from 10% to 20% in alkaline (1.19 million USD/yr), acidic (1.02 million USD/yr), CaO closed loop (0.51 million USD/yr), and CaO open blended and open loop (0.17 million USD/yr) transesterification processes. This trend is due to more operational blocks in alkaline, acidic, and CaO closed loop processes. Generally, the increase in FFA molar content from 10% to 20% has an insignificant impact on total capital expenditures across the transesterification processes, attributed to consistent mapping and sizing of operational blocks in the process.

3.5. *Effect of oil flow rate on product purity*

Increasing the amount of oil while keeping the amount of ethanol constant leads to less ethanol relative to the oil. This consequently affects the efficiency and propagation of transesterification process as

highlighted in a number of literatures [106,120]. In addition, when the oil mass flow rate is increased while maintaining a constant ethanol mass flow rate, it leads to a decrease in the quantity of un-reacted excess ethanol present in the process. Therefore, this decrease in un-reacted ethanol contributes to a reduction in the molar purity of the ethanol that is recovered from the process. This effect becomes more pronounced as the oil mass flow rate is increased. Depending on how the process is set up, changes in oil amounts can make the quality of the biodiesel product better or worse. This section presents more insight on the effect of disturbances in oil flow rate on molar purity of produced products in acidic, alkaline and CaO catalyzed transesterification process.

The impact of raising the oil mass flow rate from 4000 to 12,000 kg/h on the molar purity of biodiesel (Biodiesel-1and Biodiesel-2), recovered ethanol (R-EtOH2), glycerol, calcium sulfate ($CaSO_4$), and the waste product in the acidic catalytic transesterification process is depicted in Fig. 9. At 4000 kg/h, the molar purity of biodiesel and glycerol products is low because of the significant presence of unreacted ethanol in the products. Consequently, this leads to a high ethanol molar concentration in both the recovered ethanol and the waste product. When the oil mass flow rate is increased from 4000 kg/h to 5000 kg/h, there is not only a sharp rise in the molar purity of biodiesel and glycerol but also a reduction in the molar purity of $CaSO_4$ and the ethanol molar concentration in both the recovered ethanol and the waste product.

Moreover as illustrated in Fig. 10, an increase in the mass flow rate of oil from 5000 kg/h to 12,000 kg/h leads to changes in the molar purity of glycerol and $CaSO_4$, as well as variations in the ethanol molar concentration in both the recovered ethanol and waste product. The decrease in the molar purity of $CaSO_4$ can be attributed to the increase in water molar content resulting from the esterification conversion reaction of FFA. In addition, an increase in the oil mass flow rate from 5000 kg/h to 12,000 kg/h results in a relatively stable molar purity of biodiesel-2. However, beyond 6000 kg/h, the molar purity of biodiesel-2 experiences a decline. This finding emphasizes the crucial oil flow rate at which the intended process's greatest molar biodiesel purity is attained.

In the context of the alkaline catalytic transesterification process, the plotted data in Fig. 11 unveils fascinating insights. The shifts in oil mass flow rate are intricately linked to changes in the molar purity of various elements, providing illumination on the dynamics of the process. Within the span of 5000–6000 kg/h for oil mass flow rate, elevating this parameter simultaneously elevates the molar purity of biodiesel (Biodiesel-1 and Biodiesel-2), glycerol, and sodium phosphate (Na_3PO_4). Furthermore, there is an upsurge in the molar content of biodiesel within waste stream W–S2. However, a converse trend is noticeable for ethanol and the molar content of biodiesel in the recovered ethanol stream (R-EtOH2) and waste stream W–S3, respectively. Once the oil mass flow rate surpasses the 6000 kg/h threshold, a more intricate pattern unfolds. Specifically, the molar purity of biodiesel-1 continues to ascend, while biodiesel-2, glycerol, ethanol, and the molar content of biodiesel in R-EtOH2 and waste stream W–S2 witness a decline. Particularly, the molar purity of Na_3PO_4 and the biodiesel molar content within waste streams W–S1 and W–S3 maintain a relative constancy during this phase. These collective observations imply that, beyond an oil mass flow rate of 6000 kg/h, the process attains a state of stability. The complicated relationship among these variables suggests a consistent, steady-state operation within the alkaline catalytic transesterification process.

The findings in Fig. 12 depicts the impact of different oil flow rates in a CaO catalytic transesterification process. The process includes biodiesel (biodiesel-1, biodiesel-2, and biodiesel-3), glycerol, recovered excess ethanol (R-EtOH), and unreacted oil (R-oil). Primarily, the rise in biodiesel-1, biodiesel-2, and biodiesel-3 purity with increasing oil flow rates from 4000 to 12,000 kg/h suggests a better transesterification reaction progress. This indicates that higher oil flow rates improve conversion rates and increase biodiesel purity as highlighted in a study by Refs. [121,122]. Moreover, the significant surge in glycerol purity as the oil flow rate hits 5000 kg/h, followed by a slight drop, reveals a complex interaction between reaction kinetics and mass transfer. The initial increase may indicate better glycerol formation kinetics [123], but the subsequent decrease points to a rise in unreacted oil levels, impacting glycerol purity [124].

The decrease in recovered excess ethanol (R-EtOH) and unreacted oil (R-oil) purity with rising oil flow rates can be explained by various factors. The drop in R-EtOH purity is due to increased ethanol needed to complete the reaction at higher oil flow rates [125]. On the contrary, the lower R-oil purity stems from higher final product purity, indicating better oil conversion to biodiesel and glycerol. The outcomes in Fig. 12 emphasize the link between oil flow rates, reaction kinetics, and product purity during transesterification [124,126]. The results suggest that optimizing oil flow rate is crucial for achieving high yields and purity of biodiesel and by-products in CaO catalytic transesterification.

Similar observations are illustrated in Fig. 13, illustrating the effects of disturbances in the oil mass flow rate on the molar purity of biodiesel, glycerol, recovered excess ethanol (R-EtOH), and unreacted oil (R-oil). These observations pertain to a CaO catalytic process and encompass both open blended and closed-loop transesterification processes. The increase in the oil mass flow rate from 4000 to 12,000 kg/h results in an increase in the molar purity of biodiesel. It does, however, reduce the molar purity of R-EtOH and R-oil. In addition, as the oil mass flow rate

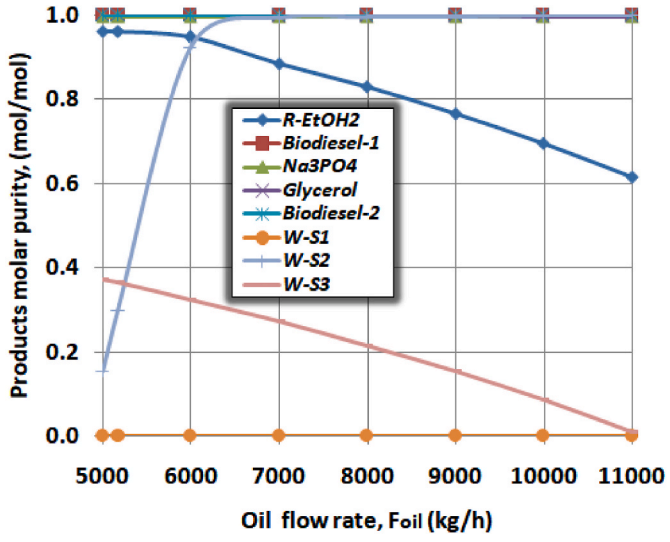

Fig. 11. Effect of oil flow rate on product purity in Alkaline catalytic transesterification process. (Key: W–S1═W–S2 = W–S3 = waste products).

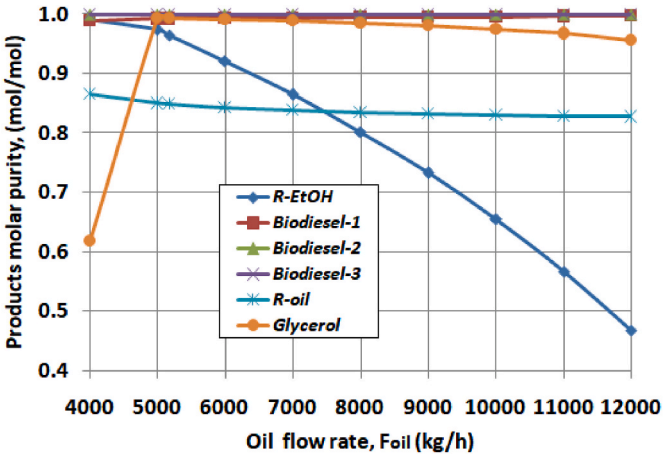

Fig. 12. Effect of oil flow rate on product purity in CaO catalysis open loop transesterification process (Key: R-ETOH = recovered ethanol, R-OIL = recovered oil).

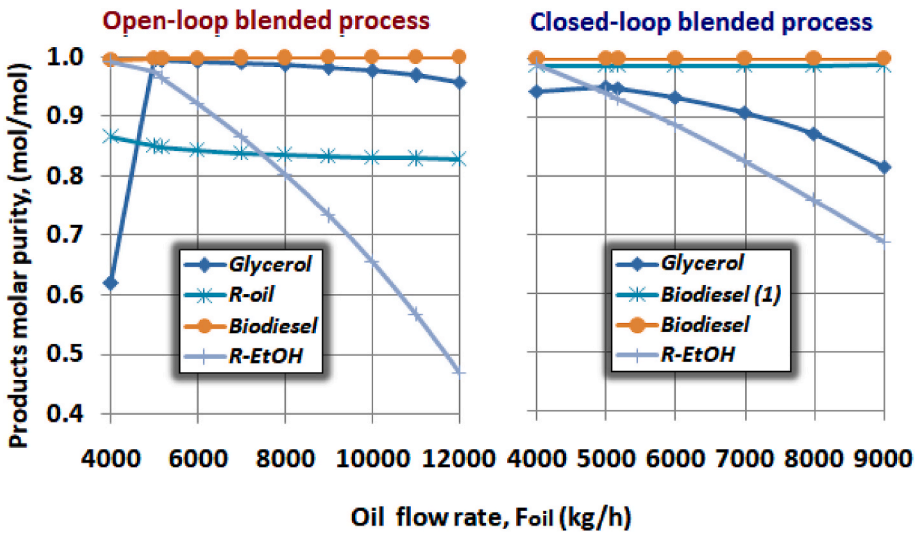

Fig. 13. Effect of oil flow rate on product purity in CaO catalysis open loop blended and closed loop transesterification process.

increases from 4000 kg/h to 5000 kg/h, the molar purity of glycerol begins to decline significantly due to an increase in the amount of unreacted oil.

The entire course of the transesterification process, its effectiveness, product purity, operational expenses, and energy needs are all significantly impacted by variations in the oil flow rate. Elevating the oil mass flow rate to the critical threshold yields higher product yields, improved purity, increased energy demands, and heightened operational expenses. However, this increment in operational expenses is offset by the augmented value of the products, attributed to their enhanced quality. Furthermore, pushing the oil mass flow rate beyond this critical point may introduce operational challenges. These include a reduction in oil conversion efficiency due to shorter reaction residence times and an increase in process downtime. Thus, establishing the critical oil flow rate becomes imperative to ensure both the effectiveness and efficiency of the transesterification process. Based on the outcomes obtained, it is recommended that the optimal oil flow rate for the designed biodiesel production processes falls within the range of 4000 to 6000 kg/h.

3.6. Effect of ethanol flow rate on product purity

The ethanol mass flow rate stands as another operational parameter exerting influence on the efficiency and advancement of the transesterification process. When the ethanol flow rate is kept at a low level, the transesterification reaction tends to come to a halt due to an imbalance in the stoichiometric reaction. Equally, when a moderate ethanol flow rate is employed, the transesterification reaction may linger incompletely and even reverse, which in turn affects the yields of both biodiesel and glycerol. On the other hand, elevating the ethanol flow rate to a high level promotes the forward progression of the reaction, ultimately favouring the production of biodiesel and glycerol. As a result, it becomes vital to ascertain the optimal flow rate that can lead to effective and efficient biodiesel production with an augmented level of molar purity.

Effect of increasing ethanol mass flow rate, ranging from 2000 to 5000 kg/h, on the molar purity of various products within the acidic catalytic transesterification process is illustrated in Fig. 14. The variations in ethanol mass flow rate interplay with the resulting molar purity of biodiesel (Biodiesel-1 and Biodiesel-2), recovered ethanol (R-EtOH2), glycerol, calcium sulfate ($CaSO_4$), and the waste product. Upon increasing the ethanol mass flow rate from 2000 to 2500 kg/h, a distinguished surge in the molar purity of biodiesel-1, $CaSO_4$, and the ethanol molar concentration in both the R-EtOH2 and waste product is evident. Further elevating the ethanol mass flow rate beyond 2500 kg/h

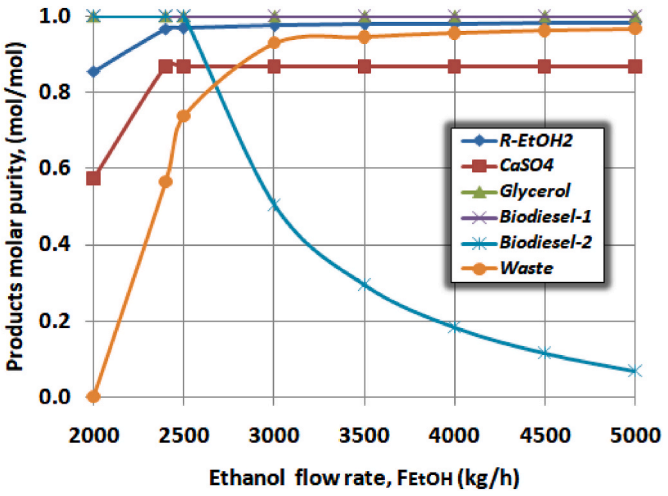

Fig. 14. Influence of the rate of ethanol flow on the purity of the product in an acid-catalyzed transesterification process.

while maintaining a constant oil flow rate leads to an increase in ethanol molar content across the process streams. So, this rise contributes to improved molar purity of biodiesel-1 through increased forward triglyceride conversion. This effect extends to ethanol molar content within the recovered ethanol stream (R-EtOH2) and the waste product. However, this progression is accompanied by a decline in the molar purity of glycerol and biodiesel-2. Furthermore, the molar purity of $CaSO_4$ exhibits an increase, attributed to higher FFA conversion efficiency, which can be linked to a substantial neutralization of acid within the acid removal reactor [127].

The molar purity trends for biodiesel (Biodiesel-1 and Biodiesel-2), recovered ethanol (R-EtOH2), glycerol, sodium phosphate (Na_3PO_4), and the waste by-products (W–S1, W–S2, and W–S3) resulting from an alkaline catalytic transesterification process are depicted graphically in Fig. 15. These graphs illustrate how variations in ethanol mass flow rates impact these substances. As the ethanol mass flow rate is increased from 2000 to 2500 kg/h, a noticeable reduction in the molar purity of biodiesel (Biodiesel-1and Biodiesel-2), sodium phosphate (Na_3PO_4), and the molar content of biodiesel in W–S2 becomes apparent. This decline primarily results from the increased presence of unreacted ethanol in the product mixture. Furthermore, raising the ethanol mass flow rate from 2000 to 2500 kg/h also leads to a significant increase in the molar

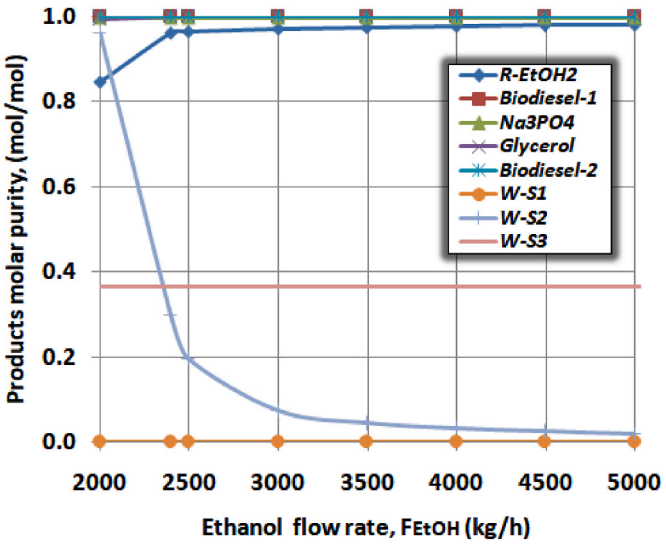

Fig. 15. Influence of ethanol flow rate on product purity in the alkaline catalytic transesterification process (Key: W–S1═W–S2 = W–S3 = waste products).

concentration of ethanol in the recovered ethanol and glycerol. This change is a consequence of an additional glycerol purification step introduced into the process. Beyond the threshold of 2500 kg/h, as indicated in the graphical representation, further increases in the ethanol mass flow rate not only improve the molar purity of biodiesel-2, glycerol, and recovered ethanol but also contribute to a reduction in the molar purity of biodiesel-1 and the molar content of biodiesel in W–S2. Throughout these variations in ethanol mass flow rates, the molar content of biodiesel in both W–S1 and W–S2 remains constant, signifying the effective separation of trays within the biodiesel purification column.

In addition, Fig. 16 displays the impact of ethanol mass flow rate on the molar purity of biodiesel-1, biodiesel-2 and biodiesel-3, glycerol, recovered excess ethanol (R-EtOH), and unreacted oil (R-OIL) generated in a CaO catalytic open-loop transesterification process. Increasing the ethanol mass flow rate from 1500 to 2000 kg/h results in a significant surge in the molar purity of biodiesel-2 and biodiesel-3, R-EtOH, and glycerol. This is primarily attributed to the heightened ethanol-to-oil ratio, which improves the conversion of triglycerides into biodiesel and glycerol. Therefore, this leads to a marked decrease in the molar content of triglycerides in the unreacted recovered oil. Likewise, raising the ethanol mass flow rate beyond 2000 kg/h leads to a decrease in the molar purity of biodiesel-1 and R-oil, but it also results in an increase in the molar purity of biodiesel-3 and R-EtOH due to the greater presence of excess ethanol in the products. Further elevating the ethanol mass flow rate beyond 2000 kg/h causes a reduction in the molar purity of glycerol and biodiesel-2. However, the molar purity of biodiesel-2 and recovered ethanol remains steady as the ethanol mass flow rate exceeds 3000 kg/h. This is primarily because the plant operates consistently with high efficiency under this flow rate, although it significantly raises operational costs while maintaining product purity and value, consequently reducing overall sales profits.

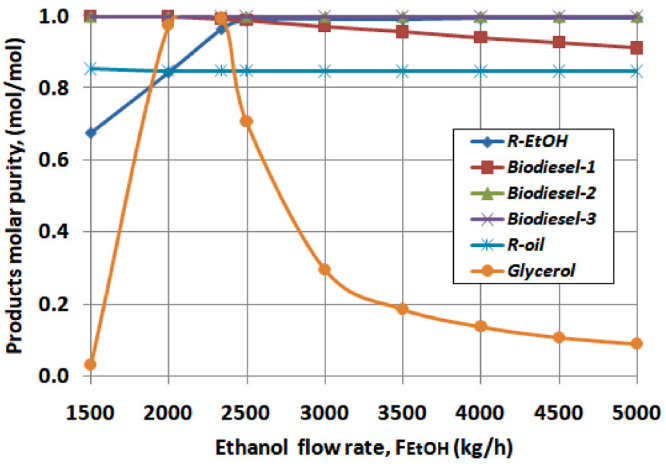

Fig. 16. Effect of ethanol flow rate on product purity in CaO catalysis open loop transesterification process.

The relationship between increasing ethanol mass flow rate and the resulting molar purity of biodiesel, glycerol, recovered excess ethanol (R-EtOH), and un-reacted oil (R-oil) is depicted in Fig. 17. This correlation is established within the context of a CaO catalytic open blended and closed loop transesterification process. From both processes, an increase in ethanol mass flow rate from 1500 to 5000 kg/h and from 2000 to 5000 kg/h, respectively results into increase in the molar purity of R-EtOH and R-oil. Furthermore, the molar purity of glycerol increases sharply with increase in oil mass flow rate from 1500 kg/h to critical flow rate (2500 kg/h) and begin to exponentially decrease because of increase in the amount of ethanol in the process streams.

In the CaO catalytic open blended loop transesterification process, the quality of biodiesel purity decreases as the flow rate of ethanol increases from 1500 to 5000 kg/h. This decline is mainly due to the increased presence of excess ethanol in the final products highlighted in Cavalcante, Penha [128]. However, in the CaO catalytic closed-loop transesterification process, there is a different trend regarding the molar purity of biodiesel. It rises as the ethanol flow rate goes up from 2000 to 5000 kg/h. This increase can mostly be attributed to the addition of an extra step for purifying biodiesel within the process. This addition is carefully implemented to counter the impact of reusing less pure components and, as a result, enhance the overall purity of the biodiesel produced. The changes in the flow rate of ethanol, as illustrated in Figs. 16 and 17, imply significant effects on the overall progression of the transesterification reaction. These effects extend to the reaction's efficiency, product purity, operational expenses, and energy requirements. An increase in the ethanol mass flow rate up to the critical point leads to an augmentation in product yield, purity, energy requirements, and operating expenses. Therefore, it is crucial to establish the critical ethanol flow rate based on reaction kinetics and conditions to ensure both effective and efficient productivity of the transesterification process. Consequently, based on the obtained results, the optimum ethanol flow rate for the planned biodiesel production processes should ideally fall within the range of 2000–2500 kg/h.

4. Conclusion

In this study, three different methods for biodiesel production from non-edible sources in Africa are assessed, focusing on both technical and economic aspects. The optimal flow rates of oil and ethanol are found to be in the range of 4000–6000 kg/h and 2000–2500 kg/h respectively for acidic, alkaline, and CaO catalytic transesterification. Despite a rise in the FFA content from 10% to 20%, all three methods consistently generate biodiesel that meets EN14213, EN14214, ASTM D6751, ANP42, IS15607, and JASOM360 international standards, thereby enhancing their economic viability. The by-products obtained during the production process, such as glycerol and calcium sulfate, also contribute to the economic feasibility of these methods. Notably, the acid-catalyzed process requires significantly higher energy compared to the alkaline and CaO methods, resulting in higher operating expenses. On the other hand, the CaO catalysis method proves to be economically favourable due to its simplicity and adaptability in various configurations, leading to reduced energy and cost requirements. Specifically, the CaO method reduces costs by 11.59% and energy consumption by 13.31% for closed-loop systems, and by 41.78% for open and open blended loops. These economic findings highlight the financial

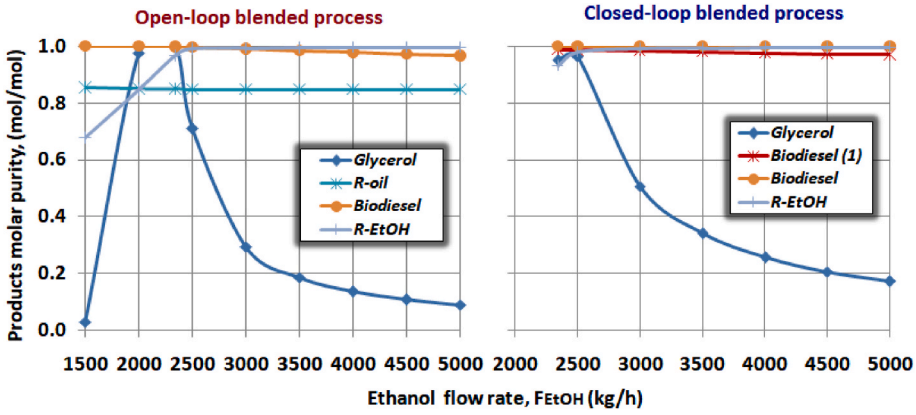

Fig. 17. Effect of oil flow rate on product purity in CaO catalysis open loop blended and closed loop transesterification process.

advantages of utilizing the CaO catalytic process, which complements its technical efficiency in biodiesel production from non-edible feedstocks in Africa.

CRediT authorship contribution statement

Thomas Kivevele: Writing – review & editing, Methodology, Funding acquisition, Conceptualization. **Baraka Kichonge:** Software, Methodology, Formal analysis, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.energy.2024.131302.

Note: COL-1, G – COL, ET – COL and P – COL are all RadFrac distillation columns.

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Nomenclature

RSTOIC: Stoichiometric reactor
AFO: Animal fat oil
HSOD: Waste derived catalyst
FFA: Free fatty acid
CaO: Calcium oxide
COL-1: Distillation column
G-SEP: Gravity two-phase liquid-liquid separator
G – COL: Glycerol separation column
C-SEP: Component separator
ET – COL: Ethanol recovery column
EX – COL: Extractive column
R – NUTRAL: Neutralization reactor
P – COL: Purification column
R – ETOH: Recovered ethanol stream
S12: Material stream
RadFrac: The main separation block in Aspen Plus
FFX: Free fatty acid conversion reactor