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Base-Catalyzed Transesterification vs. Supercritical Methanol Transesterification in the Optimization, Rigorous Model Simulation, and Heat Integration for Biodiesel Production

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Abstract: Biodiesel production is worthy of continued study and optimization of production procedures due to its environmentally beneficial attributes and renewable nature. This study aims to investigate the optimum conditions and optimum production unit for the production of biodiesel from waste vegetable oil. Two production processes were considered: one using base-catalyzed transesterification, and the second is non-catalytic transesterification (using methanol at very high temperature and pressure). Through optimizing the process variables that affect the yield and purity of biodiesel, optimal transesterification conditions that produce maximum biodiesel yield were reached. Furthermore, the optimum production process that consumes less heating and cooling energy and has less environmental impact was identified. The surface plot, contour plot, and the Pareto chart were used to represent and relate the influence of the process variables on biodiesel yield. The parameters were correlated with the biodiesel yield using linear regression analysis. HYSYS model was developed for both techniques using the optimum conditions to figure out the optimum reactor dimensions required for the two processes at these conditions. A detailed comparison between the two processes was discussed, including the CO_2 emissions for the two processes, the energy required for both, and energy integration to minimize the energy supplied as possible. Finally, economic aspects and cost analysis were also discussed.

Keywords: base-catalyzed transesterification, supercritical methanol transesterification, Pareto chart, contour plot, surface plot, heat integration.

碱催化酯交换与超临界甲醇酯交换在生物柴油生产的优化、严格模型模拟和热集成中的应用

摘要：生物柴油生产因其对环境有益的属性和可再生性而值得继续研究和优化生产程序。本研究旨在探讨利用废弃植物油生产生物柴油的最佳条件和最佳生产装置。考虑了两种生产工艺：一种使用碱催化酯交换，第二种是非催化酯交换（在非常高的温度和压力下使用甲醇）。通过优化影响生物柴油产量和纯度的工艺变量，达到了产生最大生物柴油产量的最佳酯交换条件。此外，还确定了消耗较少加热和冷却能量并且对环境影响较小的最佳生产工艺。表面图、等高线图和帕累托图用于表示和关联过程变量对生物柴油产量的影响。使用线性回归分析将参数与生物柴油产量相关联。HYSYS 模型是针对两种技术开发的，使用最佳条件来确定在这些条件下两种工艺所需的最佳反应器尺寸。讨论了这两个过程之间的详细比较，包括两个过程的二氧化碳排放量、两者所需的能量以及尽可能减少能源供应的能量整合。最后，还讨论了经济方面和成本分析。

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关键词：碱催化酯交换、超临界甲醇酯交换、帕累托图、等高线图、曲面图、热积分。

1. Introduction

Transesterification is the process used to produce the mono-alkyl esters from triglycerides in the presence of alcohol. A successful transesterification reaction is signified by the ease of separation of the ester and glycerol layers after the reaction time. The transesterification reaction is controlled by some parameters; their controlling and optimizing will yield the optimum conversion. The process variables or reaction parameter optimization greatly affect the yield and purity of biodiesel [26]. From this point, the biodiesel yield could be significantly maximized by identifying the optimal conditions. The extent of transesterification and side reactions depend mainly on the feedstock and catalyst types, catalyst loading, alcohol to oil molar ratio, reaction temperature and time.

Any animal or plant lipid could be a ready substrate for biodiesel production, as they represent a fatty acid source used in preparing biodiesel. The feedstock type as the source of triglycerides is chosen according to its availability in each region or country. Hence, rapeseed and sunflower oils are used in the European Union, palm oil is used in tropical countries, and soybean oil and animal fats are considered the main feedstock in the United States [1]. The feedstock availability, cost, storage properties, and engine performance are the factors that promote one feedstock over another to be potentially used for massive production of ME. Nowadays, the recent focus is to use non-edible oil or waste edible oil as a feedstock for biodiesel production to not compete with the food supply. The new biodiesel production process trends aim to produce biodiesel from waste frying oils instead of virgin vegetable oils. The new trend of using WVO as a feedstock produces biodiesel of quality comparable to that of virgin vegetable oil biodiesel. Besides, using waste frying oil as a feedstock lowers production costs due to reduced raw material costs. Commonly, the waste oil is drained into sewage, causing environmental problems. Hence, from a waste management standpoint, it is highly recommended to reuse the waste frying oil to produce biodiesel. It is highly beneficial as it provides a cleaner and safer way of disposing these wastes [2].

Alcohol is one of the main parameters that affect the transesterification reaction. Short-chain alcohols such as methanol, ethanol, and butanol are the most widely used. Using different alcohols in the transesterification will cause some differences in the reaction kinetics and affect the final yield of esters. Therefore, selecting the type of alcohol for the transesterification is based mainly on its cost, performance, and availability [3]. Commonly, the produced esters are methyl esters, which is associated mainly with the use of methanol more than other alcohols. Methanol is considered the least expensive alcohol and the most widely available. However, some countries, such as Brazil, use ethanol instead of methanol due to its high availability and low price. The methyl ester is considered the prime chief commercial product for biodiesel. As a result, its production was studied, demonstrated, and modeled [4]. The ethanol production from renewable resources is independent of petroleum-based alcohols [3, 5]. Mostly, methanol is produced using natural gas worldwide. However, the current interest is to produce methanol from renewable biomass resources to maintain its capability of being an advantage over ethanol.

Some production techniques, such as supercritical methanol and co-solvent transesterifications, are performed without catalysts. However, in some other techniques like base-catalyzed or acid-catalyzed transesterification, the reaction depends mainly on the presence of either a base or acid catalysts, respectively. The most alkaline catalysts used in biodiesel production are potassium hydroxide (KOH) and sodium hydroxide (NaOH), considered cheap catalysts, widely available, and easy to transport or store. For large continuous flow production, it is preferable to use an alkyl oxide solution like sodium methoxide or potassium methoxide in methanol [6]. Many researchers believe that potassium hydroxide is the best alkaline catalyst to produce biodiesel with better properties [7-9]. However, many other studies have achieved their best results using NaOH [10-12]. When discussing catalyst formulation, we must focus on the loading of catalyst used. Yaakob et al. found that using NaOH instead of KOH will provide higher biodiesel yields using a lower concentration [13].

Many researchers stated that increasing the reaction temperatures in the transesterification process decreases the time required to reach maximum conversion [4]. In other words, the process would take a shorter time at high temperatures. For base-catalyzed transesterification, the reaction temperature range extends from the room temperature to the boiling point of the alcohol used [14]. Thus, the usual temperature used during transesterification in most literature is 25-65°C. A serious problem is encountered if the reaction temperature exceeds the boiling point of the used alcohol. This problem causes alcohol vaporization and alcohol bubbles in the reaction medium that will inhibit the transesterification and decrease the biodiesel yield [15]. Many researchers have tried different temperatures to reach the optimum for the transesterification reaction. Refaat et al. [16] found

that, at a temperature approaching 65°C, an optimum conversion is achieved. Meng et al. [15] observed the optimum conversion at 50°C. Yaakob et al. [13] related the temperature and time with the biodiesel yield and found that the optimum yield is achieved at 60°C.

One of the main drawbacks of base-catalyzed transesterification is the time spent for the reaction to occur. Most investigators have recorded the optimum reaction time to be 1 h. [15-17]. It was reported that allowing a longer reaction time will not increase the conversion that much. Instead, it favors the backward reaction (hydrolysis of esters), reducing the product yield [16]. Felizardo et al. [12] noticed that the highest ME yield is achieved after 1 h. of reaction using a methanol to oil molar ratio of 4.8:1 and a catalyst concentration of 0.6% (by wt of oil). However, using another non-catalytic approach, methanol at very high temperature and pressure, under supercritical conditions (350-400ºC and > 80 atm) and at high (42:1) alcohol to oil ratio, the reaction is complete in about 4 minutes with a high yield of methyl esters reach 98 % [14].

Several approaches have been proposed to decrease the FFA content in the oil. One of the most famous techniques is acid esterification with methanol and sulphuric acid [15]. For reducing water content, heating to above 100°C is required for the WVO sample [15, 16]. Alternatively, vacuum distillation (0.05 bars) is used at the industrial scale [12]. Besides, suspended solids, phospholipids, and other impurities can be washed away with hot water or removed by centrifugation and paper filtration [13]. Other processes were introduced: neutralization, steam injection, and column chromatography. The filtered oil is dried by heating up to 100 °C for at least 15 min. with continuous stirring to ensure an anhydrous medium [11].

Biodiesel production from used cooking oil is similar to that from refined oils. Many approaches are involved, but some limitations must be considered for selecting a particular process. The process selection depends on the amount of free fatty acid and water content of the used cooking oil. It is reported that the refined vegetable oil, crude vegetable oil, used cooking oil, animal oil, and trap greases generally contain 0.05%, 0.3%–0.7%, 5%–30%, and 40%–100% of free fatty acid, respectively [14, 15].

The most commonly used technique for biodiesel production from waste vegetable oils is believed to be base-catalyzed transesterification. Also, it is known to be the most economical process. This belief is associated with the fact that it requires low operating temperatures and pressures, achieves over 98% conversion yield (provided the starting oil is low in moisture and FFA), and no intermediate compounds are involved. As a result, no special materials for construction are needed [6]. However, this approach has some limitations. The most important limitations are its high sensitivity to FFA and water contents in the feedstock oils. Base-catalyzed transesterification cannot tolerate more than 1% w/w FFA content. Otherwise, a saponification reaction occurs, the catalyst efficiency is reduced, and the viscosity is increased. Also, the oils used in transesterification should be substantially anhydrous (0.06% w/w) to prevent soap and gel formation and ease the recovery of glycerol. Moreover, base-catalyzed transesterification is an energy-intensive process. This is because of the difficulty of recovering glycerol, removing the alkaline catalyst, and treating the alkaline wastewater [18].

However, in the past few years, several new production approaches have been developed from laboratory-scale research to reduce biodiesel production costs. One such approach uses alcohol in its supercritical state and eradicates the need for a catalyst. This process solves some of the drawbacks of the base-catalyzed process. Supercritical methanol transesterification can reach a very high conversion in a short period. Also, it can tolerate up to 36 wt.% and 30 wt.% for FFAs content and water content in the feedstock, respectively. However, it requires an elevated pressure and temperature for the reaction to occur. Higher alcohol to oil molar ratio is employed in the reaction medium. The synthesis of biodiesel using supercritical methanol is a promising technology resulting in sustainable biodiesel production [19, 20].

The research involved techniques for reaction parameters optimization and thus embedded optimum values into a simulation-based design procedure for overall energy optimization/integration and emissions reduction. Literature experimental reaction data for the two technologies (base-catalyzed and supercritical) conduct an optimization for biodiesel production. The state-of-the-art process flowsheets for the two processes were used for the study. This optimization was done for the most affecting parameters on the production processes. The experimental results from the literature for the two techniques were optimally analyzed using the Pareto chart, contour plot methodology, and surface plot methodology. The research revealed that catalyst loading was the key variable for the base-catalyzed process. On the other hand, for the supercritical methanol process, the most prominent variable was the methanol to oil ratio. The optimal process conditions were used to build an ASPEN HYSYS rigorous simulation model for the previous techniques. The supercritical based-process was chosen for further studies for its better economic performance. Pinch Analysis principles through ASPEN Energy Analyser software were employed to analyze the energy performance of the overall optimum model obtained from ASPEN HYSYS. The energy targets were calculated for biodiesel production using the supercritical methanol approach. Compared with the original process, composite curves were developed to calculate heating and cooling requirements for the

optimized process. Finally, a heat exchanger network was developed to accomplish the energy targets proposed by the composite curves. The resulting integrated process flowsheet has better energy-saving opportunities.

2. Methodology

2.1. Base-Catalyzed Transesterification

The process starts with vigorous mixing to dissolve the catalyst (NaOH) in methanol. The oil is transferred in the first step from triglycerides to diglycerides. During further methanolysis and stirring, the diglycerides are converted into monoglycerides and then to glycerol. In the biodiesel reactor, the final mixture is stirred vigorously for 3 h. at 65°C. A successful transesterification reaction produces two liquid phases: ester and crude glycerin. Because of the high viscosity of crude glycerin, it is collected at the bottom of the settler. After 10 min., the phase separation is noticed and can be completed within 2 h. of settling. Some investigators recorded 20 h. to be the sufficient time required for complete settling. After the complete settling, water is stirred with the mixture for 5 min. The glycerin is allowed to settle again. A water solution at a rate of 28% by volume of oil and 1 g of tannic acid per liter of water is mixed with ester for washing purposes. Continuous stirring with water takes place until the biodiesel layer becomes pure. For final washing, only water is added at 28% by volume of oil after settling [17].

2.1.1. Experimental Data

Vincente et al. [21] obtained the following experimental results (Table 1). The conversion of triglycerides to biodiesel is correlated with the temperature of the reaction, the catalyst loading, and the methanol to oil molar ratio. The time of reaction was fixed at 3 hours. The optimum conditions were at 25˚C, 1.3% catalyst loading, and a 6:1 methanol to oil molar ratio.

Table 1 Base-catalyzed experimental data [21]

Temp.	Cat. %	Meth:oil	Conv. %
65	1.5	4.5:1	90.43
65	1.5	7.5:1	89.52
65	0.5	4.5:1	98.7
65	0.5	7.5:1	98.32
25	1.5	4.5:1	97.17
25	1.5	7.5:1	96.88
25	0.5	4.5:1	96.96
25	0.5	7.5:1	99.28

2.1.2. Process Flowsheet

The process flowsheet of biodiesel production using the conventional method for base-catalyzed transesterification is shown in the following figure. First, the oil is filtered and then pumped into a pre-heater before reaching the reactor, while methanol and the base catalyst are mixed and pumped into the reactor. In the biodiesel reactor, the transesterification reaction occurs; then, the mixture is directed to a methanol recovery column to recycle the unreacted methanol. Finally, the bottom stream of crude biodiesel and glycerol are washed and stirred by water, as previously discussed, to obtain pure biodiesel and glycerol [25].

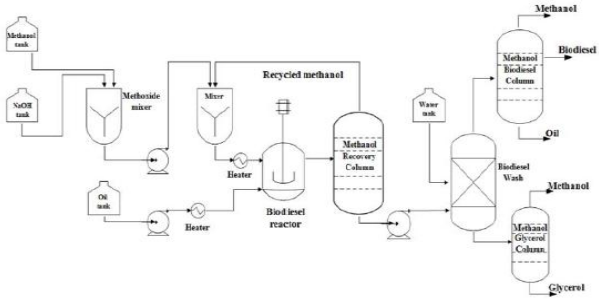

Fig. 1 Base-catalyzed transesterification process flowsheet [25]

2.2. Supercritical Methanol Transesterification

Supercritical transesterification is a possible alternative to the typical catalytic routes. Supercritical methanol transesterification shows nearly a complete conversion in a relatively short period (2-8 min.) [22]. For the reaction to occur, high temperatures and large alcohol to oil ratios are employed to achieve high conversion levels. The operating temperature could reach 350˚C, and the alcohol to oil ratio is about 42:1 [23].

2.2.1. Experimental Data

Kusdiana and Saka [23] developed the following experimental data for supercritical methanol transesterification (Table 2). They correlate the conversion of triglycerides into biodiesel with the reaction time in minutes and the methanol to oil molar ratio. The optimum conditions that provided almost complete conversion were 8 minutes and 42:1 methanol to oil molar ratio.

Table 2 Supercritical methanol experimental data [23]

Meth:oil	Time (min.)	Conv. %
4.5:1	2	50
4.5:1	4	60
4.5:1	6	62
4.5:1	8	72.7
6:1	2	53
6:1	4	63.5
6:1	6	68

Continuation of Table 2		
6:1	8	76.5
21:1	2	62
21:1	4	78.5
21:1	6	82
21:1	8	85.4
42:1	2	90
42:1	4	95.4
42:1	6	98
42:1	8	100

2.2.2. Process Flowsheet

The typical process flowsheet of supercritical methanol transesterification is represented in the following figure. Methanol and waste oil are mixed and then heated to elevated temperatures before being introduced to the reactor. The products from the biodiesel reactor are then directed to a methanol recovery column. The bottom stream is then left to settle for a few minutes. Further, distillation takes place, one for oil and methanol and the second for glycerol and methanol, to finally obtain refined biodiesel and glycerol [20].

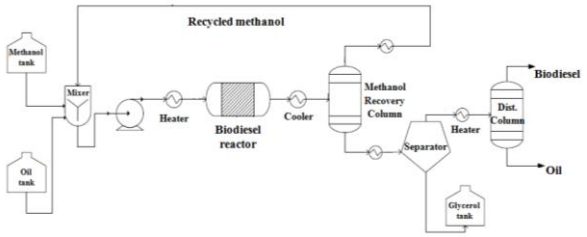

Fig. 2 The typical process flowsheet of supercritical alcoholysis (SCA) [20]

2.3. Economic Comparison

This section briefly describes an economic comparison between base-catalyzed transesterification and supercritical methanol transesterification. Glisic and Orlovic [20] showed an economic analysis to compare the two processes from the economic point of view. They stated that biodiesel production using supercritical conditions of methanol (SCA) is a promising technique compared to alkali-catalyzed alcoholysis (HACA). SCA is environmentally more beneficial than HACA, and that is mainly associated with the generation of wastewater after the purification of products upon using HACA. Also, SCA can tolerate higher FFAs in the feedstock than HACA, i.e., lower-cost feedstock [20].

The obtained results showed that the value of the capital investment for SCA and HACA is almost the same (4.6552 and 4.8008 million US $ for 8000 t/year of biodiesel production capacity). This conclusion opposes the common belief that supercritical technology will require higher capital investment.

Table 3 summarizes the total cost required for the two processes for the same production capacity (8000 t/year).

Table 3 Total cost at 100% capacity (million US $ per year)

	HACA	**SCA**
Capital cost	0.48008	0.46552
Production cost	6.5504	5.8488
Total cost	7.03048	6.31432

The previous table concludes that biodiesel production using supercritical methanol technology will save almost $716,000 per year compared to the homogeneous alkali-catalyzed process for a production rate of 8000 t/year.

3. Results and Discussion

3.1. The Pareto Chart

The purpose of the Pareto chart is to highlight the most important among a set of factors. In quality control, it often represents the most common sources of defects, the highest occurring type of defect. Commonly, the Pareto chart is used to analyze the data about the frequency of problems or causes in a process. It is also used when there are many problems or causes, and it is necessary to focus on the most significant, or when analyzing broad causes by examining their specific components.

The Pareto chart is commonly applied using Minitab software to study an effect's magnitude, influence, and degree of importance. The software shows a red line on the chart. This line is termed the "reference line." The effect is considered potentially important as long as it extends beyond this reference line. As the interval extended beyond the reference line becomes longer, the influence or the degree of importance of this effect increases. The reference line depends mainly on the existence of an error term. If no error term exists, pseudo-standard error (PSE) is used. This error is based on the sparse effects assuming that the changes in the smallest effects happen because of a random error. However, if an error term exists, Minitab draws the reference line (t), where t is (1 - α/2) quantile of a t-distribution. Minitab takes α = 0.05 by default.

The parameters that affect the base-catalyzed transesterification are studied using the experimental data stated in Table 1. The Pareto chart for this approach is presented in Fig. 3. It is clear from the figure that the factor that affects the yield of biodiesel the most is mainly B (catalyst loading) followed by AB (catalyst and temperature). So, we can conclude that the catalyst loading is the most affecting parameter that highly influences base-catalyzed transesterification, which agrees with the analysis of Vicente et al. [21].

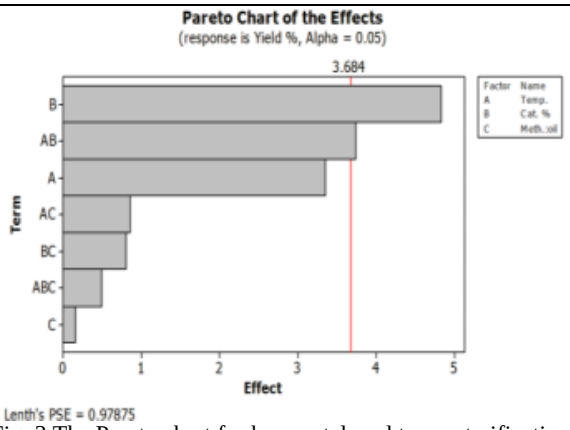

Fig. 3 The Pareto chart for base-catalyzed transesterification

The parameters that affect the supercritical trans-esterification are all studied using the experimental data stated in Table 2. The following figure shows the Pareto chart for supercritical methanol trans-esterification. The chart below describes the importance of each methanol to oil molar ratio (A) and the time of reaction (B) to the biodiesel conversion.

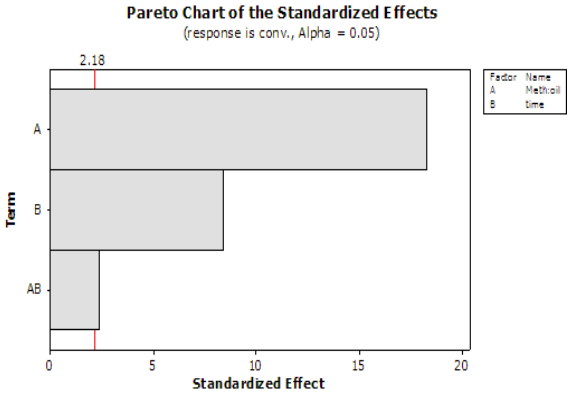

Fig. 4 The Pareto chart for supercritical methanol transesterification

The above chart shows that methanol to oil molar ratio and reaction time affect biodiesel conversion. However, the methanol to oil ratio is the most affecting. So, the alcohol molar ratio with oil is the controlling parameter for supercritical methanol transesterification. Hence, any methanol to oil molar ratio change will greatly affect the conversion. We can achieve the highest conversion with the molar ratio of methanol being 42, which completely matches what Kusdiana et al. [23] had concluded.

3.2. Contour Plot Methodology

Contour plots are used to investigate the potential relationship between three variables (while holding other variables constant, if any). Contour plots present the 3-dimensional relationship on x-y coordinates. Predictors (variables) are plotted on x- and y-scales, and the response is displayed by contours.

The following figure shows the effect of catalyst loading (y) and temperature (x) on the yield (contours) of the produced biodiesel. The darker regions identify higher z-values. The contour levels show a peak on the L.H.S at 0.5% (catalyst loading) and 25˚C (temp.). Quality scores in this region are greater than 98%.

Fig. 6 is quite similar to the previous figure, except that this one shows the effect of the catalyst loading (y) and methanol to oil molar ratios (x) on the yield (contours) of the produced biodiesel. The darker regions identify higher z-values. The contour levels reveal a peak on the bottom L.H.S at 0.5% (catalyst loading) and 4.5:1 (methanol to oil ratio). Quality scores in this region are greater than 98%.

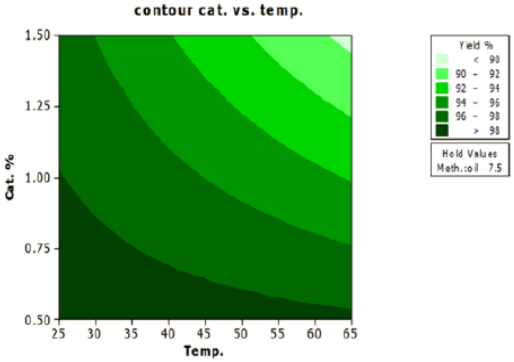

Fig. 5 Biodiesel yield contour plot for the effect of temperature and catalyst loading

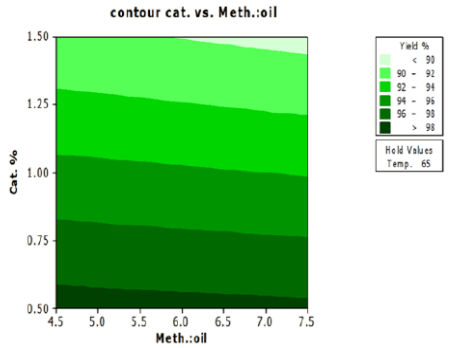

Fig. 6 Biodiesel yield contour plot for the effect of methanol to oil molar ratio and catalyst loading

For the supercritical methanol process, the following figure describes the relationship between the time (y) and the molar ratio of methanol to oil (x), affecting the conversion (contours) of biodiesel. The darker regions identify higher z-values. The contour levels reveal a peak at the top R.H.S in almost 8 minutes (time) and 42:1 (meth:oil), and that completely matches what Kusdiana et al. [23] had concluded. In addition, the quality scores in this region are greater than 100%.

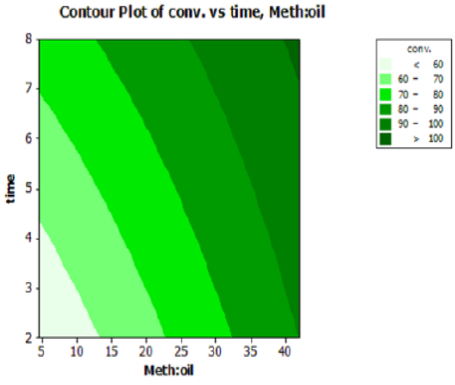

Fig. 7 Biodiesel conversion contour plot for the effect of methanol to oil ratio and time

3.3. Surface Plot Methodology

Contour response surface methodology (RSM) builds an experimental model conducted by collecting mathematical and statistical data. An optimized response (output variable) can be easily obtained with the experimental results previously discussed. For the base-catalyzed approach, several independent variables (input variables) influence that response. It can be noticed that the reasons for output response variations are the variations in the input variables.

As discussed earlier, the base-catalyzed transesterification is mainly influenced by temperature, % catalyst, time, and methanol:oil. In the surface plots shown in Fig. 9 and 10, the response, pure biodiesel yield, is measured under the influence of the previously mentioned variables while fixing the reaction time at 1 h. as discussed by Vicente et al. [21].

Fig. 8 describes the effect of methanol ratio with oil and catalyst loading on the yield while holding temperature at 65˚C.

Fig. 9 describes the temperature and catalyst loading effect on the biodiesel yield while holding the third parameter at 7.5:1.

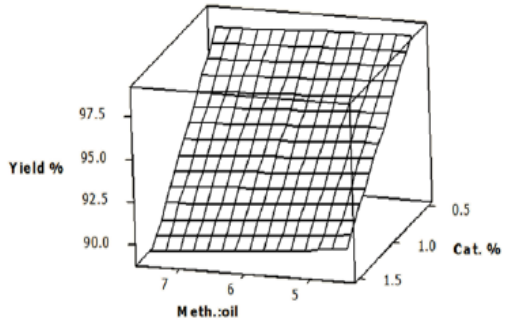

Fig. 8 Biodiesel yield surface plot with methanol to oil ratio and catalyst

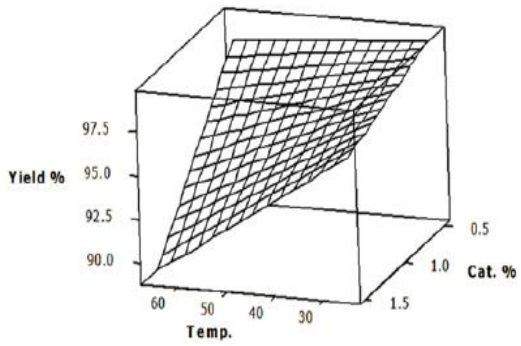

Fig. 9 Biodiesel yield surface plot with temperature and catalyst

The supercritical methanol transesterification is mainly influenced by the methanol to oil ratio, reaction time, and reaction temperature of the methanol entering. In the surface plot shown in Fig. 10, the response, biodiesel conversion, is measured under the influence of two independent variables, methanol ratio with oil and time, while the inlet methanol stream temperature is held at 350˚C, as recommended by Kusdiana et al. [23].

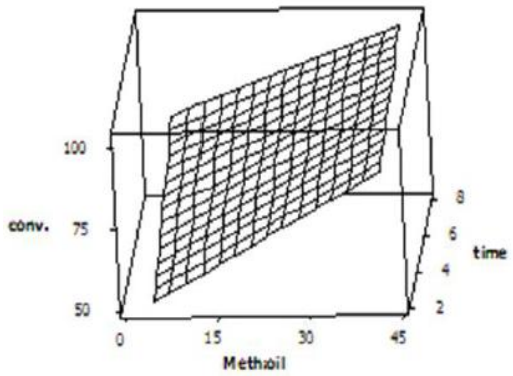

Fig. 10 Biodiesel conversion surface plot with methanol to oil ratio and time (min.)

The above plot represents the reaction time in minutes, which means that the whole reaction takes only a few minutes.

3.4. Linear Regression Analysis

Contour Linear regression analysis creates an equation that statistically relates the input variables (predictors) to the output variable (response). Commonly, regression analysis uses the least-squares method to generate the linear regression equation. It minimizes the sum of the squared residuals.

Regression results provide information about the relationship between a predictor and response, including the direction, the size, and the statistical significance of each predictor.

Eq. 1 shows the results obtained by the regression analysis, whereas other information supported by this analysis is further discussed in Table 4.

% Yield = 104.2 – 0.0839 A - 4.84 B + 0.053 C (1)

where A - temperature, B- catalyst loading, C - methanol to oil molar ratio.

Table 4 The regression results of % yield versus temp., % catalyst, and methanol to oil ratio

Predictor	Coeff.	SE Coeff.	*T*	*P*
Constant	104.189	5.050	20.63	0.00
Temp.	-0.08387	0.04946	-1.70	0.165
% Cat.	-4.840	1.978	-2.45	0.071
Meth.:Oil	0.0533	0.6595	0.08	0.939

For supercritical methanol transesterification, Eq. 2 shows the results obtained by the regression analysis. The regression results indicating the direction, size, and statistical significance are shown in Table 5.

% Conv. = 42.75 + 0.88971 A + 3.143 B (2)

where A - methanol to oil molar ratio, B - reaction time.

Table 5 The regression results of % conversion versus methanol to oil ratio and reaction time

Predictor	Coeff.	SE Coeff.	*T*	*P*
Constant	42.752	2.333	18.33	0.00

Continuation of Table 5

Meth.:Oil	0.88971	0.05652	15.74	0.00
Time	3.1425	0.3814	8.24	0.00

3.5. HYSYS Simulation

HYSYS simulation model for biodiesel production from waste vegetable oil using NaOH as an alkaline catalyst is developed. Fig. 11 illustrates the model for this approach. Unit operating conditions for the base-catalyzed HYSYS model are summarized in Table 6.

Table 6 Summary of unit operating conditions for the base-catalyzed process

Processes	**Operating conditions**	
Transesterification	Catalyst	NaOH
	Reactor type	CSTR
	Temperature (˚C)	60
	Pressure (kPa)	400
	Methanol to oil ratio	6:1
	Residence time (hr.)	4
	Conversion (%)	95
Methanol recovery	Reflux ratio	2
	Number of stages	5
	Condenser/ Reboiler	20/30
	% Recovery	94
	Distillate flowrate (kgmol/h)	3.47
	Distillate purity (%)	100
Glycerin separation	Water flow rate (kg/h)	11
Catalyst neutralization	Neutralizing agent	H_3PO_4
Biodiesel purification	Reflux ratio	2
	Number of stages	10
	Condenser/ Reboiler	10/20
	Final purity	99.9

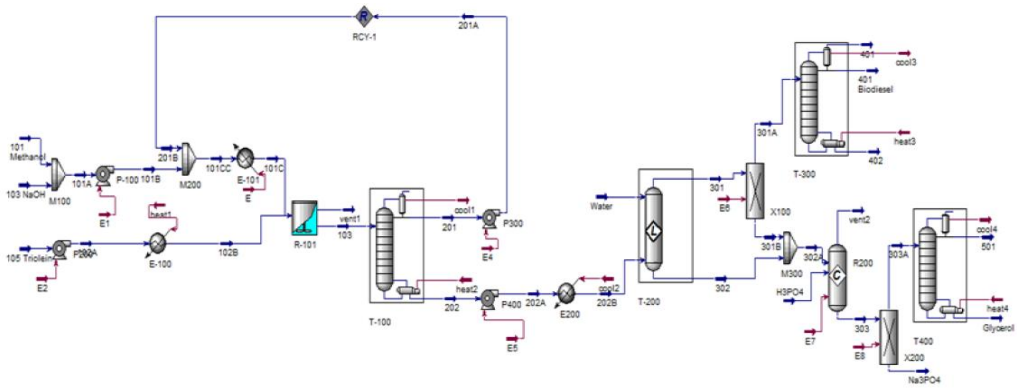

Fig. 11 HYSYS model for base-catalyzed process

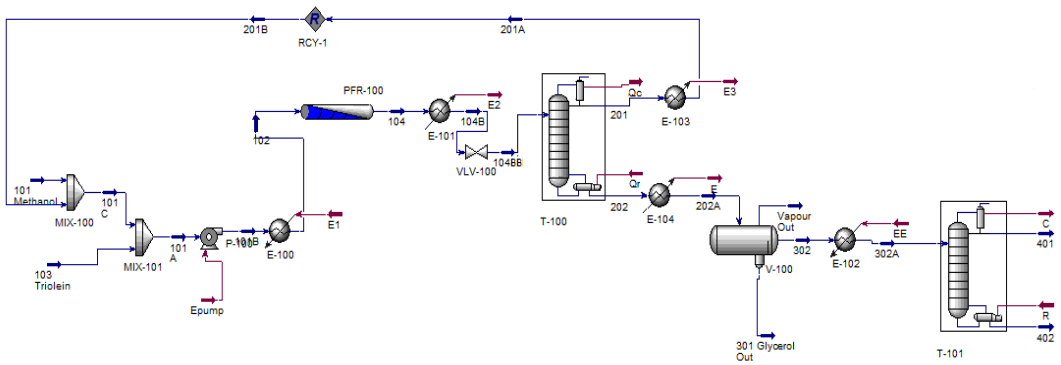

Fig. 12 HYSYS model for a supercritical methanol process

The previously simulated HYSYS model for the base-catalyzed process is based on the capacity stated before, which is 8000 t/year. The operating conditions for the process model are based on the optimum operating conditions discussed in Table 1 that were validated by the Pareto chart, contour plots, and surface plots.

HYSYS model for biodiesel production from WVO using supercritical methanol is developed. Fig. 12 illustrates the model for this approach. Unit operating conditions for the supercritical methanol HYSYS model are summarized in Table 7.

The previously simulated HYSYS model for the supercritical methanol process is based on the capacity stated before, which is 8000 t/year. The operating conditions for the process model are based on the optimum operating conditions discussed in Table 2 that were validated by the Pareto chart, contour plots, and surface plots.

Table 7 Summary of unit operating conditions for the supercritical methanol process

Processes	**Operating conditions**	
Transesterification	Catalyst	N/A
	Reactor type	PFR
	Temperature (˚C)	280
	Pressure (kPa)	20x103
	Methanol to oil ratio	42:1
	Residence time (hr.)	0.333
	Conversion (%)	98
Methanol recovery	Reflux ratio	3.42
	Number of stages	12
	Condenser/ Reboiler	101/105
	% Recovery	99.3
	Distillate flowrate	46.2
	(kgmol/h)	99.99
	Distillate purity (%)	
Biodiesel	Reflux ratio	2
purification	Number of stages	8
	Condenser/Reboiler	101/111
	Final purity	98.8

3.6. Energy Integration and Targeting

3.6.1. Composite Curve

HYSYS This curve represents a relation between the temperatures of streams and their enthalpy. The plot contains two composite curves: the hot and cold curves. For the supercritical approach, Fig. 13 is a plot between temperature and enthalpy using a minimum temperature difference (ΔT_{min}) of 10˚C. In Fig. 14, the two streams overlap in the graph middle. This region highlights the quantity of heat to be recovered for the process. For this process, the possible amount of heat to be recovered (Q_{REC}) is about 1 MW. The rest of the two streams cannot be heated or cooled by integrating energy between them. However, to satisfy their energy requirements, either heating or cooling, utilities should be supported for both cold and hot streams, respectively. For this process, the minimum requirement for the hot utility is denoted as (Q_{Hmin}) and has a value of 3.8 MW, and the minimum requirement for the cold utility (Q_{Cmin}) has a value of 3.7 MW [24].

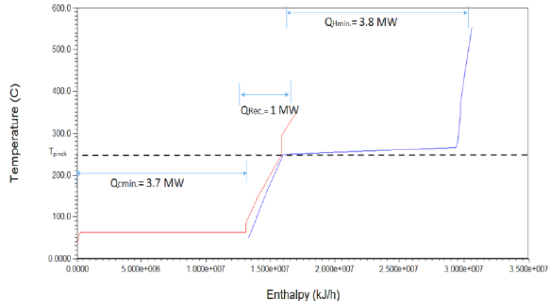

Fig. 13 Composite curve for the supercritical methanol process

3.6.2. Grand Composite Curve

The grand composite curve represents the process data as a set of temperatures against temperature energy flows. The pinch point splits the network into hot and cold ends. Above is the heat sink that requires a heating utility, while below is the heat sourcing that requires only a cooling utility. It determines the amount of heat that can be feasibly recovered. Fig. 14 represents the GCC for biodiesel production using supercritical methanol [24].

3.6.3. Utility Generation Curve

This curve represents the type and load of utilities offered by the process. The utilities offered and the amount of heat recovered by the integrated process would save a lot for the whole process. Fig. 15 shows the utility generation curve; it also represents the load of steam that would be produced. Table 8 shows the loads, costs, and pressures of HP, MP, and LP steam produced from the process.

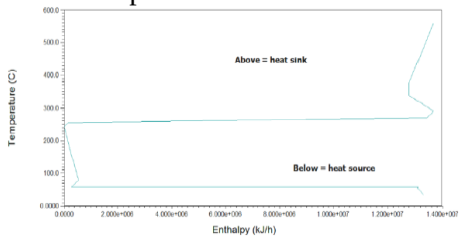

Fig. 14 Grand composite curve for the supercritical methanol process

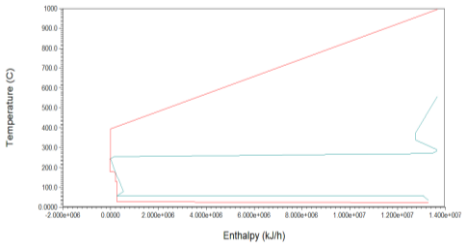

Fig. 15 Utility generation curve for the supercritical methanol process

Table 8 Utility generation data

	High pressure	**Medium pressure**	**Low pressure**
Pressure (kPa)	4201	1135	690
Load (kW)	13	60	17
Cost ($/ ton)	16.64	13.71	12.68

3.6.4. CO_2 Emissions

Carbon dioxide emissions are one of the main and critical emissions that must be estimated for any process, especially the new ones. These emissions are due to burning some kinds of fuels to produce sufficient heat to satisfy the heating requirements of the desired process (biodiesel production process). Commonly, the fuel used for this purpose is either natural gas or heavy fuel oil. Table 9 supports some information about both fuels.

Table 9 Fuel combustion in furnaces considered the source of CO_2 emissions

	NHV (kJ/kg)	% Carbon
Heavy fuel oil	39.771	86.5
Natural gas	51.60	75.4

Gadallah et al. [25] derived Eq. 3 to calculate carbon dioxide emissions. Carbon dioxide emissions are estimated for the original and integrated processes. Table 10 shows that the emissions of the integrated process are lower than those of the original process upon using both kinds of burning fuels. The percentage reduction of carbon dioxide emissions was almost 21%.

$$[CO_2]_{Emiss} = \left(\frac{Qfuel}{NHV}\right)\left(\frac{C\%}{100}\right)\alpha \quad (3)$$

where:
$Q_{Fuel} = QH/\eta$;
η - the furnace efficiency (taken 0.9);
NHV - net heating value (kJ/kg);
C% - carbon %;
α - ratio of molar masses of CO_2 and C (= 3.67).

Table 10 CO_2 emissions for the original and integrated processes using natural gas and heavy fuel oil

	Original process emissions (t/h)	Integrated process emissions (t/h)
Heavy fuel oil	1.53	1.03
Natural gas	1.213	0.815
% reduction	21 %	20.7 %

3.6.5. Heat Exchanger Network (HEN)

Heat exchanger network analysis identifies the hot and cold streams from the mass and energy balance standpoints. Let us consider a heat source and a heat sink with supply and target temperatures and enthalpy change for both streams. Steam is available at 180˚C, and cooling water is at 30˚C. Consequently, heating the cold stream with steam and cooling the hot stream by cooling water are possible. However, recovering the heat between the process streams is preferable as it would save an excessive energy cost. Fig. 16 shows the proposed HEN for biodiesel production using the supercritical methanol approach. This HEN shows how the integration between hot and cold streams would achieve energy targeting and possible heat recovery.

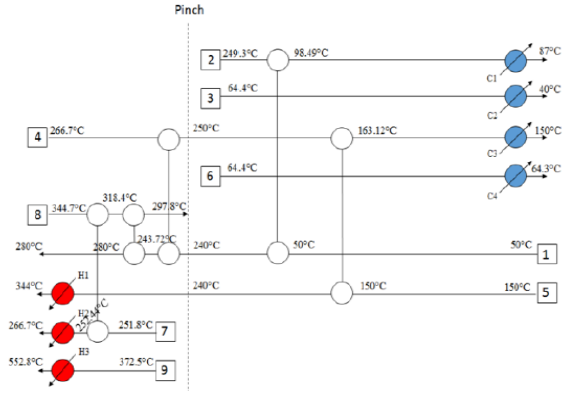

Fig. 16 Heat exchanger network (HEN) for supercritical methanol process

Table 11 CO_2 emissions for the original and integrated processes using natural gas and heavy fuel oil

	Indication on HYSYS	Inlet temp.(°C)	Outlet temp. (°C)	Enthalpy (kW)	MCp (kW/C)
1	101B	50	280	777.22	3.378
2	104	249.3	87	690.833	4.256
3	201	64.4	40	66.472	2.724
4	202	266.7	150	87.833	0.7528
5	302	150	344	140.889	0.7264
6	T-100 (top)	64.4	64.3	3566.667	35666.7
7	T-100 (bottom)	251.8	266.7	3633.33	243.9
8	T-101 (top)	344.7	297.8	278.889	5.95
9	T-101 (bottom)	372.5	552.8	241.5	1.339

In Table 11, the stream identification in the HEN is expressed in detail. It describes the stream number on the HEN and what this stream means in the HYSYS simulation model. It also shows the inlet and outlet temperatures of this stream in the original process, the enthalpy needed to achieve this temperature difference, and the calculated MCp from the energy analyzer.

Table 12 shows, in detail, every heat exchanger, its cold and hot streams (as identified in Table 11), and the duty required for each exchanger.

Table 12 Heat exchangers' duties and connections

Equipment	Cold stream	Hot stream	Duty (kW)
Hex-1	2	1	641.82
Hex-2	4	1	12.56
Hex-3	8	1	122.56

Continuation of Table 12			
Hex-4	4	5	65.376
Hex-5	8	7	156.495
C1	2	-	48.9288
C2	3	-	66.4656
C3	4	-	9.874
C4	6	-	3566.67
H1	-	5	75.5456
H2	-	7	3477.615
H3	-	9	241.4217

The minimum energy required for cooling is calculated as follows:

$Q_{Cmin.}$ = C1 + C2 + C3 + C4 = 48.9288 + 66.4656 + 9.874 + 3566.67 = 3691.9384 kW

The minimum energy required for heating is calculated as follows:

$Q_{Hmin.}$ = H1 + H2 + H3 = 75.5456 + 3477.615 + 241.4217 = 3794.5823 kW

Table 13 provides the energy requirements for the process before and after the integration to compare the expected requirements from the composite curve.

Table 13 Cooling and heating requirements for the original and integrated processes and composite curve

	Original process	**Composite curve**	**Integrated process**
Cooling requirements (MW)	4.7	3.7	3.69
Heating requirements (MW)	4.8	3.8	3.79

3.6.6. Integrated Process Flowsheet

The following process flowsheet shows the energy integration by implementing the HEN on the designed process. The flowsheet in Fig. 17 achieves the proposed energy target for minimizing the total heating and cooling energy requirements.

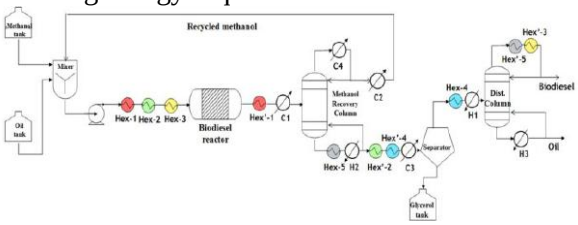

Fig. 17 Integrated process flowsheet

4. Conclusion

The results showed an optimization for biodiesel production using base-catalyzed and supercritical methanol processes. The experimental results were validated using parameter analysis that was carried out using the Pareto chart, contour plots, and surface plots. It was found that the most affecting variable for the base-catalyzed process was the catalyst loading, and the optimum conditions were 25˚C, 1.3% NaOH, and 6:1 methanol to oil molar ratio. For the supercritical methanol process, the most affecting variable was the methanol to oil ratio, and the optimum conditions were 8 minutes and 42:1 methanol to oil ratio. A simplified linear regression analysis was also performed to correlate the biodiesel yield with the process parameters. The optimal process conditions were used to build an HYSYS model for those production techniques. Process optimization was performed for the reactor volume and the reflux ratios of the distillation columns. The composite curve was used to determine the minimum energy requirements for the process, which were 3.4 and 3.7 MW for heating and cooling requirements, respectively. The grand composite curve was represented to show the operating pinch point and the total energy requirements for the original process, found to be 4.4 and 4.7 MW. The energy consumption of the base case has been reduced by 25%, hence a substantial cut in the CO_2 emissions. A utility curve was generated to determine loads of utilities. Finally, a heat exchanger network was developed to accomplish the energy minimization target proposed from the composite curve.

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