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Optimisation of biodiesel synthesis from waste cooking oil in the reactive distillation column using taguchi methodology

Tepkimeli damıtma kolonunda taguchi metodolojisi ile atık yemeklik yağdan biyodizel sentezi optimizasyonu

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Optimisation of Biodiesel Synthesis from Waste Cooking Oil in the Reactive Distillation Column Using Taguchi Methodology

Highlights

- *The effect of the four parameters on FAME conversion was analyzed by statistical ANOVA method.*
- *FAME conversion and steady state time were obtained between 72.99−99.52% and 1.67−6.25 hours, respectively.*
- *it was deduced high conversion and economically feasible biodiesel could be probable by using this methodology.*

Graphical Abstract

Taguchi orthogonal arrays were used as experimental design to reduce number of experiments significantly. Optimum conditions at the maximum conversion of 99.48% and at steady state time of 1.69 hour were determined as WCO flow rate of 2.90 ml/min, methanol/oil molar ratio of 8.19 and reboiler heat duty of 0.419 kW by numerical optimization.

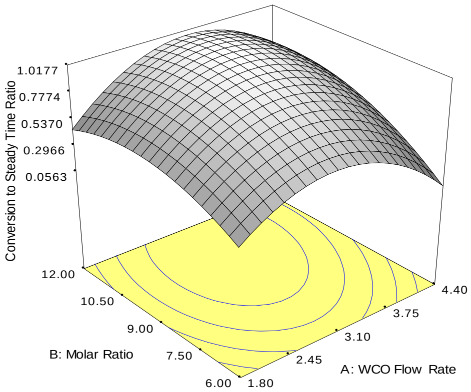

***Figure** 3D surface plot of parameter A and B*

Aim

*In this study, economic and high efficient production of continuous–flow biodiesel was aimed in the heterogeneous basic catalyst–packed RD column***.**

Design & Methodology

Taguchi orthogonal arrays were used as experimental design to reduce number of experiments significantly.

Originality

Optimum parameters were found by using Taguchi method for biodiesel production from waste cooking oil in the reactive distillation column

Findings

Optimum conditions at the maximum conversion of 99.48% and at steady state time of 1.69 hour were determined as WCO flow rate of 2.90 ml/min, ethanol/oil molar ratio of 8.19 and reboiler heat duty of 0.419 kW by numerical optimization.

Conclusion

Considering results were quite compatible with literature, it was understood Taguchi, ANOVA and numerical optimization were carried out successfully.

Declaration of Ethical Standard)

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Optimisation of Biodiesel Synthesis from Waste Cooking Oil in the Reactive Distillation Column Using Taguchi Methodology

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(This study was presented in ULIBTK 2019 Conference)

Araştırma Makalesi / Research Article

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ABSTRACT

Traditional biodiesel methods have disadvantages of excessive alcohol demand, short catalyst life, high manufacturing cost. Reactive distillation (RD) simplifies operations by combining reaction and separation. In literature, there was a few experimental study on continuous–flow biodiesel in RD column with heterogeneous catalyst. So, it was aimed to develop economical continuous process for producing fatty acid methyl esters from low price waste cooking oil (WCO) in RD column packed with cheaper basic heterogeneous calcium oxide. Taguchi orthogonal arrays were used as experimental design to reduce number of experiments significantly. Conversions and steady state times were obtained in range of (72.99–99.52)% and (1.67–6.25) hour, respectively. Effects of four parameters were analyzed by statistical analysis of variance (ANOVA) and numerical optimization was performed by programs embedded in Design–Expert 6.0. Optimum conditions at the maximum conversion of 99.48% and steady state time of 1.69 hour were determined as WCO flow rate of 2.90 ml/min, methanol/oil molar ratio of 8.19 and reboiler heat duty of 0.419 kW by numerical optimization. Considering results were quite compatible with literature, it was understood Taguchi, ANOVA and numerical optimization were carried out successfully. Consequently, it was deduced high conversion and economically feasible biodiesel could be probable by using this methodology.

Keywords: Reactive distillation column, biodiesel, waste cooking oil, optimization.

Tepkimeli Damıtma Kolonunda Taguchi Metodolojisi ile Atık Yemeklik Yağdan Biyodizel Sentezi Optimizasyonu

ÖZ

Biyodizel üretiminde; aşırı alkol talebi, kısa katalizör ömrü ve yüksek üretim maliyeti geleneksel yöntemlerin dezavantajlarındandır. Tepkimeli (TD), reaksiyon ve ayırmayı birleştirerek işlemleri basitleştirir. Literatürde heterojen katalizörlü TD kolonunda sürekli akışlı biyodizel üzerinde çok az deneysel çalışma yapılmıştır. Bu çalışmada, daha ucuz bazik heterojen kalsiyum oksit ile dolgulu RD kolonunda, düşük fiyatlı atık yemeklik yağından (WCO) yağ asidi metil esterlerinin üretilmesi için ekonomik sürekli bir prosesin geliştirilmesi amaçlanmıştır. Deneysel tasarım metodu olarak, deney sayısını önemli ölçüde azaltan Taguchi ortogonal dizinleri kullanılmıştır. Dönüşüm ve yatışkın hal süreleri sırasıyla %(72.99-99.52) ve (1.67-6.25) saat aralığında bulunmuştur. Design-Expert 6.0'da gömülü programlar yardımıyla, dört parametrenin etkisi istatistiksel varyans analizi(ANOVA) ile incelenmiş ve sayısal optimizasyon yapılmıştır. Maksimum % 99,48 dönüşüm ve 1.69 saatlik yatışkın hal süresinde, optimum koşullar; 2.90 ml/dk WCO akış hızı, 8.19 metanol/yağ molar oranı ve 0.419 kW kazan ısıtma yükü olarak nümerik optimizasyonla belirlenmiştir. Sonuçların literatürle oldukça uyumlu olduğu düşünüldüğünde Taguchi, ANOVA ve sayısal optimizasyonun başarılı bir şekilde gerçekleştirildiği anlaşılmıştır. Sonuç olarak, yüksek dönüşümlü ve ekonomik olarak uygulanabilir biyodizel üretiminin bu metodolojiyle mümkün olabileceği görülmektedir.

Anahtar Kelimeler: Tepkimeli damıtma kolonu, biyodizel, atık yemeklik yağ, optimizasyon.

1. GİRİŞ (INTRODUCTION)

Environmentally friendly and renewable alternative resources are still being explored as an alternative to fossil fuels due to the global negative effects of greenhouse gases. Biodiesel is one of the most investigated and in definition it is the long chain fatty acid methyl ester obtained by transesterification of long chain fatty acids (FA) from vegetable and animal oils in the presence of a suitable catalyst with methanol and glycerol as a by-product [1].

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Mostly, homogeneous and heterogeneous alkali and acid catalysts are used in biodiesel reactions. Heterogeneous catalysts have some advantages such as being easily seperable from the product and being partly cheaper. Heterogeneous basic catalysts include alkali earth metal oxides such as CaO [2,3]. Inexpensive and easily available CaO has been reported to have superior catalytic performance in biodiesel production [4,5].

In respect of the high price of crude vegetable oil as a source of triglycerides, how to make biodiesel as lucrative emerged as the main challenge. Regarding to economical reviews, raw material composed a substantial part of total manufacture expenditure. So as to reduce the biodiesel cost, WCO could be used in place of pure vegetable oil [6]. Recently, the usage of low price WCO has increased [7,8]. It has been informed the market price could be reduced in the range of 60−90% by WCO due to it being 2−3 times cheaper than vegetable oil [9].

Another important factor affecting biodiesel price is the production facility. With this regard, it has been seen that RD column has some advantages. In customary processes, extreme quantity of equipment and energy are required to remove excess alcohol and impurities, which are operated to achieve high conversion [10]. The toll of biodiesel obtained by using RD column has been lower than that by using conventional plant [11]. Cost–reducing considerations of RD column can be summed up; (1) simultaneous reaction and separation, (2) thus, shifting the equilibrium reaction through product side, (3) ensuring the necessary heat integration and (4) exploitation of less constructive material due to its compactness [12]. Wang *et.al* performed methyl acetate hydrolysis by RD process and achieved 10% less energy consumption and 50% increase in production compared to those produced by using fixed bed reactor.

In literature, it is possible to encounter a large number of experimental designs studies using Response Surface Method (RSM), Central Composite Design (CCD), etc. Amongst them, Taguchi experimental design method is a useful tool for getting high quality system design. It standardized orthogonal queues by sets in tabular form and simplified their usage. Thus, it becomes feasible to make a large number of variables with only a few experiments [13]. Besides, there were numerous studies on biodiesel manufacturing by transesterification of methanol in batch reactors with CaO catalyst [14,15]. However, there was a few study including biodiesel synthesis in continous–flow CaO–catalyzed process [16]. Noshadi *et.al* fed the WCO stream and the mixture of heterogeneous HPA acid catalyst and methanol stream to RD column, separately. They investigated biodiesel production and the impacts of parameters on conversion by using RSM, and also performed optimization.

In this study, economical and high efficient synthesis of continuous–flow biodiesel was aimed in heterogeneous basic catalyst–packed RD column. To achieve this goal, low–cost WCO, cheaper, easily recoverable and superior catalytic CaO catalyst were used in the intensified RD column process. Following completion the experiments defined according to Taguchi methodology, the influences of WCO flow rate, methanol/WCO molar ratio, reboiler heat duty and feed inlet temperature on biodiesel conversion were scrutinized by ANOVA and optimum operating conditions were determined.

2. MATERIAL and METHOD

2.1. Materials

CaO catalyst and methanol in analytical purity were obtained from MERCK. The catalyst intended to be used as fillers in RD column was procured in small marble pieces (~ 3−20 mm). Then, WCO utilized in the experiments was obtained from a domestic establishment. The water and sediment content of WCO was completely removed by operations such as thick and thin filtration and heating. Finally, the proportion of free FA was brought down to acceptable value (<0.5%) by neutralization.

The FA composition of WCO was determined by Perkin Elmer Clarus 500 model gas chromatography (GC) using Agilent HP−88 (100 m x 0.25 mm x 0.20 μm) capillary column and Flame Ionization Detector according to the method of "CoI/T.20/Doc.No.17, 2001" and was presented in Table 1. The oven temperature was programmed at 175 °C for 12 minutes and raised to 225 °C at a velocity of 2 °C/min for 12 minutes. In addition, the injector and detector temperatures were hold at 250 °C and 280 °C, respectively.

Table 1. FA composition (w%) and properties of WCO

Parameters	Value
palmitic	20.99
stearic	4.92
oleic	38.12
linoleic	29.73
water content	0.09%
acid value	1.09 (mg KOH/g oil)
color	golden yellow

2.2. Experimental Setup and Procedure

The experiments were carried out in a laboratory scale RD column having a diameter of 5 cm. The system consisted of two reactant supplies, a condenser, a reboiler and a product collection line as shown in Figure 1. The RD column was divided into two zones for reaction and stripping phases. The upper reaction region, 80 cm in height, was filled with Raschig rings and CaO catalyst. Besides, bottom stripping zone, 40 cm long, filled with Raschig rings was suffixed to decompose excess methanol. In addition, two BT100−1F brand digital pumps were used to feed WCO and methanol separately. The mixture of WCO and methanol, added to the 4 liter glass boiler, was bubbled up with a JP Selecta sa brand mantle heater having a capacity of 700 W. Thanks to the control unit annexed to the system, the flow rate of the pumps and the heating power were adjusted automatically by a computer.

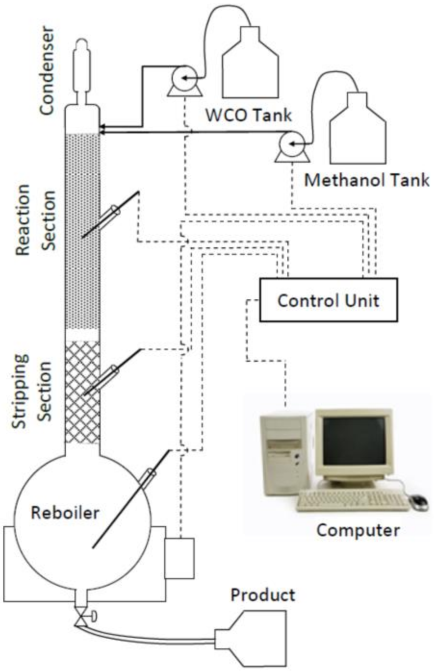

Figure 1. Schematic diagram of packed RD system

Initially, a mixture of WCO and methanol with a total volume of 2,025 mL, having the same molar ratio with feed stream, was put into the 4 liter glass boiler. During heating at the setted power, methanol vapour condensed in RD column upon facing with cold environment and flew back through the boiler. RD column temperature increased by means of rising methanol steam in time and became steady approximately in 40−50 minutes. The steam methanol reaching top of RD column was completely condensed in the condenser and returned to the column. At this moment, depending on the molar ratio, WCO and methanol streams were provided individually at the top of RD column via pumps. Each of feed stream was heated separately before entering the column by circulating water bath (MAY) and fed to the column as a single line after combining two streams with a "t" connectıon element. Following the arrival of the feed stream to the boiler, the liquid level of boiler was tried to keep constant within a certain interval via the ball valve eked out to the outlet.

To determine the duration of the experiments, the literature was searched It was declared that a steady state was reached at 7 hours in CaO−packed RD column for biodiesel manufacturing from WCO [14]. It was also notified that a steady state was reached at 6 hours in RD column with homogeneous KOH catalyst for biodiesel synthesis from palm oil [10]. Accordingly, the time of experimental studies was specified to be 7 hour. In each experiment, 10 samples were taken from the boiler outlet. 6 samples of them were taken in every 30 minutes of the first 3 hours. As for the remaining 4 samples, they were taken in every 60 minutes of following 4 hours. Every sample was placed in a 50 ml screw capped container and allowed to stand for 30 minutes in a cold environment to reduce the temperature and prevent the proceeding of the reaction.

2.3. Analysis of Samples by FTIR

First of all, each sample of 50 ml was taken into tubes of 25 ml and centrifuged at 3,000 rpm for 3 minutes. The upper biodiesel phase in it was carefully extracted by an automatic pipette and placed in a 50 ml glass flask. Following the dissociation, the methanol in biodiesel phase was removed by a rotary evaporator through treating 11 minutes at 80 rpm in a water bath with an average temperature of 90 ^{o}C. Following methanol removal, the kinematic viscosity at 40 ^{o}C (mm^2/s, cSt) and the refractive index of the samples were measured.

The final FAME conversion was determined by FTIR. There were many studies in the literature about qualitative and quantitative analysis of biodiesel by using FTIR. It was noticed that the main frequency domain in which soybean oil and biodiesel mixture could be partitioned was of 1,500−900 cm^{-1} and that the peak at frequency of 1,446 cm^{-1} was occured only in biodiesel spectrum [17]. Also, the peak at 1,196 cm^{-1} was the another characteristic peak for biodiesel [18]. Furhermore, it was found that the amount of biodiesel in the mixture of soybean oil and biodiesel could be detected with 98.11% accuracy by calculating the peak areas in frequency range of 1,425−1,447 cm^{-1} and 1,188−1,200 cm^{-1} by using an improved program [19]. In addition, the quantity of biodiesel in mixture of soybean oil and biodiesel was found with 99.91% precision by using the partial least squares regression method in the 1,800–600 cm^{-1} interval [20].

Taking advantage of the information given above, a calibration curve was established in order to identify the biodiesel conversion ratio of the sample taken from the boiler outlet in each experiment. For this purpose, the known biodiesel ratios of WCO and biodiesel blends were prepared and their FTIR spectrums were drawn. Then, characteristic peak areas of biodiesel at 1,435 cm^{-1} and 1,195 cm^{-1} were calculated and plotted against the biodiesel conversion. Thus, Figure 2 was obtained and used for the quantitative analysis of FAME.

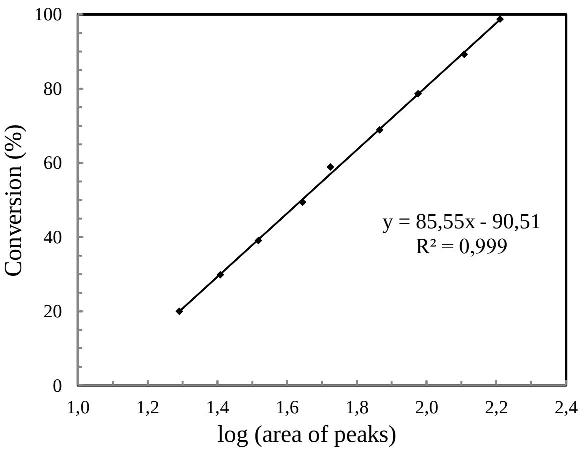

Figure 2. Calibration graph based on FTIR analysis

2.4. Design of Experiments (DoE) Using Taguchi Orthogonal Arrays

A new method was developed by G. Taguchi to explore the effects of parameters on a mean and variance in a procedure. It is a statistical method that the number of experiments could be reduced significantly by using it [21]. Thus, it could be possible to save time and resources by minimum number of experiments. Moreover, Taguchi method leads to the determination of the factors affecting the product quality. In short, it could be said that Taguchi experimental design method is very useful tool for high quality system design.

In fact, reducing the number of experiments could be done easily by using orthogonal rows when one designs the experimental configuration [22]. But, Taguchi standardized orthogonal arrays by sets in tabular form and simplified its use. In the methodology, only a few pairs were searched for instead of all possible combination of parameters. Thus, it became feasible to make a large number of variables with only a few experiments. The orthogonal array to be exploited is selected according to the number of parameters (P) and the variation level (L) of each parameter by using Eq. (1) [23],

$$N = (L - 1) * P + 1 \quad (1)$$

where N is the minimum number of experiments. For example, Taguchi L_9 design was presented in Table 2. Accordingly, 9 experiments are performed for 3 levels of 4 parameters and this is called L_9 design. By use of this scheme, the number of configurations of 3^4 i.e. 81 work could be degraded to 9 studies. Additionally, experiments with very large number of configuration could yield much more gains. For instance, when we test 13 parameters in 3 levels, only 27 experiments will be sufficient to perform studies by L_{27} design instead of 3^{13} i.e. 1,594,323 configurations [22].

Table 2. Taguchi L_9 orthogonal array (4 parameters, 3 levels)

Exp.Nu.	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

3. RESULTS AND DISCUSSIONS

3.1. Experimental Results

In the study, WCO flow rate, molar ratio of methanol to WCO, reboiler heat duty and feed inlet temperature were chosen as parameters and the effects of them on conversion were investigated. The operating boundary of factors were selected as 1.80, 3.30, 4.40 ml/min for flow rate, 6, 8, 12 for the molar ratio, 280, 350, 420 watt for the heat duty and 45, 50, 55 °C for the feed inlet temperature. The Taguchi L_9 experimental design and final FAME conversion values determined by FTIR were presented in Table 3.

Table 3. Taguchi design and FAME conversion values

Exp. Nu.	WCO flowrate (ml/min)	Molar ratio	Heat duty (watt)	Inlet temp. (°C)	FAME conv. (%)
1	1.80	6:1	280	45	90.00
2	1.80	8:1	350	50	91.60
3	1.80	12:1	420	55	96.56
4	3.30	6:1	350	55	91.35
5	3.30	8:1	420	45	98.17
6	3.30	12:1	280	50	99.52
7	4.40	6:1	420	50	72.99
8	4.40	8:1	280	55	86.66
9	4.40	12:1	350	45	97.38

Upon inspection of each group in itself, an increase in the FAME conversion was observed in parallel with the increase of molar ratio. Especially, when we take into account the first six experiments, it was observed that FAME conversions augmented reasonably in parallel with the raise of flow rate for the same molar ratio. The greatest FAME conversion among all experiments was obtained to be 99.52% at the Experiment 6.

It could be benefited from viscosity, one of the product characteristic, to observe the degree of reaction occurring in the reactor. The decrease in viscosity and relating increase in biodiesel conversion versus time was presented graphically in the literature. It was stated that the viscosity of the used oil of 30.73 cSt lowered to 3.30 cSt at the end of the reaction and remained constant at the relating conversion of 96.60% depending on the condition of parameters [24]. In another study, kinematic viscosities of biodiesel produced from three different canola oil were found to be 4.67, 5.01 and 4.64 mm^2/s (cSt) at 40 °C [25].

Furthermore, it was stated that there was at least three periods in the methanolysis of sunflower oil in the presence of CaO catalyst, and the diminishing in TG concentration was sighted as a sigma curve. It was also noted that the spending rate of TG was slow at the begining stage due to the mass transfer restriction, then it rised in the middle stage under kinetic regime control, and finally slowed down as the completion of the reaction approached. Likewise, such kinetics was also observed in homogeneous basic catalysed methanolysis. This sigma curve could be related to the growth in solubility of methanol in oil−FAME phase [26].

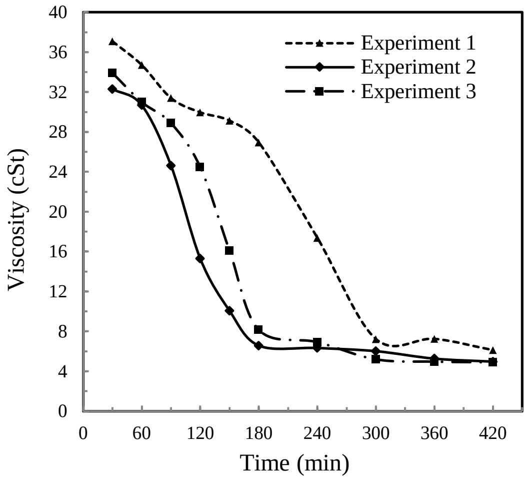

Figure 3. The change of viscosity of Experiments 1, 2 and 3

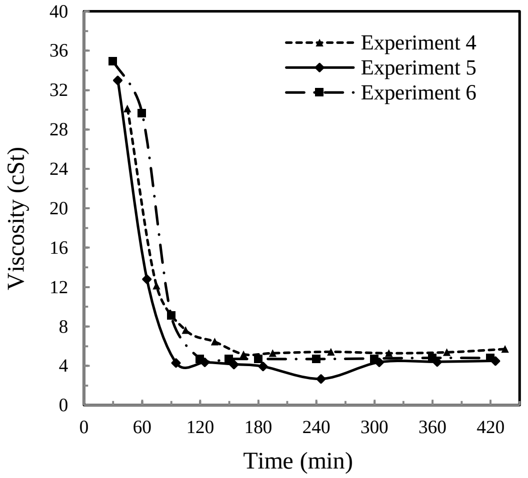

Figure 4. The change of viscosity of Experiments 4, 5 and 6

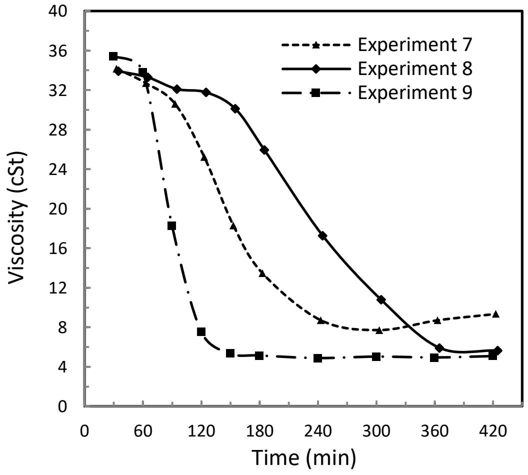

Figure 5. The change of viscosity of Experiments 7, 8 and 9

In our study, the sigma curves for the decreasing TG concentration similar to the literature mentioned above were obtained, too and submitted in Figure 3−5. Upon inspection of graphs, it could be figured out that the curves had different FAME conversion at different steady state time depending on the experimental conditions. The final viscosity of the methanol−evaporated sample mixture consisting of unreacted WCO and biodiesel diminished to the range of 8.42−4.36 cSt depending on the experimental conditions. As a consequence, it was seen that the viscosity values obtained in the study were quite compatible with the values defined in the literature [24].

Generally speaking, different magnitude initial mass transfer limitation and kinetic zone reaction rates were observed in the experiments. As seen in the figures, large conversion values could be obtained at high reaction rates in a shorter time. Likewise, low conversion could be reached at lower reaction rates in longer times. On the other hand, it was also observed that lower conversion could be obtained at higher kinetic region reaction rates, and larger conversion values might be achieved at lower reaction rates but in a longer time. Hence, in terms of conversion and steady state time consideration, it has been explored that they changed in the range of 72.99−99.52% and 1.67−6.25 hour, respectively.

It was grasped from the Figure 3 that the initial mass transfer restraint was greatest in Experiment 1 and smallest in Experiment 2. Besides, the slope in the kinetic controlled area in experiment 1 was more flater than the other two. Therefore, kinetic zone reaction rate of it was the smallest. Besides, it was viewed that the slope in the kinetic controlled district of Experiment 3 was much steeper i.e. a greater reaction rate was achieved. Figure 4 demonstrated that the curves of experiments 4, 5, and 6 were very close to each other, collected together, and seemed to be similar. Compared to all 9 experiments, the initial reaction rates of them were much larger, and the slopes in the kinetic controlled field were more perpendicular, showing up greater reaction rates. Furthermore, the curves reached the final equilibrium conversion in a shorter time in the completion phase. Analyzing Figure 5, the most scattered curves at all experiments were found in Experiments 7, 8 and 9. The initial mass transfer constraint was minimal in Experiment 9 within these three curves. Moreover, much steeper slope of it in the kinetic controlled section displayed the higher reaction rate than the other two.

3.2. Statistical Analysis Using ANOVA for FAME Conversion

As a result of numerous model studies carried out in Design 6.0 program, the FAME conversions were associated with the modified quadratic polynomial equation. In the analysis, the least squares regression method was employed to ensure whether the data were consistent with the model, or not. For definition of the interval in the program, (–1) code was chosen for the minimum and (+1) code was selected for the maximum value of the experimental parameters. Accordingly, the most compatible model contained the coded terms was obtained as polynomial Eq. (2).

$$
\begin{aligned}
(Conversion)^{2.05} = {} & 12825.80 \\
& - 256.53 * A \\
& + 1435.90 * B \\
& + 283.35 * C \\
& - 2320.64 * A^2 \qquad (2) \\
& - 695.74 * B^2 \\
& + 932.68 * AB \\
& + 865.73 * BC
\end{aligned}
$$

As seen in the equation, the impact of linear (A) was negative and the effect of linear (B) and (C) was positive. The coefficient of linear positive (B) was much larger than other linear terms. Quadratic terms (A^2) and (B^2) had negative influences and quadratic (A^2) had the greatest coefficient in the model. The effect of interaction between (AB) and of (BC) was positive. Although linear (A) had negative and partially smaller impact and (B) had positive and larger influence, the synergistic effect of both parameters (AB) on conversion was positive and equivalent to about 3 times of coefficient of (A). Likewise, although linear (B) had positive and larger influence and (C) had positive and relatively smaller impact, synergistic effect of both parameters on conversion was positive and was equivalent to about 3 times of coefficient of (C).

Table 4. ANOVA of model and process parameters

Source	Sum of squares	DF	Mean square	F value	p–value prob>F	
Model	2.65E+07	7	3.78E+06	4.65E+05	0.0011	Significant
A	2.49E+05	1	2.49E+05	3.06E+04	0.0036	
B	1.23E+07	1	1.23E+07	1.51E+06	0.0005	
C	3.18E+05	1	3.18E+05	3.91E+04	0.0032	
A^2	7.58E+06	1	7.58E+06	9.33E+05	0.0007	
B^2	7.38E+05	1	7.38E+05	9.07E+04	0.0021	
AB	2.44E+06	1	2.44E+06	2.99E+05	0.0012	
BC	1.55E+06	1	1.55E+06	1.91E+05	0.0015	
Residual	8.13	1	8.13			
Cor total	2.65E+07	8				

The fitness of the experimental data with the proposed model is designated by F−value, R^2 and p−value. In other words, each term in any model will be contemplated as significant if the p−value is less than 0.05 [27]. In the study, ANOVA analysis showing the modified quadratic model was compatible with the experiments as indicated in Table 4. The very large F−value of 4.65E+05 obtained for the model stressed that this model was meaningful and the magnitude of the F−value might be only 0.11% of the probability of being noise−induced. When examined the F and p values of each terms in the model, the linear (A), (B) and (C) terms and second order (A^2), (B^2), (AB) and (BC) terms appeared to be significant. In the modeling, the best fitting model did not included term of (D) because the impact of it on conversion was very little in the partition of 45−55 °C. Consequently, the feed inlet temperature was decided to be taken as 55 °C.

The model's adequacy is also assessed by the residual distribution analysis, which is the extent of the difference between the predicted and the actual values in the model. If the experimental errors are random, these residuals will be expected to exhibit a normal distribution, with the straight line showing that studentize residuals has a normal distribution [28]. Accordingly, in the study, the straight line in Figure 6 exhibited studentize residuals had a normal distribution. The random scattering of the residues presented in Figure 7 also indicated that the proposed model was suitable for the system.

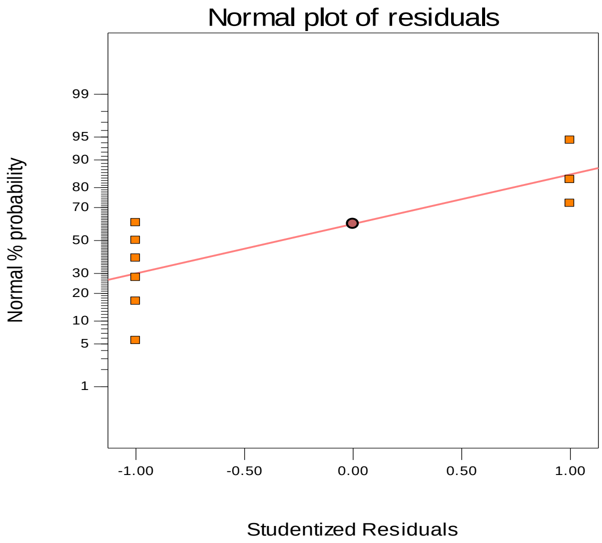

Figure 6. Normal% probability and studentized residuals

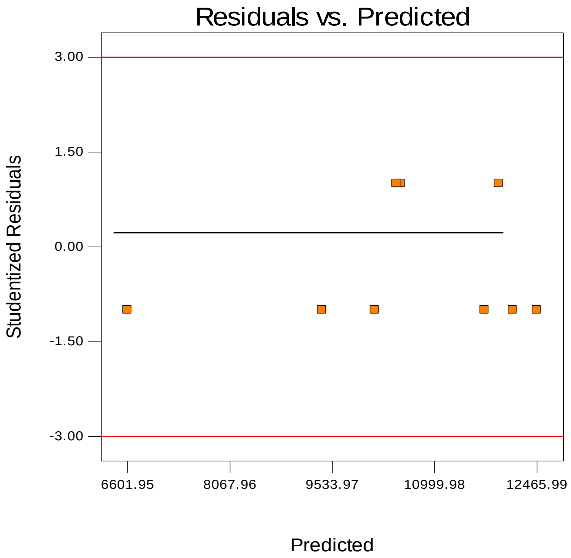

Figure 7. The studentized residuals and predicted response

In the experimental design, the R^2 value is obtained through calculating the rate of change depending on the average value obtained from the model. However, it should not be forgotten that R^2 always increases regardless of whether the term is remarkable or not when a new factor is added to the model. However, there will be no augmentation in the adjusted R^2 term, even if any factor is put into the model. In this context, large difference between R^2 and adjusted R^2 values indicates the presence of meaningless terms in the model [29].

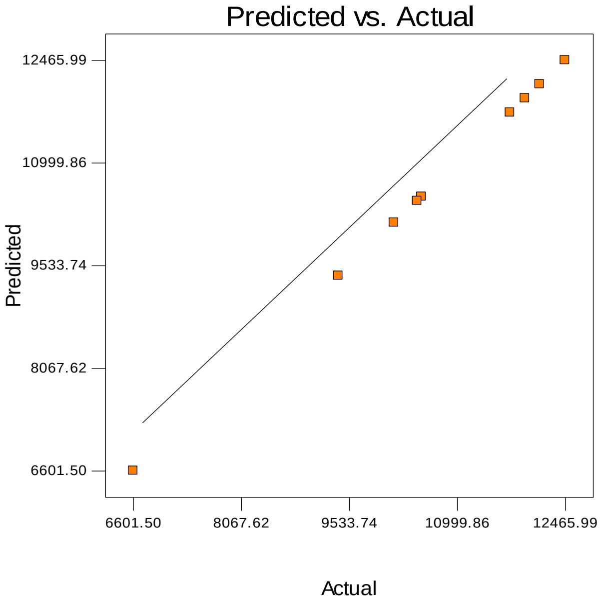

Figure 8. The actual and predicted plot

In the study, the actual and estimated FAME conversions were given in Figure 8. According to the model, R^2 and adjusted R^2 were calculated as 1.00 and 1.00 respectively and they were noticed to be highly compatible with each other. Also, the estimated R^2 was calculated to be 0.999 and was in good agreement with the adjusted R^2 value.

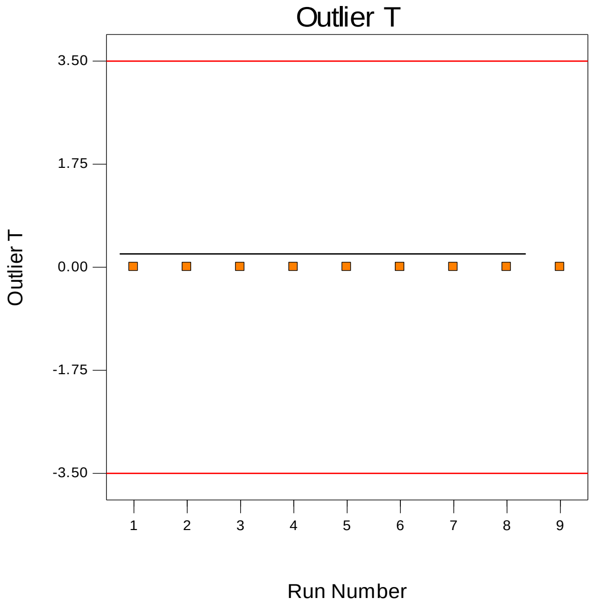

Figure 9. The outlier t plot

The t−value graph is also an important criterion, indicating the size of the residues in each study. Thus, it could be decided whether very large residual value has been obtained in any operation, or not. Typically, the standard deviation is operated as the limit value of 3 and a large part of the standard residues is expected to be within ± 3.00. An outlier value beyond this border points to a potential fault for the model or a procedural fault on the experimental ground. In the study, as seen in Figure 9, there appeared to be no data outside of interval 3, indicating that the model was consistent with all the data. Finally, the sufficient sensitivity value, an indication of the signal to noise ratio, was found to be 2181.45, which should be greater than 4. Consequently, all of these values are evident to the model being meaningful.

3.3. Effects of WCO Flow Rate and Molar Ratio on Conversion

In Figure 10 and 11, the FAME conversion rised remarkably quadratically till a certain value and declined after this maximum when it continued to increase the WCO flow rate at constant heat duty of 350 watt. This variation of parabolic flow rate at higher molar ratio related to greater conversion values. On the other hand, the molar ratio curves at the lower flow rate and heat duty become slightly parabolic. Although the change of it was almost too little, it was fathomed that the conversion raized somewhat in parallel with the increase of molar ratio at lower flow rates. But, upon alteration of molar ratio at the higher flow rates, the quadratic impact on conversion enlarged, too. Meanwhile, the gradient of profile become much steeper and conversion ascended in a like manner, when the heat duty was being kept up increase simultaneously.

The synergistic influence of both parameters on conversion varied between half cylindrical surface and light dome shape depending on the condition of parameters.

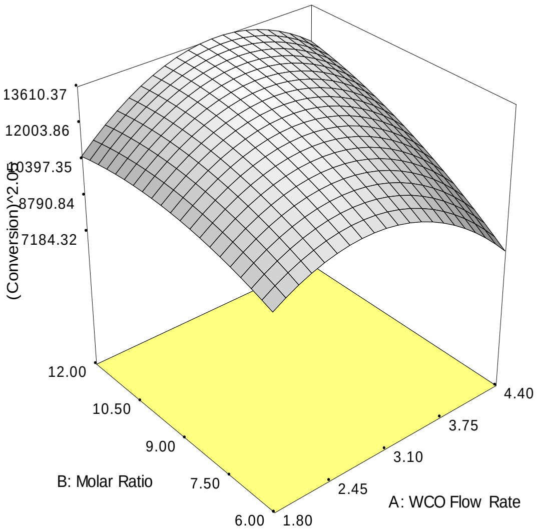

Figure 10. 3D surface plot of parameter A and B

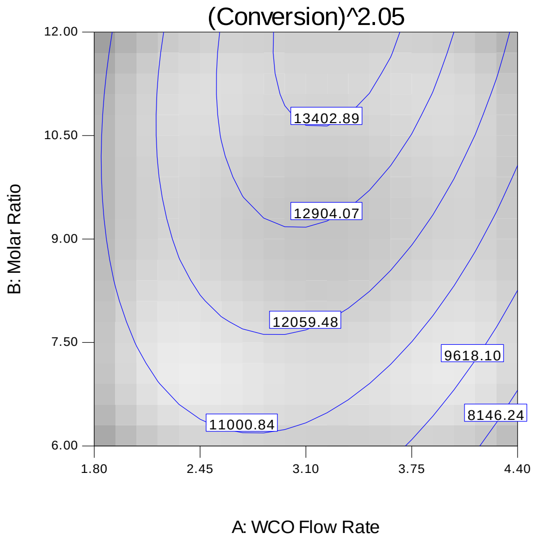

Figure 11. Contour plot of parameter A and B

3.4. Influence of Molar Ratio and Heat Duty on Conversion

Referring to Figure 12 and 13, it could be sighted that conversion versus molar ratio graphs at a stationary flow rate of 3.10 ml/min had a parabolic change, too. This alteration had much more inclination at higher heat duty. Also, much larger conversion values were acquired in parallel with the rising of molar ratio. However, the profile of the heat duty versus the conversion at the smallest molar ratio shown that a little change occurred and even it was almost close to constant. As the heat duty and molar ratio was increased simultaneously, the conversion augmented reasonably linearly. The synergistic effect of both parameters resembled to a flat surface bent slightly on the diagonal. Additionally, as long as WCO flow rate was magnified till 3.28 ml/min, all these surface conversion values surged, too. When it continued to grow up, surface conversion values started to lessen again at the all molar ratio and heat duty values.

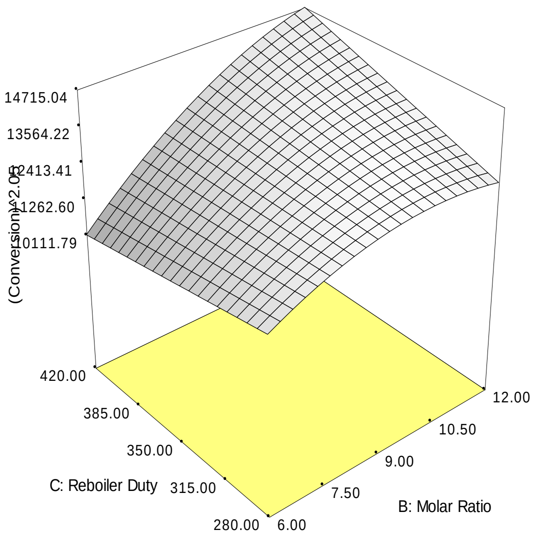

Figure 12. 3D surface plot of parameter B and C

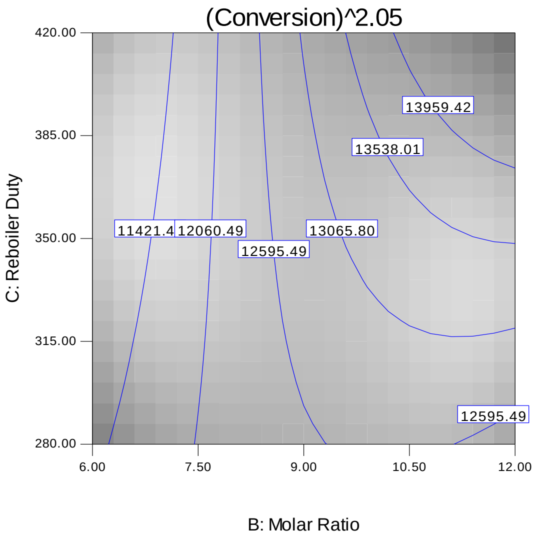

Figure 13. Contour plot of parameter B and C

3.5. ANOVA Analysis for Optimization Criteria

As stated at the begining, the objective of this study was to contribute to the cost reduction of biodiesel, which was the biggest obstacle in the industrialization of its production. Considering the experimental studies, the mass transfer restrictions and kinetic region reaction rates were described previously in Figure 3−5. It was obvious that each steady state was get at different times at different conversion values in the figures as mentioned earlier.

In terms of biodiesel price, it is clear that the production expenses will decrease if higher conversion values and lower operating times are obtained. At this point, the smallest initial mass transfer limitations and the greatest kinetic region reaction rates became most important factors. Accordingly, an optimization criteria factor, the ratio of conversion to steady state time, was determined for each state experimentally and presented in Table 5. It was used in numerical optimization, thus including both initial mass transfer constraints and kinetic reaction rates at the same time.

Table 5. Optimization criteria values

Exp. Nu.	Steady sate time (min)	FAME conv. (%)	Optimization Criteria
1	315	90.00	0.286
2	180	91.60	0.509
3	210	96.56	0.459
4	165	91.35	0.554
5	100	98.17	0.982
6	120	99.52	0.829
7	300	72.99	0.243
8	375	86.66	0.231
9	150	97.38	0.649

The most compatible model containing coded terms was obtained as polynominal Eq. (3). Looking at the equation, the (A^2) term had a negative quadratic and the greatest impact, the largest coefficient and F–value in the model. Then, the second largest coefficient was of negative quadratic (B^2) and had a coefficient close to linear positive (B). Likewise, linear (C) had a positive influence and had about a half effect of linear positive (B). The synergistic influence of the interaction (AB), (AC) and (BC) were positive, but the parameters had lower values than the individual coefficients. Lastly, synergistic impact of (BC) had the smallest value in the model.

$$
\begin{aligned}
\textit{Optimization Criteria} &= 0.97 \\
&+ 0.19 * B \\
&+ 0.10 * C \\
&- 0.42 * A^2 \\
&- 0.20 * B^2 \quad (3) \\
&+ 0.11 * AB \\
&+ 0.10 * AC \\
&+ 0.019 * BC
\end{aligned}
$$

As viewed in Table 6, the higher F−value of 2273.96 of modified second order model pointed out its significance, indicating the probability of noise induced F−value of this magnitude might be only 1.61%. It was also observed that linear (B), (C), and second order (A^2), (B^2) and (AB) terms were meaningful when F and p values of each one were checked. Although p values of (AC) and (BC) were greater than 0.05, these interacted terms, however, were taken place in the model because the parameters (A), (B) and (C) were significant, individually.

Table 6. ANOVA of model and process parameters

Source	Sum of squares	DF	Mean square	F value	p–value prob>F	
Model	0.540	7	0.078	2273.96	0.0161	Significant
B	0.046	1	0.046	1346.73	0.0173	
C	0.026	1	0.026	746.60	0.0233	
A^2	0.210	1	0.210	6012.54	0.0082	
B^2	0.026	1	0.026	758.44	0.0231	
AB	0.010	1	0.010	294.61	0.0370	
AC	5.23E-03	1	5.23E-03	152.73	0.0514	
BC	5.08E-04	1	5.08E-04	14.84	0.1617	
Residual	3.42E-05	1	3.42E-05			
Cor total	0.540	8				

Relating to R^2 and adjusted R^2 values, they were calculated as 0.999 and 0.999, respectively, and seemed to be very compatible with each other. Also, estimated R^2 of 0.974 well matched with the adjusted R^2 value. Finally, the sufficient sensitivity value, which should be greater than 4, was found to be 136.02. All of these values are evident that the model is very eloquent.

3.6. Effects of WCO Flow Rate and Molar Ratio on Optimization Criteria

In Figure 14 and 15, it was gripped that the optimization criteria increased substantially quadratically till a certain value and fallen after this maximum, provided the growth of WCO flow rate continued at a fixed heat duty of 350 watt. Upon lessening the heat duty at all molar ratios, all optimization criteria values of the profile dropped in the same way. Likewise, optimization criteria increased in parallel with the increase of heat duty. However, the changes in optimization criteria profiles were obtained partially lesser, in comparison.

In addition, all of the above was true for the molar ratio profiles obtained at constant WCO flow rates and for those exchanged parallel with the heat duty. The synergistic effect of the two parameters on the optimization criteria was quite pronounced as a dome.

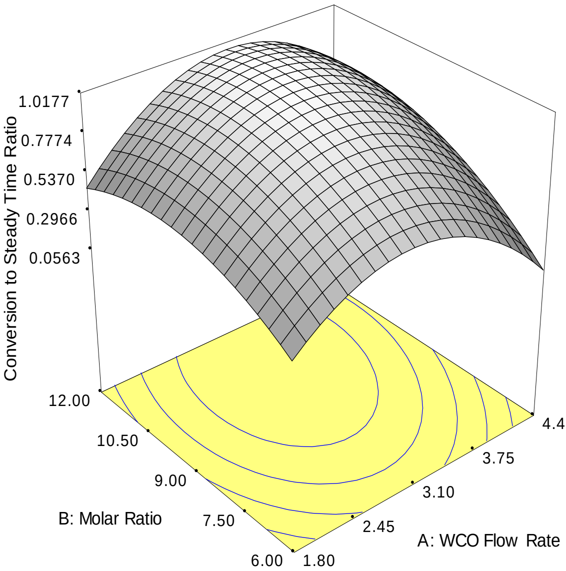

Figure 14. 3D surface plot of parameter A and B

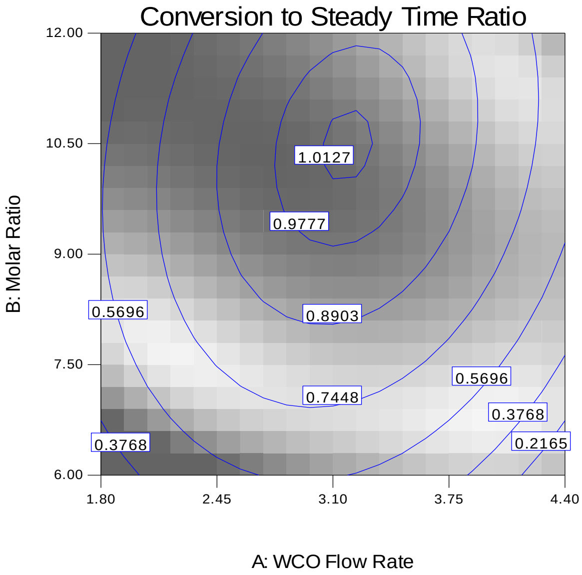

Figure 15. Contour plot of parameter A and B

3.7. Effects of WCO Flow Rate and Heat Duty on Optimization Criteria

As presented in Figure 16 and 17, the optimization criteria rised squarely till a certain value and declined after this maximum as long as the augmentation of WCO flow rate was maintained at the constant molar ratio of 9. It was also found that this profile had higher optimization criteria values at larger heat duty. Also, different heat duty profiles were obtained during the research. Accordingly, the change of optimization criteria versus heat duty profile was almost constant at the smallest flow rate. Then, the gradient of line grew slightly linearly in parallel ascent of flow rate. The synergistic effect of both parameters emerged as a semi–cylindrical lateral surface. The conversion values of this cylindrical surface grew increasingly when the molar ratio was magnified till 10.70 and when it was continued to increase, all optimization criteria started to diminish again.

3.8. Influence Of Molar Ratio and Heat Duty on Optimization Criteria

As for Figure 18 and 19, the optimization criteria was found to rise squarely till a certain value and diminished after this maximum depending on molar ratio at constant WCO flow rate of 3.10 ml/min. It was seen that the influence of the heat duty, however, almost disappeared at the lower flow rates. In other way, all of the molar ratio profiles were almost superimposed regardless of heat duty values at the lower flow rates. On the other hand, upon boosting of the flow rate, this linear profile had an increasing slope with parallel growth of heat duty.

The synergistic effect of both parameters emerged as a semi−cylindrical lateral surface. Optimization criteria values of that cylindrical surface surged while the flow rate was raised till 3.35 ml/min, and when it was kept to magnify, optimization criteria started to lessen again.

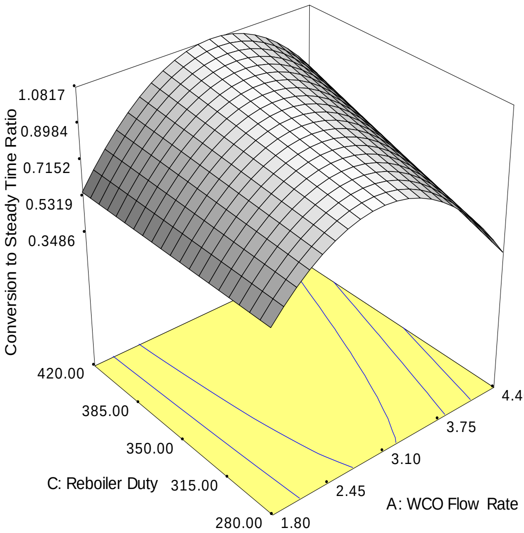

Figure 16. 3D surface plot of parameter A and C

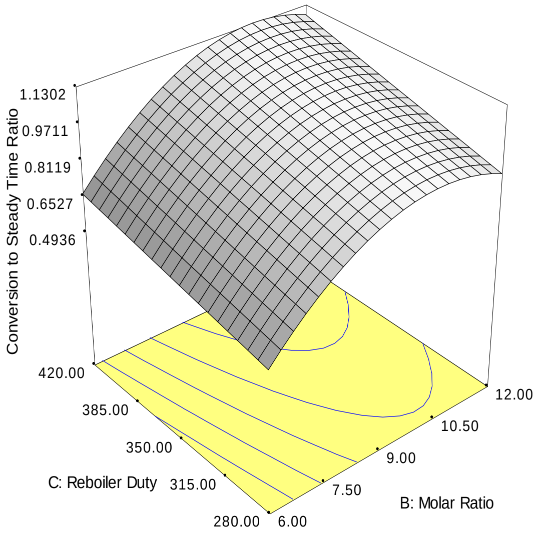

Figure 18. 3D surface plot of parameter B and C

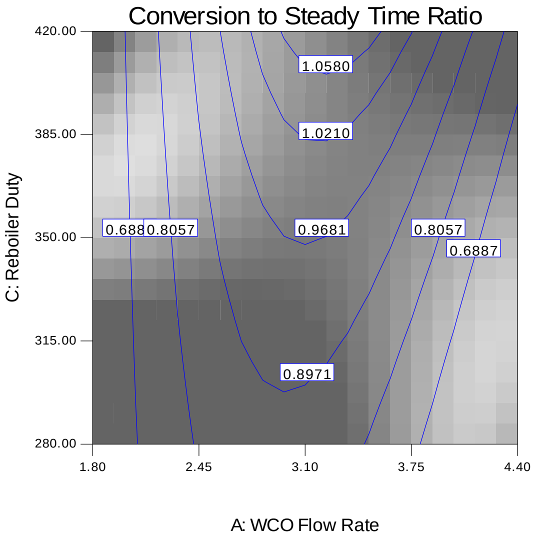

Figure 17. Contour plot of parameter A and C

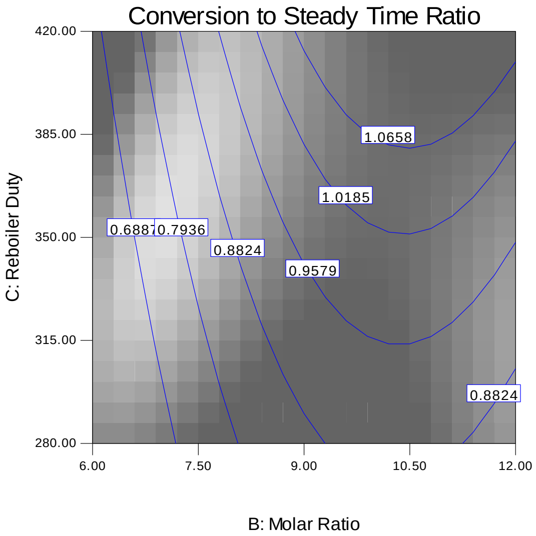

Figure 19. Contour plot of parameter B and C

3.9. Optimization

Numerical optimization is the simultaneous finding of the combination of all factors that meets the desired requirements. For this purpose, upper and lower limits for WCO flow rates, methanol/oil molar ratios, reboiler heat duty were defined in Design 6.0 program. The maximum value of optimization criteria was appointed as the final target. Constraints for each factor were shown in Table 7.

Table 7. Constraints for the numerical optimization

Parameter	Target	Lower limit	Upper limit
WCO flow rate (ml/min)	in the range	1.80	4.40
Molar ratio	in the range	6.00	12.00
Heat duty (watt)	in the range	280.00	420.00
FAME conversion (%)	in the range	72.99	99.52
Optimization criteria	maximum		

Four possible solution that meets all specified criteria set were given in Table 8. Among all solutions, Number 4 was nominated as the optimum conditions. Accordingly, depending on the highest conversion value of 99.48% and steady state time of 1.69 hour; WCO flow rate of 2.90 ml/min, methanol/oil molar ratio of 8.19, reboiler heat duty of 0.419 kW were obtained.

Table 8. Optimum conditions of parameters

Sol. Nu.	WCO flow rate (ml/min)	Molar ratio	Reboiler heat duty (watt)	FAME conv. (%)	Optimization Criteria
1	3.35	8.01	420.00	97.99	0.982
2	3.07	8.02	419.78	98.83	0.983
3	4.05	9.68	419.46	98.98	0.983
4	2.90	8.19	419.74	99.48	0.982

4. CONCLUSIONS

In accordance with Taguchi experimental design, continuous–flow biodiesel production from WCO was carried out via transesterification of methanol in CaO catalyst−packed RD column. Depending on the experimental conditions, FAME conversion and steady state time were obtained between 72.99−99.52% and 1.67−6.25 hours, respectively. Optimum conditions at the maximum conversion of 99.48% and at steady state time of 1.69 hour were determined as WCO flow rate of 2.90 ml/min, methanol/oil molar ratio of 8.19 and reboiler heat duty of 0.419 kW by numerical optimization. In addition, as mentioned before, the feed inlet temperature was opted for 55 °C.

The effect of the four parameters on FAME conversion was analyzed by statistical ANOVA method in which good F and p values were obtained. It was realized that the most important parameter was negative quadratic (A^2) term in both model. Then, second important one was the linear positive B and the ratio of both of them was similar in both models. The negative quadratic impact of (B^2) increased in the second model and reached almost the value of linear positive (B). The synergistic influences in both models were positive, but they diminished somewhat in the second model. The synergistic (AB) and (BC) took part in both models whereas the effect of (BC) substantially marked down in the second model. Finally, only showing up in the second model, (AC) had a close coefficient to (AB).

There were numerous studies in the literature on biodiesel manufacture with transesterification of methanol in a batch reactors with CaO catalyst. By using waste cooking oil, conversion values of 94.25% in 12:1 molar ratio [14], 95.84% in 18:1 molar ratio [15], 99.58% in 6.03:1 molar ratio [19] and 99.00% in 12:1 molar ratio [2] were obtained. Furthermore, conversion values of 99.85% in 9:1 molar ratio from canola oil [30], 99.00% in 12:1 molar ratio from karanja oil and jatropha oil [31] and 96.50% in 12:1 molar ratio from rapeseed oil [32] were found. Besides, by using 12:1 molar ratio and soybean oil, conversions of 95.00% [3] and 93.00% [2] were obtained. On the other hand, there was very few study on biodiesel production in CaO−catalyzed continuous flow systems. By using waste cooking oil in a continuous flow process, conversion values of 94.00% in 25:1 molar ratio in fixed bed reactor [16] and 94.41% in 6:1 molar ratio in packed RD column [14] were obtained.

It was viewed that the good findings obtained in the study were in good agreement with the literature. The Taguchi experimental design method, ANOVA analysis and numerical optimization seemed to be accomplished quite successfully. This process could be considered both economically and environmentally friendly due to the using of low priced waste cooking oil, easily available and cheaper heterogeneous CaO catalyst and compact RD column.

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DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

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