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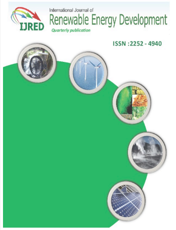

Research Article

Experimental Investigation and Optimization of Non-Catalytic In-Situ Biodiesel Production from Rice Bran Using Response Surface Methodology Historical Data Design

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ABSTRACT. Rice bran oil (RBO) is claimed to be a potential feedstock for biodiesel production. Non-catalytic in-situ biodiesel production from a low-cost feedstock (rice bran) using subcritical ethanol-water mixture was investigated in this study. The influence of four independent variables, i.e., addition of co-solvent, ethanol concentration, temperature, and time of reactions, on the yield of biodiesel was examined. The results showed that the most effective co-solvent was ethyl acetate and the optimum ethanol concentration, temperature and reaction time were 80% v/v, 200 °C and 3 hours, respectively. The maximum yield of biodiesel was found to be around 80%. The optimization of operating conditions was carried out by response surface methodology (RSM) with historical data design (HDD). The statistical method also suggested similar optimum operating conditions, i.e., 78.44% (v/v) ethanol concentration, 200 °C, and 3.2 hours reaction time with ethyl acetate as a co-solvent. The predicted maximum biodiesel yield was also slightly lower, i.e., 76.98%. Therefore, this study suggests that biodiesel production from rice bran through a non-catalytic in-situ process using a subcritical ethanol-water mixture with ethyl acetate as a co-solvent is very feasible since the yield can reach 80%. The study also found that RSM with HDD can predict the optimum operating conditions with a good accuracy.

Keywords: Rice bran; Biodiesel; Historical data design; Subcritical ethanol-water mixture

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1. Introduction

Dependence on fossil fuels is an important concern nowadays. In Indonesia, the country with the 4th largest population in the world, the consumption of petroleum was recorded at 1,785,000 barrels/day while the production of petroleum was only 778,000 barrels/day in 2019 (British Petroleum 2019, Dewan Energi Nasional 2019). The consumption of fossil fuels is also proven to be the main cause of climate change due to the emission of greenhouse gases into the atmosphere (Syafiuddin *et al.* 2020). Therefore, an environmental- friendly alternative fuel is required to replace conventional fossil fuels.

Biodiesel is an environmental-friendly fuel that is suitable to replace conventional diesel fuels since it is easily biodegradable in nature, non-toxic, and has low sulfur and aromatic contents (Syafiuddin *et al.* 2020, Jahirul *et al.* 2021). In addition, biodiesel has high fuel efficiency, low emissions, and can be used as fuel in diesel engines without modifications (Sundar & Udayakumar, 2020, Bathia *et al.* 2021). However, there are still obstacles in the production process of biodiesel, including a long process stage and uneconomical feedstock (Zullaikah *et al.* 2017, Zullaikah *et al.* 2019).

Rice bran is an alternative feedstock for biodiesel production since it has high lipid content between 15-23 wt.%, depending on the rice type and degree of milling (Nguyen *et al.* 2019, Chen *et al.* 2020). However, rice bran oil (RBO) is significantly higher in free fatty acids (FFA) content than other edible oils due to the presence of an active lipase. Hence, 60-70% of the global production of RBO is used in non-food applications. Therefore, RBO is a

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non-edible oil with high FFA content and can be considered as a low-cost feedstock for biodiesel production (Choi *et al*. 2018, Hoang *et al*. 2021). The potential of RBO production in Indonesia is estimated to reach 4.8-6 million tons annually if all rice bran is utilized to produce crude RBO.

Several catalytic biodiesel production processes using RBO have been studied, i.e., base-catalyzed, acid-catalyzed, and lipase-catalyzed transesterification processes. Base-catalyzed alcoholysis is generally regarded as the most advantageous owing to short reaction time and high efficiency. However, alkali-based transesterification required oil with low FFA and water contents (Chen *et al*. 2020, Hoang *et al*. 2021) and therefore, it is unsuitable for RBO with high FFA content. The base catalyst will react with FFA to produce soap that could decrease the yield of alkyl esters substantially and makes the separation and purification steps complicated. On the other hand, acid- and lipase-catalyzed transesterification reactions are more suitable for biodiesel production from RBO since they can tolerate high FFA content. However, they also have some drawbacks. Acid-catalyzed transesterification has lower reaction rate and difficulty in the recovery of glycerol while lipase-catalyzed transesterification is expensive and has low reaction rate (Choi *et al*. 2018, Hoang *et al*. 2021). The lower reaction rate of acid catalyst, however, could be compensated by employing high pressure, high temperature, and longer reaction time.

Current commercial production facilities of biodiesel mostly operate in batch mode which require intense mixing and long reaction time because the trans/esterification reactions only occur at the interface between oil phase and alcohol phase. This problem can be overcome by using supercritical trans/esterification method since oil is soluble in supercritical alcohol (Athar & Zaidi, 2020). However, this process requires intense energy input since the reactions occur in extremely high pressure and temperature.

Alternatively, the non-catalytic *in situ* biodiesel production using sub/sub/supercritical water-ethanol-CO_2 mixture combined with co-solvent developed in this study can offer some advantages. The energy demand is lower than that under supercritical condition since this process runs under subcritical condition. The raw material used in this process is raw rice bran rather than rice bran oil, and therefore can eliminate the costs associated with oil extraction and purification. In this method, both extraction and trans/esterification reactions occur simultaneously. The ethanol serves both as a solvent for oil extraction as well as the reactant for trans/esterification reactions. The oils are miscible with ethanol in near-critical condition leading to higher fatty acid ethyl esters (FAEE) formation rate since the trans/esterification reactions occur in a single phase rather than in two separate phases. Subcritical water can also serve as solvent to extract oil from the bran since the polarity of water in the subcritical condition is close to those of organic solvent and therefore, can reduce the amount of ethanol required. This method is not sensitive to FFA and moisture contents (Zullaikah *et al*. 2017). The use of subcritical water and supercritical CO_2 assisted with co-solvent can decrease both the medium pH and polarities of solvents leading to the higher rates of extraction, hydrolysis, and trans/esterification reactions, and therefore can decrease processing time and increase FAEE formation rate (Zullaikah *et al*. 2019, Hassan *et al*. 2020a, Hassan *et al*. 2020b). The developed process is completely green since ethanol is used instead of methanol (Syafiuddin *et al*. 2020). Moreover, since FAEE has a longer carbon chain than fatty acid methyl esters (FAME), it has higher cetane number (CN) and heating value (Bathia *et al*. 2021).

The objective of this study was to investigate the yield of biodiesel (FAEE) produced from rice bran by using a non-catalytic *in situ* process with a subcritical ethanol-water mixture. A statistical design was used subsequently to optimize the operating conditions (ethanol concentration, type of co-solvent, temperature, and reaction time). Response surface methodology (RSM) is a reliable statistical technique of design of experiments (DOE) to predict the relationship between the responses and independent variables. RSM can optimize the response function and predict future responses. A statistical design has been used to optimize catalytic biodiesel production processes from high-quality oil with low content of FFA (< 5%, w/w) (Soria-Figueroa *et al*. 2020, Yusuff *et al*. 2020, Sharma *et al*. 2021) but it has rarely been used to optimize non-catalytic biodiesel production from low-quality oil with high content of FFA.

2. Materials and Methods

2.1 Materials

Two kinds of rice bran (Rice bran 1 and Rice bran 2) used in this study were of IR 64 rice variety originating from Banyuwangi, Indonesia. They were obtained at different time resulting in different yields of crude RBO and their compositions. Rice bran was stored at 15-20 ℃ to maintain initial level of FFA in rice bran oil (RBO). As a benchmark, RBO was extracted from rice bran using hexane as a solvent and biodiesel was obtained using acid-catalyzed ethanolysis of RBO according to Zullaikah *et al*. (2005) and the results were summarized in Table 1. The yield of crude RBO and crude biodiesel (CBD) were calculated according to equation 1 and 2, respectively.

CO_2 as a pressurized gas was obtained from Aneka Gas (Surabaya, Indonesia), NaOH was obtained from Merck (Kenilworth, NJ, USA), ethanol and demineralized water were obtained from Smart-Lab (Tangerang, Indonesia), n-hexane and ethyl acetate were obtained from Fulltime (Anhui, China), chloroform was obtained from Sigma Aldrich (St. Louis, MO, USA), and phenolphthalein (pp) indicator was obtained from Cahaya Kimia (Surabaya, Indonesia).

$$Yield\ of\ Crude\ RBO\ (\%) = \frac{Crude\ RBO\ (g)}{Rice\ bran\ (g)}\ x\ 100\% \qquad (1)$$

$$Yield\ of\ CBD\ (\%) = \frac{CBD\ (g)}{Crude\ RBO\ (g)}\ x\ 100\% \qquad (2)$$

2.2 Non-catalytic in situ biodiesel production from rice bran using a subcritical ethanol-water mixture.

The experimental procedure of non-catalytic in situ biodiesel production from rice bran using a subcritical ethanol-water mixture is explained in detail in the previous work (Zullaikah et al., 2017). In essence, 10 g of rice bran was mixed with 80 ml of ethanol-water mixture and 20 ml of co-solvent in a hydrothermal reactor under CO_2 atmosphere (80 bars) and then the mixture was heated to a pre-determined temperature. The mixture was quenched to room temperature after a pre-determined reaction time. The crude biodiesel (CBD) was then extracted by using ethyl acetate and it was recovered by evaporating the solvent. CBD was then stored for further analyses. CBD is biodiesel containing impurities such as unreacted oils and unsaponifiable matters including bioactive compounds (γ-oryzanol, phytosterols, tocopherols, tocotrienols, etc.) that are rich in RBO.

All experiments parameters are shown in Table 2 and 3, respectively. The optimum type of co-solvent and ethanol concentration were investigated by using Rice bran 1. To investigate the best type of co-solvent, the ethanol concentration was set to 50% v/v and the effect of three different co-solvents, i.e., n-hexane, chloroform, and ethyl acetate, on biodiesel yield was investigated. On the other hand, to investigate the optimum ethanol concentration, the experiments were carried out without co-solvent and the ethanol concentration was varied from 20 - 80% v/v. Other parameters (operating pressure, temperature, reaction time, and stirring speed) were kept constant in both cases as shown in Table 2. Rice bran 2 was used to investigate the optimum temperature and reaction time since the quantity of Rice bran 1 was not sufficient. To investigate the optimum operating temperature, the reaction time was kept constant at 3 h while the temperature was varied from 120 to 200 ^{o}C. To investigate the optimum reaction time, the temperature was set at 200 ^{o}C while the reaction time was varied from 1 to 4 hours. Other parameters (operating pressure, co-solvent, ethanol concentration, and stirring speed) were kept constant in both cases as shown in Table 3. In all cases, each run was repeated at least twice and the average result from each run was presented in this work since the difference between repetitions was found to be less than 5%.

The CBD was analyzed by using high temperature gas chromatography (Shimadzu GC-2010 Plus, Kyoto, Japan) equipped with a flame ionization detector (FID) to determine the concentration of biodiesel (FAEE) and other impurities. The yield of FAEE and extraction efficiency were calculated according to equation 3 and 4, respectively.

$$Yield\ FAEE\ (\%) = FAEE\ content\ (\%) x\ EA\ (\%) \qquad (3)$$

$$Extraction\ Efficiency, EA\ (\%) = \frac{CBD\ (g)}{Crude\ RBO\ (g)}\ x\ 100\% \qquad (4)$$

Table 1
Yield of crude RBO and maximum yield of CBD obtained using acid-catalyzed ethanolysis.

	Rice bran 1	Rice bran 2
Yield of crude RBO (%)	15.52 ± 0.11	13.21 ± 0.10
Yield of CBD (%)	84.69 ± 1.45	88.19 ± 0.27
Crude RBO composition:		
Free fatty acids (FFA)	63.59	83.12
Monoacylglycerols (MAG)	1.48	2.05
Diacylglycerols (DAG)	5.40	2.25
Triacylglycerols (TAG)	24.94	9.21
Others*	4.59	3.37

*Mainly unsaponifiable matters

Table 2
The operation conditions of the non-catalytic in-situ biodiesel production from rice bran (1) using a subcritical ethanol-water mixture.

	Ethanol concentration (%, v/v)	Co-solvent
P = 8 MPa	50	Without co-solvent
T = 160^{o}C		n-Hexane
t = 2 h		Chloroform
N = 400 rpm		Ethyl acetate
Ratio of rice bran: solvent: co-solvent= 10 (g): 80 mL: 20 mL	20 - 80	Without co-solvent
The pressurized gas: CO_2		

Table 3
The operation conditions of the non-catalytic in-situ biodiesel production from rice bran (2) using a subcritical ethanol-water mixture.

	Temperature (^{o}C)	Time (h)
P = 8 MPa	120 - 200	3
N = 400 rpm		
Ethanol concentration = 80% (v/v)		
Co-solvent = ethyl acetate		
Ratio of rice bran: solvent: co-solvent= 10 (g): 80 mL: 20 mL	200	1 - 4
The pressurized gas: CO_2		

2.4 Optimization of operating conditions by using a DOE.

The evaluation of the equation model was carried out using the analysis of variance (ANOVA) and the residual test. The Design Expert 12 software provided the recommendations for equation models including linear, two-factor with interaction (2FI), quadratic, and polynomial equations above second order. Linear recommendation indicates that the factors that have significant influence only came from the form of the linear equation, namely the independent variables. The 2FI recommendation indicates that the equation is increasingly significant with the interaction of every two factors from the experimental data. Meanwhile, the quadratic recommendations and polynomial equations indicate that the quadratic form in the equation makes the equation even more significant. The residual tests were carried out using the normality test, the error of the equation model, and the difference between the predicted and experimental results. Optimization of analysis results was carried out on all variables with a choice of several treatments, including minimum, maximum, in range, target optimization, and none.

3. Results and Discussion

3.1 Non-catalytic in situ biodiesel production

Table 4 shows that the most effective co-solvent is ethyl acetate that give FAEE yield of 52.81% (at 160 °C, 2 hours reaction time, and 50% v/v ethanol) while the optimum ethanol concentration is 80% v/v that give FAEE yield of 51.64% (at 160 °C, 2 hours reaction time, and without co-solvent). The addition of ethyl acetate increases FAEE yield by more than two-fold (Table 4) compared to that without the addition of co-solvent indicating that the addition of co-solvent significantly increases the extraction rate of oil which is the limiting step in the non-catalytic in-situ biodiesel production from rice bran (Zullaikah *et al*., 2017). Among the three co-solvents used in this work, ethyl acetate has the highest polarity index (polarity index of ethyl acetate = 4.4). Consequently, it will extract more lipids in rice bran, since the rice bran used in this work has high level of free fatty acids (FFA > 60%). Besides, the more polar the co-solvent, the easier it is to penetrate the cell wall of biomass which consist of lignocellulosic compounds (Zhang *et al*, 2015).

FAEE yield also increases with higher ethanol concentration. Increasing ethanol concentration from 50% v/v to 80% v/v also increase FAEE yield by more than two-fold (Table 4). In this system, ethanol plays a role as a reactant and solvent. Increasing the concentration of ethanol also increases the yield of crude RBO since the solubility of oil is higher in ethanol than that in water (Zullaikah *et al.* 2019). Besides, according to the Le Chatelier's principle, adding additional reactant to a system will shift the equilibrium towards the products side. Since both transesterification and esterification reactions are reversible reactions, the FAEE yield can be increased by increasing the concentration of ethanol.

Table 5 shows that FAEE yield increases with reaction time up to 3 hours and then decreases slightly as the reaction time is extended to 4 hours. Longer reaction time more than 3 hours decreases FAEE yield probably due to polymerization and degradation of unsaturated fatty acids in rice bran oil (Zullaikah *et al.,* 2017). On the other hand, FAEE yield increases with temperature up to 200 °C. The extraction rate of oil from rice bran increases with increasing temperature due to the increase of diffusion coefficient between oil and the ethanol-water mixture. Besides that, the oil is also more soluble in the ethanol-water mixture at higher temperature because the ethanol-water mixture has lower dielectric constant at higher temperature (Zullaikah *et al.* 2017). The maximum FAEE yield of 80.09% is achieved at 200 °C and 3 hours reaction time (at 80% v/v ethanol concentration and with ethyl acetate as co-solvent).

3.2 Optimization of operating condition by using RSM

Response surface methodology (RSM) is a collection of statistical and mathematical techniques used to set up a series of experiments (design) for adequate prediction of a response (Y), fitting a hypothesized (empirical) model to data obtained under the chosen design, and determining the optimum conditions on the model's input (control) variables that lead to the maximum or minimum response within a region of interest (Yusuff *et al*. 2020). Unlike the Box-Behnken designs (BBD) and Central Composite designs (CCD) which perform design experiments, the historical data designs (HDD) use data that has already been gathered to predict the optimum response as a function of the independent variables. Historical data creates a blank design layout to accept components and factor settings and responses from an existing data set. Design limits must be determined beforehand to find the minimum or maximum setting from the components and factors.

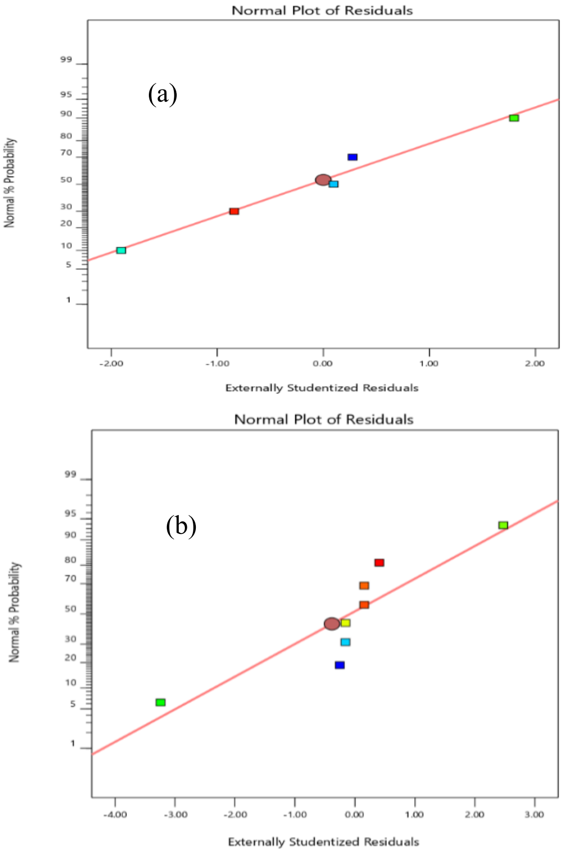


Fig. 1 Graphical representation of residuals for the model from (a) rice bran 1 and (b) rice bran 2.

The HDD was a suitable design for modelling post-experimental results by importing available data whether it is numerical or categorical data (Nookaraju *et al.* 2020). In this work, two sets of experiments were carried out. The first set of experiment was carried out by using rice bran 1 to find the optimum ethanol concentration and co-solvent with high FFA level (> 60%). Hence, for the first set of experiment, the independent variables were ethanol concentration (X_1) and co-solvents (X_2), while the response was FAEE yield (Y) as shown in Table 4. The second set of experiment was carried out by using rice bran 2 to determine the optimum reaction time and temperature. The optimum ethanol concentration and co-solvent obtained from the first set of experiment were employed in the second set of experiment. Hence, for the second set of experiment, the independent variables were reaction time (X_1) and reaction temperature (X_2) as shown in Table 5. The correlation between experiments using rice bran 1 and rice bran 2 is shown in Fig. 1 and it shows that a data set is well-modelled by a normal distribution.

The quadratic polynomial equation is used to fit the response of each experimental data because it has the highest F-value and R^2 and the lowest P-value. The empirical model of FAEE yield from Rice bran 1 was expressed by equation 5-8 for n-hexane, ethyl acetate, chloroform, and without co-solvent, respectively. Meanwhile, the empirical model of FAEE yield as a function of reaction time and temperature from ice bran 2 is shown in equation 9.

$$Y = 0.01\,X_1^2 - 0.28\,X_1 + 9.59 \tag{5}$$

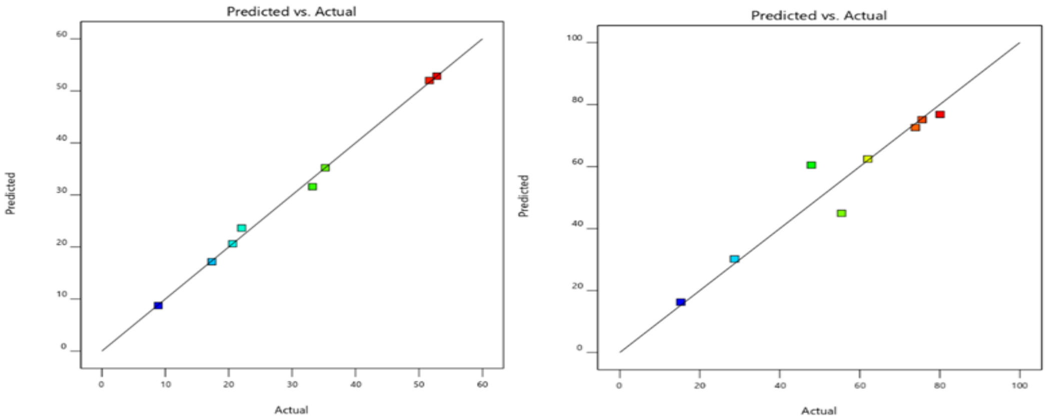
$$Y = 0.01\,X_1^2 - 0.28\,X_1 + 41.78 \tag{6}$$

$$Y = 0.01\,X_1^2 - 0.28\,X_1 + 24.18 \tag{7}$$

$$Y = 0.01\,X_1^2 - 0.28\,X_1 + 22.04 \tag{8}$$

$$Y = 0.001\,X_1^2 - 2.96\,X_2^2 + 0.44\,X_1 + 19.03\,X_2 - 125.09 \tag{9}$$

Multiple regression analysis technique included in the historical data RSM design was employed to obtain the coefficients of the empirical model. The model coefficients with positive sign represent synergistic effect, while those with negative sign represents antagonistic effect.



(a) (b)

Fig. 2 Graphical representation of actual and predicted values from (a) rice bran 1 and (b) rice bran 2

Table 4
Historical data experimental design of the independent variables and responses (rice bran 1)

Run	Ethanol concentration, % (X_1)	Co-solvent (X_2)	FAEE Yield, % (Y)	Predicted FAEE Yield, % (Y’)	Error, %
1	50	n-hexane	20.63	20.63	0.00
2	50	Ethyl acetate	52.81	52.81	0.00
3	50	Chloroform	35.22	35.22	0.00
4	50	-	22.04	23.64	-1.60
5	80	-	51.64	51.98	-0.34
6	60	-	33.21	31.59	1.62
7	40	-	17.36	17.18	0.18
8	20	-	8.89	8.75	0.14

Table 5
Historical data experimental design of the independent variables and responses (rice bran 2)

Run	Time of reaction, h (X_1)	Temperature of reaction, °C (X_2)	FAEE Yield, % (Y)	Predicted FAEE Yield, % (Y')	Error, %
1	1	200	62.02	62.44	-0.43
2	2	200	73.89	72.61	1.28
3	3	200	80.09	76.84	3.25
4	4	200	75.58	75.15	0.43
5	3	120	15.25	16.26	-1.01
6	3	140	28.69	30.18	-1.49
7	3	160	55.47	44.92	10.55
8	3	180	47.90	60.47	-12.57

Table 6
ANOVA for Surface Response Quadratic Model (rice bran 1)

Source	SS	DF	MS	F- value	P- value
Model	1777.15	5	355.43	133.61	0.0074
Ethanol Concentration, X_1	1038.43	1	1038.43	390.35	0.0026
Co-solvent, X_2	737.99	3	246.00	92.47	0.0107
X_1^2	0.0000	0			
Residual	46.92	1	46.92	17.64	0.0523
Total	5.32	2	2.66		

Table 7
ANOVA for Surface Response Quadratic Model (rice bran 2)

Source	SS	DF	MS	F-value	P-value
Model	3496.40	4	874.10	9.20	0.0494
Time, hour, X_1	2831.01	1	2831.01	29.79	0.0121
Temperature, X_2	90.25	1	90.25	0.9495	0.4017
X_1^2	0.0000	0			
X_2^2	2.70	1	2.70	0.0284	0.8769
Residual	36.26	1	36.26	0.3815	0.5805
Total	285.13	3	95.04		

ANOVA is another statistical approach used to analyse the adequacy of the model. The ANOVA results for the model in equation (5-8) were shown in Table 6 and for the model in equation (9) were shown in Table 7. As shown in Table 6, the F-value of 133.61, as well as the p-value of < 0.0074 suggest that the model for the first set of experiment using rice bran 1 is significant. Meanwhile, Table 7 shows that the model for the second set of experiment with rice bran 2 is also significant with the F-value and p-value of 9.20 and less than 0.0494, respectively. Although, the interaction between factors was aliased due to the lack of the data amount available.

Fig. 2 demonstrates the actual against the predicted yields of FAEE. It shows that the predicted yield of FAEE is around the actual yield of FAEE suggesting a moderately decent connection between the predicted and actual yields of FAEE. The residuals depict a normal distribution because essentially every one of the focuses pursue a straight-line curve. This diagram shows that Eq. (5-9) is the most suitable model for the historical data design RSM on FAEE yield of non-catalytic in-situ biodiesel production from rice bran under subcritical ethanol-water mixture.

Table 7
Summary of optimized operation conditions of a non-catalytic in-situ biodiesel production from rice bran using subcritical ethanol-water mixture.

Source	Variables	Optimized condition	Optimized yield of FAEE
Rice bran 1	Ethanol concentration	78.44%	79.35%
	Co-solvent	Ethyl Acetate	
Rice bran 2	t of reaction	3.2 h	76.98%
	T of reaction	200 °C	

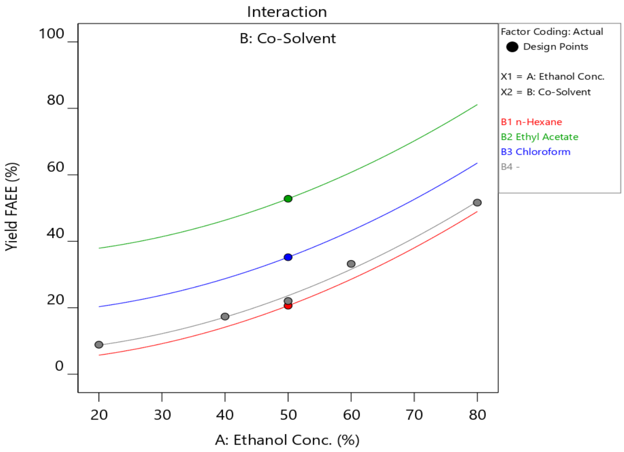


Fig. 3 Effects of ethanol concentration and co-solvent on yield of FAEE (rice bran 1).

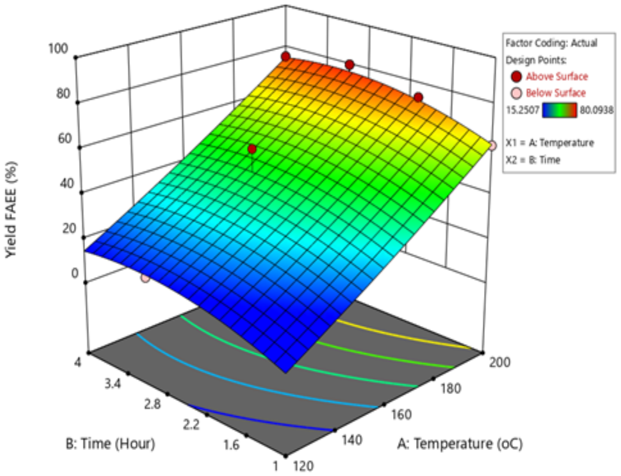


Fig. 4 Effects of reaction time and temperature on yield of FAEE (rice bran 2).

Fig. 3 demonstrates the interaction between ethanol concentration and co-solvent on yield of FAEE. The yield of FAEE increases with increasing ethanol concentration. The types of co-solvent also have significant impact on the yield of FAEE. Among the three co-solvents used in this work, ethyl acetate will extract more lipids in rice bran due to their similar polarity. Fig. 4 demonstrates the interaction between time and temperature of reactions on yield of FAEE. The highest yield of FAEE was achieved after 3 h of reaction time and 200°C.

Numerical optimization of equations 6 and 9 was finished by utilizing the Design Expert programming (Design-Expert 12, Stat-Ease, Inc.) to decide the optimum ethanol concentration, reaction time and temperature which produce the maximum yield of FAEE. The summary of optimized operating conditions of a non-catalytic in-situ biodiesel production from rice bran using subcritical ethanol-water mixture is shown in Table 7. The optimum operating conditions were found to be 78.44% (v/v) ethanol concentration with ethyl acetate as co-solvent for rice bran 1 and the optimum FAEE yield was 79.35% (at 160 °C and 2 hours reaction time). For rice bran 2, the optimum reaction time and temperature were found to be 3.2 h and 200°C (at 80% v/v ethanol concentration and with ethyl acetate as co-solvent), respectively, and the optimum FAEE yield of 76.98%.

4. Conclusion

The non-catalytic in-situ biodiesel production from rice bran using subcritical ethanol-water mixture has been investigated and optimized by using response surface methodology (RSM) with historical data design (HDD). The highest biodiesel (FAEE) yield was found to be 80.09% at the following operating condition: 200 °C, 3 hours reaction time, 80% v/v ethanol concentration, and with ethyl acetate as co-solvent.

The HDD was chosen as the proper design due to its capacity to model the existing experimental data. The quadratic polynomial was selected to fit the experimental data. The optimization of operating conditions was performed by using response surface optimizer on the Design-Expert 12 (Stat-Ease, Inc.). The predicted optimum conditions were 78.44% (v/v) ethanol concentration with ethyl acetate as co-solvent and 3.2 h reaction time at 200°C. The predicted maximum FAEE yield under these optimum conditions was 76.98%.

Therefore, this study suggests that rice bran can potentially be employed as a cheap feedstock for biodiesel produced through a non-catalytic in-situ process using a subcritical ethanol-water mixture with ethyl acetate as a co-solvent. Higher biodiesel yield can be achieved by removing biodiesel (FAEE) produced to shift the trans/esterification to the products side. This study also shows that RSM with HDD can be used to predict the optimum operating conditions with good accuracy.

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