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Optimisation of Biodiesel Production via In-Situ Esterification for Spent Bleaching Earth Waste (SBEW) using Response Surface Methodology

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ABSTRACT

Spent Bleaching Earth Waste (SBEW) is a solid waste generated during the degumming and bleaching of edible oils containing up to 40%(wt.). SBEW is utilised in biodiesel production via in-situ esterification in a deep eutectic solvent (DES). Optimisation of the reaction time (80 to 160 min) and DES/Methanol ratio (5 to 25%) were carried out using response surface methodology (RSM) involving central composite design (CCD) at a fixed temperature (65 °C). A quadratic model was set up to predict the biodiesel yield. The high value of R^2 was 0.99 and R^2_{adj} 0.98 for FAME yield, indicating that the fitted model agrees with predicted and actual crude and FAME yield. The RSM result exhibit that the optimized condition for the in-situ esterification process was 160 min with a 5% DES/methanol ratio. The predicted FAME yield was 96.13%, and the actual experimental value was 97.56%. The produced biodiesel from spent bleach earth shows the property fulfilled the standard requirements EN14214 and ASTM D6751.

Keywords: *Spent Bleaching Earth Waste (SBEW), deep eutectic solvent, in-situ esterification, FAME yield, Response Surface Methodology (RSM)*

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INTRODUCTION

Global energy demand for the transportation sector has a significant impact on fossil fuel stocks' depletion and air quality degradation. The adverse effects of fossil fuel combustion lead to global warming and ozone layer depletion. Carbon dioxide (CO_2) emissions are forecast to reach 4.1 billion metric tons between 2017 and 2021, with an estimated 8.6 billion tons of CO_2 by 2035. Therefore, renewable energy sources such as biodiesel are being explored as it is renewable, biodegradable, and non-toxic [1].

Recently, biomass and biodegradable component from municipal and industrial waste have been identified as possible sources of biodiesel. It reduced overall production costs while improving environmental sustainability [2]. Spent bleach earth waste (SBEW) from edible oil refinery processes containing waste vegetable oil has emerged as a previously overlooked source of biodiesel. As an industrial waste primarily generated by edible refineries, SBEW removes harmful components and unpleasant odours. Nearly 2 million tonnes of SBEW are produced globally [3]. SBEW was usually dumped directly into landfills, which was costly and required much space [4]. Its residual oil may oxidise, posing fire hazards and environmental concerns. According to Huang and Chang [5], the methyl ester derived from SBEW's residual oil could be used in place of commercial petroleum diesel due to their similar properties.

Transesterification is a standard method for producing biodiesel. In the case of residual oil, extensive research has been conducted on the in-situ production of biodiesel from SBEW [5], [6]. In-situ esterification is preferred as the extraction, and transesterification processes occur concurrently. Sedghamiz et al. [6] and Suryani et al. [7] converted residual SBEW's oil to methyl ester, yielding 72.90 and 84.9% biodiesel, respectively, by in-situ esterification in the presence of NaOH as a catalyst. Thus, these studies verified that the in-situ esterification of SBEW can produce a high amount of biodiesel. However, saponification occurs when alkali catalyses the reaction, resulting in a lower FAME yield due to a high FFA value SBEW (>5%). Thus, a new green solvent, deep eutectic solvent (DES), was discovered to act as a catalyst for the synthesis and purification of biodiesel. DES has been shown to enhance catalytic abilities, avoid saponification, and improve separation and purification efficiency [8, 9]. Liu and Wang [10] demonstrate the capability of the postulated DES(P-DES) catalyst by yielding 98.66% biodiesel under optimal conditions:8% P-DES catalyst, 8:1 MeOH: Oil ratio and at temperature 110 °C.

Statistical experimental designs have been used to aid the optimisation of experimental processes in recent years. These tools assist in the determination of optimal method parameters and significantly reduce the number of experiments required by 'one-factor-at-a-time' methodologies [11]. The response surface methodology (RSM), optimisation by central composite design (CCD), and factorial design are commonly used statistical tools for assessing the effects of at least two independent variables and determining the statistical significance of the factor's impact on the desired variable [12, 13]. Hence, it increases productivity and reduces the time and cost

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required for optimisation. Therefore, this study's novelty was producing biodiesel from SBEW using deep eutectic solvent via in-situ esterification. This work uses a standard RSM design called central composite design (CCD) to optimise the reaction time and DES to methanol ratio (vol %) to obtain the highest FAME yield from SBEW oil.

EXPERIMENTAL

Residual oil extraction

In a 250 mL round bottom flask with a thimble chamber, SBEW oil residues were extracted. The SBEW to hexane ratio was fixed at 1:4 (w/w). Hexane was boiled and vaporised inside the condenser. The extraction began when the solvent encountered SBEW and lasted 6 hours until the hexane turned colourless. Separation of the cooled hexane-oil mixture was accomplished using a rotary vacuum evaporator. The residual oil was dried in an oven for 12 hours at a temperature of 107 ± 2 °C. Then the per cent of residual oil was calculated as in equation 1.

$$\text{Oil extracted} = \text{wt of oil extracted} / \text{wt of SBEW} \times 100 \quad (1)$$

Preparation of deep eutectic solvent (DES)

The DES was prepared by dissolving choline chloride (ChCl) in ethylene glycol in a 1:2 molar ratio and stirring at 300 rpm for 1 hour at 80 °C until homogenous and transparent.

In-situ transesterification of SBEW

The in-situ transesterification was carried out in a 250 mL 2-neck round bottom flask equipped with a reflux system, magnetic stirrer, and heater. The reaction with different DES to methanol mixtures ranging from 5 – 25 vol% was conducted at 65 °C for 80 – 160 minutes with continuous stirring of 25 g SBEW (at 18% oil content) to give a 5 mL/g solvent to SBEW ratio. The extracted product was then transferred to a separation funnel and allowed to settle for one hour. The bottom layer is a mixture of glycerol, methanol, and DES removed before an equal mix of hexane and distilled water is added to remove any excess methanol. A rotary evaporator evaporated the hexane, yielding pure FAME. The weight of crude oil and biodiesel yield was measured using equation 2.

$$\text{Biodiesel yield} = (\text{wt of oil biodiesel product}) / (\text{wt of starting material}) \times 100 \quad (\mathbf{2})$$

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Experimental design

Response Surface Methodology (RSM) based on a central composite design (CCD) was used to determine the effect of parameters in the in-situ transesterification reaction and the optimum for the crude biodiesel yield from SBE. In RSM, the design of experiments (DOE) is crucial for understanding the optimised responses. CCD is a fundamental response surface experiment that combines fractional and factorial designs to measure contours using axial and center points [14]. This study selected the reaction time and DES to methanol ratio (vol %) as independent variables. Table 1 shows the range and levels of the variables that affect the esterification reaction. The regression analysis and graphical presentation were done using the Design Expert 7.15 software.

Table 1: Experimental range and levels of esterification parameters

Parameters	**-1**	**+1**
Reaction time (min)	80	160
DES/ methanol ratio (v%)	5	25

Physicochemical characterisation of fatty acid methyl ester

The biodiesel that has been purified from transesterification was tested and evaluated the FAME properties using a standard method: density (ASTM D854), kinematic viscosity at 40 °C (ASTM D445), free fatty acid content (ASTM D974), acid number (ASTM D664).

RESULTS AND DISCUSSION

The reaction time and DES to methanol ratio (vol%) as independent variables and biodiesel yield (%) as dependent variables evaluated in this research are shown in Table 2. The table indicates that the experimental design determines the interaction between each intersecting parameter and response. Eight experiments with five replications at the centre points were carried out in this study. A random run of the experimental series was performed to minimalise errors and uncontrollable factor influences.

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Table 2: Design of experiment

Exp No.	Reaction time (min)	DES to methanol ratio (vol%)	FAME yield (%)
1	80	5	95.25
2	120	25	88.65
3	63.43	5	79.47
4	80	25	60.87
5	120	0.86	73.04
6	120	29.14	87.49
7	176.57	15	66.66
8	160	15	96.84
9	120	15	82.75
10	160	15	47.05
11	120	15	86.37
12	120	15	83.52
13	120	15	85.03

Design of expert (DOE) software aids in creating graphic representations of polynomial equation (3) response surface plots. The software determines the optimal factor combinations that satisfy all the criteria for each response and factor simultaneously. Figure 2 depicts the three-dimensional plots illustrating the interactions of the FAME yield (%) as a dependent variable and the reaction time and DES to methanol ratio (vol %) as independent variables. This study investigated biodiesel yields with varying DES to methanol ratio (vol %) from 0% to 25% at 80 to 160 min. Reaction time plays a significant role in various reactions, providing sufficient time for the reaction's completion.

The per cent of FAME yield increases as the reaction time or the DES/methanol ratio(v%) increases, but only up to a certain point. The FAME yield increased from 60.87% to 96.84% as the reaction time increased from 80 to 160 minutes with a fixed ratio of DES/methanol (v%) of 5%. When the DES/methanol ratio(v%) increased from 5% to 25% at a fixed reaction time of 80 minutes, the FAME yield increased from 60.87% to 95.25%. However, at a fixed higher ratio of DES/methanol(v%) of 25% and reaction times ranging from 80 to 160 minutes, the FAME yield dropped from 96.8% to 47.05%. The FAME yield decreased from 95.25% to 47.05% when the DES/methanol ratio(v%) increased from 5% to 25%, while the reaction time remained constant at 160 minutes. The decrease in FAME yield could be due to longer hydrolysis of the ester into fatty acid and alcohol [15], product absorption on DES-catalyst, or insufficient availability of free methanol molecules due to excess ratio DES in a mixture [16]. Thus, reaction time is regarded as a sensitive controlling factor, as delaying the reaction has an adverse impact on the interest yield. The data shows that the highest FAME yield is 96.84%, with a reaction time of 160 minutes and a DES/methanol ratio (v%) of 5%.

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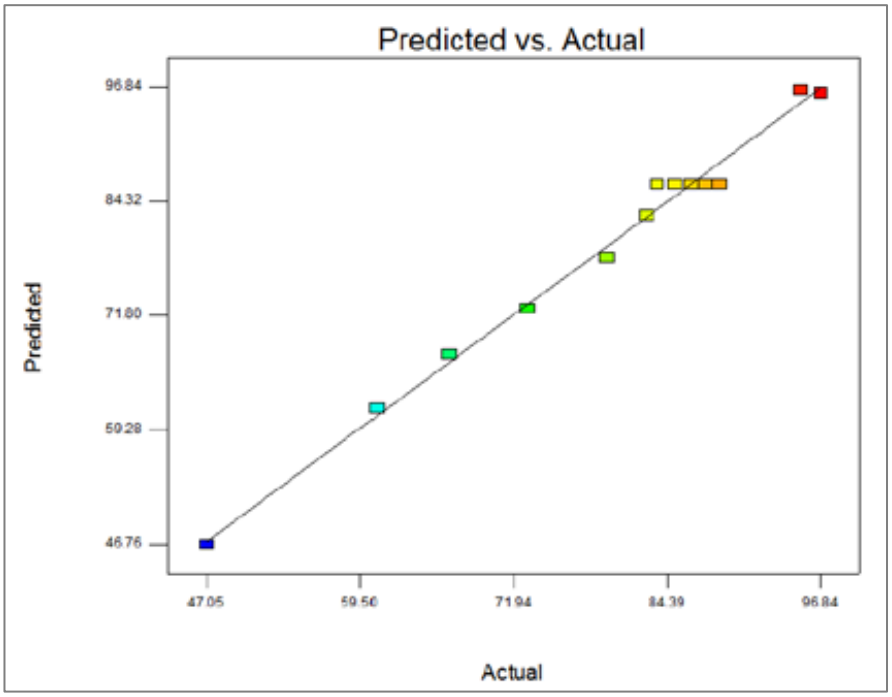

Figure 1: Plot predicted vs actual for FAME yield (%)

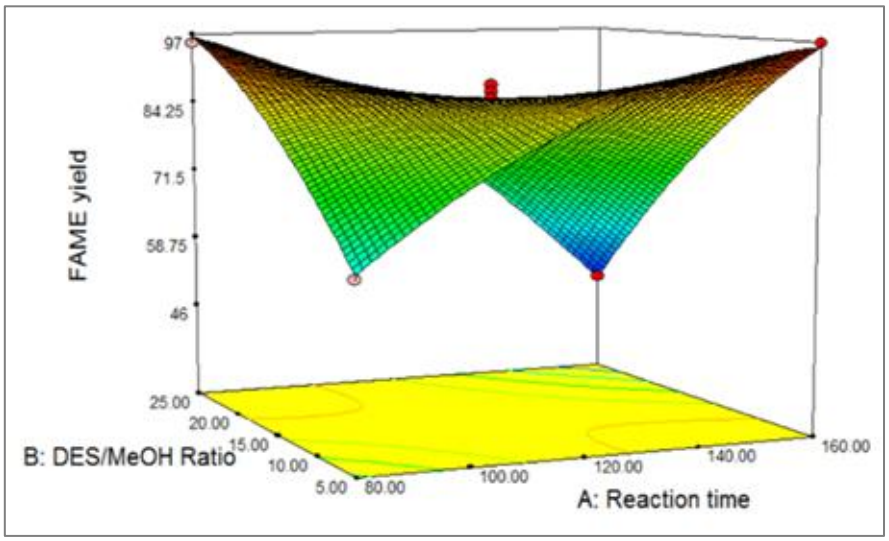

Figure 2: Response surface plots of FAME yield vs reaction time and DES/MeOH Ratio

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Optimisation of reaction conditions by RSM

According to the analysis, the quadratic model best fits the FAME yield (%). As with equation 3, the experimental response was suited to the polynomial equation using coded factors as follows:

$$Y = 86.21 – 3.79A – 3.64B – 21.04AB – 669A^2 – 4.28B^2 \quad (3)$$

where Y is the FAME yield, A is the reaction time, and B is the DES to methanol ratio(vol%).

The obtained data were evaluated using analysis of variance ANOVA to determine the goodness of fit of the quadratic response surface model by the least square method. The results of the ANOVA analysis for the response surface quadratic model for FAME Yield are summarised in Table 3. The "Model F- value" of 156.21 implies that the model is significant. There is only a 0.01% chance that such a large "Model F-value" will occur due to noise. It is important because the value of "Prob>F" is less than 0.05. In this quadratic mode, A, B, A^2, and B^2 are considered significant model terms since the values are greater than 0.1000; otherwise, the model terms are insignificant. All parameters were shown to impact the purity of FAME yield. The 0.42 for "Lack of Fit F-value" indicated a 74.8% chance that such a high "Lack of Fit F-value" could arise due to noise. Furthermore, as this model fit well, the "not significant" lack of fit is regarded as acceptable. Figure 1 depicts the predicted vs actual response for FAME yield (%). The estimated R^2 for FAME yield is 0.9743, which is very near the R^2_{adj} value of 0.9848. The statistical parameter "adequate precision" determines the signal-to-noise ratio, with a precision greater than four being preferred. In this study, adequate precision for responses above the previously mentioned limit indicates a good signal and is suitable for navigating design space.

The optimised condition for in-situ esterification of SBE samples designed by the Design Expert was 160 min with a 5% of DES/Methanol ratio (vol %). The actual FAME yield is close to the predicted value (96.13%), which was considered good. In this study, under various reaction time conditions and DES/methanol ratio (vol %), in-situ esterification of SBEW in the presence of DES yielded a minimum of 47.05% and a maximum of 97.56% FAME yield.

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Table 3: Analysis of variance (ANOVA) for response surface quadratic model for FAME yield

Source	Sum of squares	df	Mean Squares	F value	p-value Prob> F	
Model	2386.07	5	477.21	156.21	<0.0001	significant
A	115.11	1	115.11	37.68	0.0005	
B	106.16	1	106.16	34.75	0.0006	
AB	1771.15	1	1771.15	579.96	<0.0001	
A^2	311.61	1	311.61	102.00	<0.0001	
B^2	127.31	1	127.31	41.67	0.0003	
Residual	21.38	7	3.05			
Lack of fit	5.14	3	1.71	0.42	0.7480	Not Significant
Pure Error	16.25	4	4.06			
Cor Total	2407.46	12				
$R^2 = 0.9911$						
Adjusted R^2= 0.9848						
Predicted R^2=0.9743						
Adequate precision= 41.831						

Comparative study

The effectiveness of the DES was evaluated and compared to the research made in this study with and without DES and in research conducted by Suryani et al. [7]. This demonstrates that DES increases the biodiesel yield and can meet ASTM and EN standards requirements. The properties of produced biodiesel are summarised in Table 4.

Table 4: Physiochemical properties for Biodiesel yield from SBEW oil and standard biodiesel properties of EN14214 and ASTM D6751

Specification	This study With DES	This study Without DES	Suryani et al. [7] Without DES	Biodiesel Standard	
				EN 14214	ASTM D6751
Yield (%)	97.56	-	84.5	-	-
Density at 25 ^{O}C (g/cm^3)	0.89	0.91	0.855	0.86-0.90	-
Kinematic viscosity at 40 ^{O}C (mm^2/s)	4.1	5.78	5.9	3.5-5.0	1.9-6.9
Acid value (mg KOH/g)	0.31	5.65	0.71	0.5 max	0.5 max

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Characterisation of SBE oil

The extracted SBEW oil via hexane extraction has a transparent light-yellow colour with no suspended solids. From the preliminary study, it manages to recover about 20.3% (±1.6) residual oil. The physicochemical properties showed that the moisture content of SBEW oil was 3.7 wt% (±0.1), the density was 0.89 kg/m^3, the viscosity at 40 °C was 48.64 cSt, and the FFA was found to be 13.93(%).

CONCLUSION

In this study, biodiesel was prepared from SBEW oil through in situ esterification with methanol and deep eutectic solvent (DES) catalyst using response surface methodology (RSM). The findings showed that the optimum conditions were at 160 min with a 5% DES to methanol volume ratio at 65 °C. The analysis showed a quadratic model to predict the crude and FAME yield (%). Validation experiments also have evaluated the availabilities and accuracy of the model. The results show that the expected value corresponds to the experimental value of 97.57% higher FAME yield. The biodiesel physiochemical properties were compared to those from American Standard for Testing Materials (ASTM) and European standards (EN). The physicochemical properties of biodiesel are produced to meet the acceptable range of measurement as the standards.

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AUTHOR'S CONTRIBUTION

Nur Syazlinda and Izzati conducted the research and wrote and revised the article. Asnida Yanti and Muhammad Luqman conceptualised the central research idea and provided the theoretical framework. Asnida and Mohd Azlan designed and supervised the research progress; Asnida anchored the review and revisions and approved the article submission.

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CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted without any self-benefits or commercial or financial conflicts and declare the absence of conflicting interests with the funders.

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