TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC QUY NHƠN

Tối ưu hóa quá trình tổng hợp biodiesel từ dầu ăn thải trên nền xúc tác tái tạo từ quá trình nhiệt phân vỏ trứng: Một nghiên cứu dựa trên phần mềm Minitab

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TÓM TẮT

Sản xuất biodiesel đã thu hút được sự chú ý đáng kể như một phương án thay thế cho các loại nhiên liệu hóa thạch truyền thống. Một lĩnh vực nghiên cứu triển vọng liên quan đến việc sử dụng các chất xúc tác tái tạo. Trong nghiên cứu này, chúng tôi đã tổng hợp chất xúc tác bazơ dị thể được lấy từ vỏ trứng bằng cách nung vỏ trứng thô ở nhiệt độ khoảng 800°C trong 6 giờ. Các đặc trưng của vật liệu được xác định dựa trên phổ XRD, ảnh SEM và phổ EDX. Phương pháp bề mặt phản ứng (RSM) được sử dụng để thiết kế thực nghiệm và tối ưu kết quả thực nghiệm dựa trên phần mềm Minitab (phiên bản 18). Dựa trên phương pháp bề mặt phản ứng, phương trình hồi quy được thiết lập để mô tả mối quan hệ giữa điều kiện thực nghiệm và hàm lượng ester trong biodiesel, với hệ số tương quan cao (R^2 = 0.956). Kết quả nghiên cứu này chứng tỏ rằng chất xúc tác từ vỏ trứng là một loại xúc tác tái tạo, thân thiện với môi trường và hoàn toàn thay thế được cho các chất xúc tác truyền thống. Phương pháp RSM dựa trên phần mềm Minitab có thể giúp tăng cường trong việc thiết kế thực nghiệm và tối ưu kết quả thực nghiệm.

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Optimization of the biodiesel synthesis of used cooking oil using calcined eggshell as a renewable catalyst: A study using Minitab software

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ABSTRACT

The production of biodiesel has attracted significant attention as an alternative to traditional fossil fuels. One promising research area is related to the use of renewable catalysts. In this study, we synthesized eggshell-based heterogeneous base catalysts by calcining raw eggshells at approximately 800°C for 6 hours. The characteristics of the material were determined based on XRD spectra, SEM images, and EDX spectra. The response surface methodology (RSM) was used to design experiments and optimize experimental results using Minitab software (version 18). Based on the response surface methodology, a regression equation was established to describe the relationship between experimental conditions and the amount of ester in biodiesel, with a high correlation coefficient (R^2 = 0.956). The results of this study demonstrate that eggshell-based catalysts are renewable, environmentally friendly catalysts that can fully replace traditional catalysts. The RSM method based on Minitab software can enhance experimental design and optimize experimental results.

Keywords: *Biodiesel, Used cooking oil, eggshell, transesterification, RSM.*

1. INTRODUCTION

Biodiesel is generally defined as fatty acid alkyl esters produced from alternative resources through esterification, transesterification, or two-step reactions. It can be used directly or blended with petroleum diesel due to its acceptable properties. Traditionally, cooking oils have been the main resources for biodiesel production due to their low FFA content. However, relying on edible vegetable oils is a major disadvantage for commercial purposes due to their high price and potential impact on food security. As a result, non-edible oils such as waste cooking oil, Jatropha oil, and used cooking oils (UCO) have become increasingly attractive as renewable resources for biodiesel production at a lower cost.[1,2]

In this study, methyl ester was produced through the transesterification of UCO using calcined eggshell as a heterogeneous base catalyst. The objectives of this study were to: (a) investigate the production of a renewable catalyst through eggshell calcination; (b) assess the effect of MeOH/UCO molar ratio, catalyst/UCO catalyst content, and reaction temperature on the ester content in biodiesel; and (c) use response surface methodology (RSM) to design, analyze, and optimize experimental conditions.

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2. MATERIALS AND METHODS

2.1. Materials

The study collected used cooking oil (UCO) and chicken/duck eggshells from various restaurants located in Quy Nhon City, Vietnam. The necessary chemicals, such as methanol (MeOH, purity > 99 wt.%), ethanol (EtOH, purity > 96 wt.%), and sulfuric acid (H_2SO_4, purity > 98 wt.%) provided by Binh Dinh Chemical and Scientific Equipment Co. Ltd. in Vietnam, are commonly used in this work.

2.2. Catalyst preparation

To prepare the eggshells for use, they were carefully separated from their membranes and thoroughly cleaned by rinsing with tap water three times. The cleaned eggshells were then dried in a hot air oven at 60 ^oC for 12 hours.[3]

Once dry, they were ground into a fine powder using a blender and then sieved to ensure a consistent size of 0.045 mm using a burger sieve. The resulting eggshell powder was then calcined in a muffle furnace at 800 ^oC for 6 hours to create the desired catalyst. The calcined eggshells were then stored in a desiccator to prevent any reaction with moisture or CO_2 in the air, which could be harmful to the catalyst's active site.[3,4] This careful storage was necessary to ensure the calcined eggshells remained free of unwanted particles and ready for use.

2.3. Characterization results of the catalysts

The calcined catalysts were characterized using XRD, SEM and EDX. XRD characterization was used for the phase identification; it was operated using Copper K-alpha (Cu Kα) radiation with 2θ in the range between 20^o and 80^o at a scan rate of 2^o /min.[4] SEM characterization was carried out at 10,000 times magnification under 5 kV electrical potential; it was utilized for the morphological studies.[5] EDX analysis is used in conjunction with SEM to characterize the elemental composition of the analyzed volume. SEM and EDX analyses were conducted at Institute of Materials Science, Vietnamese Academy of Science and Technology, Vietnam, while XRD analysis was performed at University of Science and Technology, The University of Danang, Vietnam.

2.4. Transesterification reaction procedure and phase separation

In order to produce biodiesel from used cooking oil (UCO), a transesterification reaction was conducted using methanol and a heterogeneous catalyst made from calcined eggshells. The reaction took place in a 0.5 L three-necked flask with magnetic stirring at a speed of 600 rpm, under atmospheric pressure and with water reflux at 20 ^oC to condense the methanol vapor.[6]

Prior to carrying out the transesterification reaction, UCO was decanted to remove impurities and dried at 110 ^oC within 2 hours. And then, the feedstock oil was preheated to the desired temperature and then the methanol-catalyst mixture was added. The start time for the reaction was recorded once all the methanol and catalyst had entered the reactor. After the reaction was complete, the product was transferred to a separatory funnel and allowed to settle for 60 minutes to separate into two phases: methyl ester and glycerol. The glycerol phase was removed, and the methyl ester phase was washed three times with hot water at 70 ^oC without stirring and three times with stirring. The washed methyl esters were then dried for 90 minutes at 110 ^oC. Finally, the resulting biodiesel was weighed to determine the methyl ester content.[6,7]

All experimental runs were conducted three times to minimize errors. The reaction time was set up at 40 min for all runs.[6] Some different reaction conditions were tested, such as methanol/WCO molar ratio (4.0 – 8.0), catalyst content (0.5 - 1.5 wt.%), and reaction temperature (45 - 65 ^oC).

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Table 1. Experimental parameters used in transesterification of UCO.

Factors			Range and coded level		
Name of factor	Symbol	Dimension	-1	0	+1
MeOH/UCO molar ratio	X_1	mol/mol	4	6	8
Catalyst content	X_2	wt.%	0.5	1.0	1.5
Reaction temperature	X_3	°C	45	55	65

2.5. Approximate analysis of ester content

To determine the ester content of biodiesel, the Thailand Patty Patent No. 5060 was used. This method involves using microwave radiation to determine total glycerides content in biodiesel through transesterification. Residue glycerides react with methanol and potassium methoxide to produce methyl esters and glycerol. The glycerol amount can be determined using a correlation curve, and the total glycerides content can be converted into ester content by subtracting it from 100 wt.%.[8]

2.6. Experiment designs

Response surface methodology (RSM) is a statistical technique that is commonly used to study the behavior of a response variable [6,7]. In this study, the Minitab software (version 18) was used to design and optimize the experimental results.

To determine the best conditions for the ester formation, the Box-Behnken design (BBD) was applied. This design combines three levels (-1, 0, +1) for each parameter, as shown in Table 1. Fisher's test (F-value), probability (P-value), correlation coefficient (R), and coefficient of determination (R^2) were used to predict the response of the transesterification process. Diagnostic plots, such as standardized residual and run number plots, expected normal value and residual plots, studentized residuals and predicted values plots, and predicted values and real values plots were also used to evaluate the model.

The second order polynomial regression model equation is typically expressed as Eq. (3).

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j + \sum_{i=1}^{3} \beta_{ii} X_i^2 \quad (3)$$

Herein, Y is the predicted response (ester content); β_o, β_i, β_{ii}, β_{ij} are the regression coefficients (β_o is the constant term, β_i is a linear term, β_{ii} is a quadratic term and β_{ij} is an interaction term); X_i, X_j are coded independent factors.

Table 2. The coded independent factors, experimental results and predicted values from RSM.

Run	Independent Factors			Ester content (%)		
	X_1	X_2	X_3	Experiment	Predict	Residual
1	4	1	65	89.4	90.64	-1.24
2	8	0.5	55	91.58	92.69	-1.11
3	8	1	45	96.49	95.25	1.24
4	6	0.5	65	92.4	91.25	1.15
5	4	1	45	88.32	88.28	0.04
6	6	0.5	45	91.58	91.71	-0.13
7	6	1.5	65	97.31	97.18	0.13
8	6	1.5	45	95.49	96.64	-1.15
9	8	1.5	55	96.13	96.22	-0.09
10	4	0.5	55	86.22	86.13	0.09
11	8	1	65	92.94	92.98	-0.04
12	4	1.5	55	94.58	93.47	1.11
13	6	1	55	84.85	84.75	0.10
14	6	1	55	85.04	84.75	0.29
15	6	1	55	82.95	84.75	-1.80
16	6	1	55	86.17	84.75	1.42

Table 3. ANOVA results for the adjusted regression model.

Source/Term	Degree of freedom (DF)	Coefficient	Sum of squares (SS)	Mean squares (MS)	F-value	P-value	Remarks
Model	9		314.83	34.98	15.45	0.0017	Significant
β_o	1	229.75				0.00019	Significant
Linear	3						
X_1	1	-2.152				0.522	Insignificant
X_2	1	-30.73				0.03394	Significant
X_3	1	4.707				0.00167	Significant

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X_3	1	-4.707				0.00167	Significant
Square	3						
X_1^2	1	0.621				0.01638	Significant
X_2^2	1	19.57				0.000631	Significant
X_3^2	1	0.04551				0.000924	Significant
Interaction	3						
X_1X_2	1	-0.952				0.252	Insignificant
X_1X_3	1	-0.05788				0.175	Insignificant
X_2X_3	1	0.05000				0.751	Insignificant
Residual	6		13.59	2.264			
Lack of fit (LOF)	3		8.235	2.745	1.5391	0.366	Insignificant
Pure error	3		5.350	1.783			
Total	15		328.42				
R^2: 0.959; adjusted R^2: 0.897; R^2 for prediction: 0.570							

**P-value < 0.05: statistically significant at the confident level of 95%*

3. RESULTS AND DISCUSSION

3.1. Conversion of eggshell into potential catalyst

3.1.1. XRD pattern of calcined eggshell

In order to identify the components and crystallinity of calcined eggshell, XRD analysis was conducted. As depicted in Figure 1, a peak at 2θ values around 34° for calcium oxide only appeared after the eggshells were calcined at 800 °C for 6 hours in a muffle furnace. This was likely due to the high thermal transition that occurred in the eggshells, causing complete decomposition of the calcium carbonate into calcium oxide at 800 °C. This result can be seen in a work by MD. Putra et al.[8] Additionally, a small peak for calcium hydroxide was observed, which can be explained by the hygroscopic nature of calcium oxide. It is noteworthy that both CaO and $Ca(OH)_2$ are alkaline and have the potential to be used as catalysts for biodiesel synthesis.

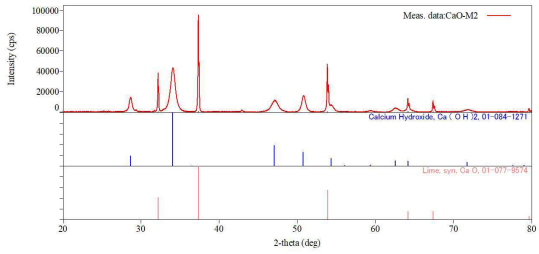

Figure 1. XRD pattern of calcined eggshell in a muffle furnace under 800 °C for 6 hours.

3.1.2. SEM characterization of calcined eggshell

The SEM image of the CaO catalyst obtained from the calcination-hydration-dehydration treatment of eggshells is presented in Figure 2. The image reveals a honeycomb-like porous surface and a regular micro morphology of

rod-like particles with a size of about 50 - 100 µm. This finding is consistent with a similar study conducted by S. Niju et al.[9]

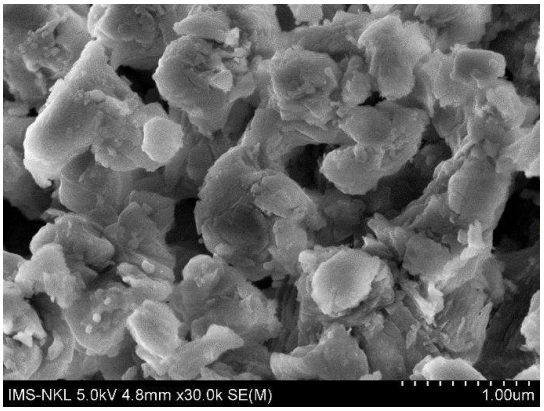

Figure 2. SEM image of calcined eggshell in a muffle furnace under 800 °C for 6 hours.

3.1.3. EDX characterization of calcined eggshell

The EDX pattern of the CaO catalyst obtained from the calcination of eggshells is shown in Figure 3. The results indicate that the EDX analysis conformed the presence of Ca, Mg and O in the sample of calcined eggshell. The main atomic components of calcined eggshells are Ca, and O, which are well-suited for serving as a potential heterogeneous base catalyst in the biodiesel synthesis process (Table 4).

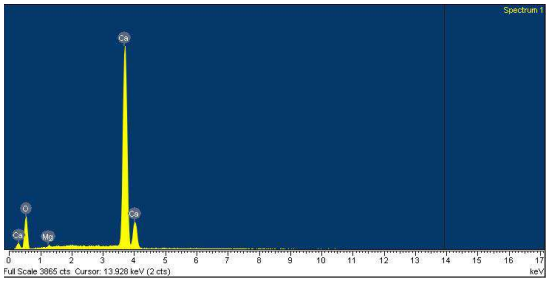

Figure 3. EDX pattern of calcined eggshell in a muffle furnace under 800 °C for 6 hours.

Table 4. The main atomic components of calcined eggshell.

Element	Weight, wt%	Atomic, %
O	53.93	74.48
Mg	0.35	0.32
Ca	45.71	25.20

from the calcination-hydration-dehydration treatment of eggshells is presented in Figure 2. The image reveals a honeycomb-like porous surface and a regular micro morphology of rod-

3.2. Regression model and statistical analysis for the ester content in biodiesel

Table 2 presents both the experimental and predicted results for the methyl ester content in biodiesel. To analyze the obtained data, the full factorial BBD approach of RSM was utilized, and the resulting data was fitted to Eq. (3). The best-fit model was determined to be described by Eq. (4):

$$Ester\ content\ (\%) = 229.75 - 30.73X_2 - 4.707\ _3 + 0.62\quad _1^2 + 19.57X_2^2 + 0.04551X_3^2 \quad (4)$$

In which, X_2 and X_3 are coded independent factors of catalyst content and reaction temperature, respectively, X_1^2, X_2^2, X_3^2 are code square factors of MeOH/UCO molar ratio, catalyst content and reaction temperature, respectively.

The results of the ANOVA for the adapted regression model are presented in Table 3. The adequacy of the designed model was assessed based on the F-value, P-value, R^2, and lack of fit (LOF). The F-value and P-value at 95% confidence level were 15.45 and 0.0017, respectively. The correlation coefficient (R^2) indicated that 95.9% of the variation in ester content was explained by the independent variables listed in Table 1, with only 4.1% attributed to random errors. Furthermore, the LOF was not significant (0.366 > 0.05), suggesting that the model was adequate for predicting the ester content in biodiesel.

Additionally, Table 4 shows that each term in the regression model was evaluated to determine its significance and its interrelation to the ester content in biodiesel. A P-value less than 0.05 indicated that the term was significant. After removing insignificant terms, the linear term of catalyst content (X_2) and reaction temperature (X_3), as well as the square terms of MeOH/UCO molar ratio (X_1^2), catalyst content (X_2^2), and reaction temperature (X_3^2) were found to be significant in Eq. (4).

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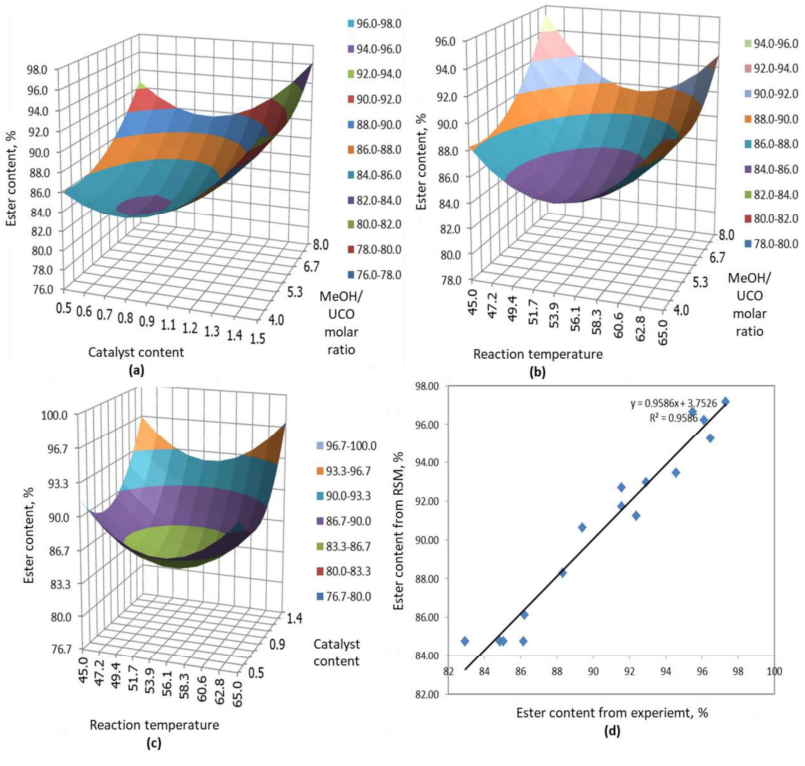

Figure 4. Interaction effects of the factors on ester content in biodiesel: (a) molar ratio and catalyst content, (b) molar ratio and reaction temperature; (c) catalyst content and reaction temperature; (d) predicted values and actual values plot.

3.3. Interaction effects of the factors on the ester content in biodiesel

The influence of interaction factors on the ester content in biodiesel was depicted in Figures 4a-4c. The contour slope indicated the degree of interaction's effect on the ester content in biodiesel, with a higher slope indicating a greater effect. The contour slope for catalyst content was higher than that for molar ratio (Figure 4a), indicating the significant effect of catalyst content in the range of 0.7 - 1.5 wt.%. The slopes of the catalyst content were higher than those of the molar ratio (Figure 4a) and reaction temperature (Figure 4c). These findings demonstrate the significance of calcined eggshell as a renewable catalyst in the transesterification reaction. The catalyst plays a crucial role in methyl ester formation, as shown in the coefficients of Eq. (4). Therefore, increasing the catalyst content accelerates the conversion of UCO to methyl esters (biodiesel). These results are consistent with previous studies.[6,10]

The predicted values were compared against real benefits and shown in Figure 4d, exhibiting linear behavior and being close to the diagonal line. As a result, the obtained model is suitable for predicting the ester content via transesterification reaction.

3.4. Optimization of variables for the ester content in biodiesel

The main objective of this study was to maximize the production of methyl ester in biodiesel. The experimental results showed that the ester content in biodiesel varied between 82% and 97%. To achieve a target ester content of 97%, the optimization was carried out using RSM. The optimal parameters were determined to be a MeOH/UCO molar ratio of 8 mol/mol, catalyst/ UCO catalyst content of 1.5 wt.%, and a reaction temperature of 52 ^{o}C. This ester content of 97% ensured that the reaction takes place completely as per the standard EN 14214.[12]

4. CONCLUSIONS

In this study, the synthesis of biodiesel using calcined eggshell as a heterogeneous base catalyst was investigated. The following conclusions were drawn:

- The eggshell pyrolysis process was successful in producing the synthesized catalysts, which were characterized using XRD, SEM, and EDX spectra.

- A model was proposed to predict the influence of variables on the ester content in biodiesel, which showed good agreement with a high correlation coefficient ($R^2 = 0.956$).

- Ester content of 97% was obtained in the experimental conditions including: MeOH/UCO molar ratio of 8 mol/mol, catalyst/UCO catalyst content of 1.5 wt.%, and a reaction temperature of 52 ^oC.

- The effects of experimental variables on acid-catalyzed esterification were explored and optimized using RSM, including the MeOH/UCO molar ratio, catalyst content, temperature, and reaction time. The results showed that catalyst content was the most significant factor in the predicted model.

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