

OPTIMIZATION OF Pd-B/ γ -Al₂O₃ CATALYST PREPARATION FOR PALM OIL HYDROGENATION BY RESPONSE SURFACE METHODOLOGY (RSM)

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Abstract - Response surface methodology was used to design and evaluate the experimental variables for Pd-B/ γ -Al₂O₃ catalyst preparation. The catalyst was prepared by impregnation and chemical reduction. Thirteen different samples of the catalyst were prepared at different KOH concentrations and annealed at various temperatures, before applying them in palm oil hydrogenation. Hydrogenation was performed on a 0.12% Pd-B/ γ -Al₂O₃ catalyst at a temperature of 393 K, hydrogen pressure of 500 kPa and agitation of 500 rpm for 1 h. The iodine value (IV) and trans fatty acids (TFAs) content responses were measured for each hydrogenated palm oil sample. The predicted models were verified for both responses and found to be statistically adequate. An optimization study was performed on the catalyst preparation variables for minimizing both IV and TFAs content. The Pd-B/ γ -Al₂O₃ prepared under optimized conditions exhibited 47% higher conversion and 22% lower trans-isomerization selectivity than Escat 1241 commercial catalyst. The Pd-B/ γ -Al₂O₃ catalyst preparation variables have a noticeable effect on palm oil hydrogenation conversion and trans-isomerization selectivity.

Keywords: Iodine value; Trans fatty acids content; Quadratic model; Hydrogenation.

INTRODUCTION

Vegetable oil hydrogenation involves full or partial oil saturation to improve the oil's oxidation stability and thermal properties (Piqueras *et al.*, 2008; Schaaf and Greven, 2010). It increases the shelf life of shortening, margarine and baking fats (Karabulut *et al.*, 2003).

The properties of hydrogenated oils are influenced by different parameters, including temperature, hydrogen pressure, agitation and catalyst type and

concentration. Among those variables, the catalyst type has been considered the most important factor (Deliy *et al.*, 2009). Conventional hydrogenation is carried out in a stirred reactor at 423 - 498 K and 69 - 413 kPa using a nickel catalyst (Fernandez *et al.*, 2009).

Palladium (Pd) catalysts have been reported to be effective in hydrogenation due to their low toxicity, ability to work under moderate conditions and also because their performance can be altered by combination with other materials (Kielhorna *et al.*, 2002; Polshettiwara *et al.*, 2009). For example, the modifi-

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cation of a monometallic palladium catalyst using a small quantity of other metals can change its attributes (Belkacemi *et al.*, 2007).

However, the application of chemically reduced supported PdO in the field of hydrocarbon hydrogenation has been rarely reported (Yu *et al.*, 2000; Xiong *et al.*, 2007).

The iodine value (IV) is an important property of vegetable oils, indicating the degree of unsaturation of the oil. In the field of oil hydrogenation, it is used for monitoring catalyst activity and measuring hydrogenation conversion (Tonetto *et al.*, 2009; McArdle *et al.*, 2011). The IV decreases during hydrogenation as a result of C = C saturation (Fernandez *et al.*, 2005). The rate of IV decline during hydrogenation is related to the nature of the oil, operating conditions and catalyst type and concentration (Schaaf and Greven, 2010).

The trans fatty acids (TFAs) formed during vegetable oil hydrogenation have been found to be harmful to human health (Oluba *et al.*, 2008). The TFAs content is strongly correlated with the extent of hydrogenation and the reaction conditions, but it can be minimized by process modification and catalyst development (Beers 2007; Singh *et al.*, 2009).

Response surface methodology (RSM) is a helpful method for statistically designing experiments and identifying the relation between different variables affecting a process. It reduces the number of runs and the time required for model-building and statistical analysis (Wu *et al.*, 2010). This technique can be used to predict oil hydrogenation responses, such as IV (Andrade *et al.*, 1998).

This study aimed to statistically analyze and optimize the Pd-B/ γ -Al₂O₃ catalyst preparation variables for the partial hydrogenation of palm oil using RSM.

MATERIALS AND METHODS

Materials

Alumina, γ -Al₂O₃ (Alfa Aesar, Ward Hill, USA) was used as a support and Pd(acac)₂ (palladium (II) acetylacetonate) (Johnson Matthey, Pasadena, USA) was used as a Pd precursor. The chemical reduction of the Pd/ γ -Al₂O₃ catalyst was performed using a 0.2 M aqueous solution of KBH₄ (Acros Organics, New

Jersey, USA). Escat 1241 commercial Pd/ γ -Al₂O₃ catalyst (BASF, Heerenveen, NL) was used as a reference catalyst. Palm oil used for catalyst testing was provided by the Yemen Company for Ghee and Soap Industry (YCGSI, Taiz, Yemen).

Methods

Design of Experiments (DOE)

Response surface methodology was used to design the layout for the catalyst preparation experiments and analyze the results. The purpose of this study was to investigate the influence of the catalyst preparation variables on the responses. A central composite design (CCD) with two variables was used to study the effect of the variables on the IV and TFAs content of hydrogenated palm oil. The independent variables include the KBH₄ solution alkalinity (KOH concentration) and catalyst annealing temperature. These two variables were coded at three levels corresponding to the minimum, target and maximum values of each variable, as shown in Table 1. The limits of each variable were deduced from previous work for the development of similar catalysts (Kuo, 1997; Xiong *et al.*, 2007).

The coded values were designated by -1, 0, +1, $-\alpha$ and $+\alpha$. Alpha is defined as a distance from the center point and has a maximum value of $2^{n/4}$, where n is the number of variables (Vicente *et al.*, 2007). Accordingly, the value of α in this study was 1.41421.

Catalyst Preparation

Pd-B/ γ -Al₂O₃ catalyst samples were prepared by wet impregnation and chemical reduction. The γ -Al₂O₃ was impregnated using a toluene solution of Pd (Acac)₂ via a method similar to that used by Tonetto *et al.* (2009). Prior to the chemical reduction, the Pd/ γ -Al₂O₃ was calcined at 773 K for 2 h in air. Pd-B/ γ -Al₂O₃ catalyst samples were prepared by chemical reduction of the PdO (Pd/ γ -Al₂O₃) using aqueous KBH₄ solutions of different KOH concentrations (based on the DOE). The KBH₄/Pd²⁺ molar ratio was equal to 3 for all samples to achieve the full reduction of PdO (Xiong *et al.*, 2007). Annealing was performed for each Pd-B/ γ -Al₂O₃ catalyst sample at the required temperature (based on the DOE) for 2 h.

Table 1: Actual and coded values of the experimental variables.

Independent Variable	Unit	Symbol	Coded Levels				
			$-\alpha$	-1	0	+1	$+\alpha$
KOH concentration	M	A	0.03	0.20	0.60	1.0	1.17
Annealing temperature	K	B	269	373	623	873	977

Catalyst Characterization

Characterization was performed for the optimized Pd-B/ γ -Al₂O₃ catalyst including the Brunauer-Emmett-Teller surface area (BET) using an ASAP 2020 (Micromeritics, Norcross, USA). The structure of the catalyst was characterized by X-ray powder diffraction (XRD) using a D8-Advance with Cu K α radiation (Bruker, Massachusetts, USA). The surface morphology was observed by scanning electron microscopy (SEM) using a 1450 VP (LEO, UK). This technology also included energy-dispersive X-ray spectroscopy (EDX) which was applied for the catalyst metals content scanning. Transmission electron microscopy (TEM) was performed for particle size measurement using a CM12 transmission electron microscope (Philips, Eindhoven, NL).

Catalyst Testing

The hydrogenation tests for the catalyst sample were performed in a 400 ml batch reactor equipped with temperature, pressure and agitation controllers. The batch consisted of 250 g of fully refined palm oil. For each run, and prior to hydrogen injection, the reactor was flushed with nitrogen gas to remove the air and dissolved oxygen (Pakdehi *et al.*, 2010). Hydrogenation was performed on the 0.12% Pd-B/ γ -Al₂O₃ catalyst at a temperature of 393 K, hydrogen pressure of 500 kPa and agitation of 500 rpm for 1h.

Analytical and Calculation Methods

The analyses of the composition of the fatty acids, TFAs content and IV were performed using the relevant American Oil Chemists' Society test methods (AOCS, 2011). The AOCS ce1b-89 method was used to determine the fatty acid composition and ca 5a-40 to determine the TFAs of the unhydro-

genated and hydrogenated samples via gas chromatography (GC). The AOCS Cd 1-25 test method was used to determine the IV.

The C = C hydrogenation conversion was calculated using the following equation, which has been used elsewhere in the literature (Tonetto *et al.*, 2009):

$$C = C \text{ conversion (\%)} = [(IV_o - IV_f) / IV_o] \quad (1)$$

where IV_o is the initial IV for palm oil (before hydrogenation) and IV_f is the corresponding IV of the hydrogenated palm oil.

Trans-isomerization selectivity (S_i) as a measure of the catalyst's tendency to form the TFAs was calculated by the following equation of Lausche *et al.* (2012):

$$S_i = \Delta(\% \text{ trans fats}) / \Delta(\% \text{ conversion}) \quad (2)$$

The catalyst activity was measured as a reduction in iodine value per minute per concentration of Pd (ppm) in palm oil by following the method previously used by Koritala *et al.* (1985).

RESULTS AND DISCUSSION

The experimental design layout applied by CCD and the response results are provided in Table 2. A total of 13 experiments were performed including four factorial points, four axial points and six replications at the center values (zero level) to evaluate the pure error.

The statistical analysis was performed by ANOVA using a quadratic model and the results are presented in Table 3. The results describe the significance and fitness of the two responses prediction models. These results also indicate the effect of the significant terms of the independent variables and their interactions on the responses.

Table 2: Experimental design results for iodine value and trans fatty acids content.

Std. Order	Run Order	Actual Values		Coded Values		Response 1 IV (g iodine/100 g oil)	Response 2 TFAs (wt. %)
		A	B	A	B		
1	7	0.2	373	-1	-1	46.31	6.10
2	3	1	373	+1	-1	48.00	8.70
3	12	0.2	873	-1	+1	46.10	8.60
4	9	1	873	+1	+1	48.00	5.10
5	11	0.03	623	- α	0	46.91	6.20
6	8	1.17	623	+ α	0	49.10	5.70
7	6	0.6	269	0	- α	46.20	8.70
8	10	0.6	977	0	+ α	46.11	8.30
9	5	0.6	623	0	0	45.90	9.20
10	4	0.6	623	0	0	45.40	9.90
11	1	0.6	623	0	0	45.30	9.40
12	13	0.6	623	0	0	46.10	8.70
13	2	0.6	623	0	0	46.00	9.30

Table 3: Statistical analysis of variance for iodine value and trans fatty acids content.

Source	Sum of Squares		DF		Mean Square		F Value		P-value Prob > F	
	IV	TFAs	IV	TFAs	IV	TFAs	IV	TFAs	IV	TFAs
Model	14.66	30.37	5	5	2.93	6.07	36.36	53.12	< 0.0001	< 0.0001
A	5.59	0.32	1	1	5.59	0.32	69.35	2.82	< 0.0001	0.1368
B	0.014	0.35	1	1	0.014	0.35	0.18	3.03	0.6871	0.1251
AB	0.011	9.3	1	1	0.011	9.30	0.14	81.36	0.7224	< 0.0001
A²	9.01	20.1	1	1	9.01	20.10	111.79	175.84	< 0.0001	< 0.0001
B²	0.32	1.26	1	1	0.32	1.26	3.92	10.99	0.0882	0.0129
Residual	0.56	0.8	7	7	0.081	0.11				
Lack of Fit	0.032	0.06	3	3	0.011	0.020	0.081	0.11	0.9670	0.9506
Pure Error	0.53	0.74	4	4	0.13	0.19				
Cor Total	15.22	31.17	12	12						
R-Squared	0.963	0.974	Standard Deviation Mean Coefficient of Variation (CV) % Prediction Error Sum of Squares (PRESS)						0.28	0.34
Adjusted R-Squared	0.936	0.956							46.57	7.919
Predicted R-Squared	0.930	0.949							0.61	4.23
Adequate Precision	17.93	17.67							1.06	1.59

The P-value for both models is less than 0.05, which implies that the models are significant for 95% confidence intervals for the predicted IV and TFAs content.

For IV, the linear term of KOH concentration (A) is significant but that of annealing temperature is not. However, both linear terms for TFAs content are not significant. In addition, the coupling term AB is significant for TFAs only. The quadratic term of KOH concentration is significant for both models, whereas the quadratic term of the catalyst annealing temperature is significant only for TFAs content.

The "Lack of Fit F-value" of both responses implies that the Lack of Fit is not significant relative to the pure error; thus, a nonsignificant "Lack of Fit" is good. The predicted R-squared values are within 0.20 of the adjusted R-squared values for both responses, indicating that both models have sufficient capability to predict the two responses.

Additionally, the accuracy and reliability of the experiments were confirmed by the coefficient of variation (CV), which was 0.61 and 4.23 for IV and TFAs content, respectively. These values were considered nonsignificant values for this study (Akhazarova and Kefarov, 1982).

The adequate precision is much greater than 4 for both models, indicating adequate model discrimination (Zabeti *et al.*, 2009).

The experimental results of the RSM and regression analysis for the coded factors yield the

quadratic polynomial equations (Eqs. (3) and (4)) for predicting the responses (the "P-value > 0.1" terms have been excluded):

$$\text{IV (g iodine / 100 oil)} = 45.74 + 0.84A + 1.14A^2 + 0.21B^2 \quad (3)$$

$$\text{TFAs Content (\%)} = 9.30 - 1.53AB - 1.7A^2 - 0.43B^2 \quad (4)$$

where: A and B are the KOH concentration (M) the catalyst annealing temperature (K) respectively.

Tables 4 and 5 compare the actual responses (IV and TFAs content) with the predicted values obtained from the models. The coefficients of determination (R^2) for IV and TFAs content were 0.962 and 0.974 respectively, which is considered sufficient to identify the correlation between the actual and predicted values (Haaland, 1989).

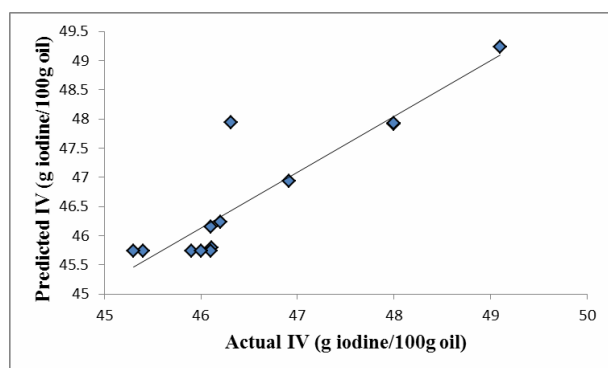
The data in Tables 4 and 5 show that the predicted values are in good agreement with the experimental values for both responses. This result was also confirmed by Figure 1 which graphically shows the correlation between the actual and predicted responses. It indicates that the proposed models could be used to predict the IV and TFAs content within the range of KOH concentrations and annealing temperatures employed in this study.

Table 4: Actual and predicted IV from the quadratic model.

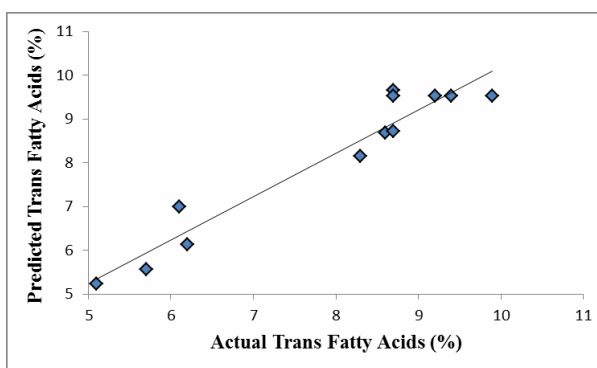
Standard order	Run order	Actual value	Predicted value	Residual
1	7	46.31	46.21	0.1
2	3	48.00	47.93	0.07
3	12	46.10	46.25	-0.15
4	9	48.00	47.93	0.07
5	11	46.91	46.83	0.08
6	8	49.10	48.86	0.24
7	6	46.20	46.16	0.04
8	10	46.11	45.74	0.37
9	5	45.90	45.74	0.16
10	4	45.40	45.74	-0.34
11	1	45.30	45.74	-0.44
12	13	46.10	45.74	0.36
13	2	46.00	45.74	0.26

Table 5: Actual and predicted TFAs content from the quadratic model.

Standard order	Run order	Actual value	Predicted value	Residual
1	7	6.10	5.64	0.46
2	3	8.70	8.70	0
3	12	8.60	8.70	-0.10
4	9	5.10	5.64	-0.54
5	11	6.20	5.91	0.29
6	8	5.70	5.90	-0.20
7	6	8.70	8.44	-0.26
8	10	8.30	8.44	-0.14
9	5	9.20	9.30	-0.10
10	4	9.90	9.30	0.60
11	1	9.40	9.30	0.10
12	13	8.70	9.30	-0.60
13	2	9.30	9.30	0



(a)



(b)

Figure 1: Actual vs. predicted (a) iodine value and (b) trans fatty acids content.

Effect of Catalyst Preparation Variables on the IV and TFAs Content

As shown in Figure 2 (a) and Equation (3), the alkalinity of the KBH₄ solution has a noticeable effect on the catalyst's ability to reduce the IV of palm oil during hydrogenation under the conditions used in this study. The KOH concentration has a linear effect on the IV in the range 0.4 - 1 M KOH, where the IV declined when the KOH concentration decreased. This behavior is likely to be a consequence of the negative effect of this variable on the IV (Zabeti *et al.*, 2009). In contrast, an inverse tendency was observed for concentrations below 0.4 M. This tendency most likely resulted from the positive influence of the quadratic term of KOH concentration on the IV response.

The statistical analysis found no significant effect

of the linear term of the catalyst annealing temperature on the IV. However, the quadratic term of this variable seems to be more significant than the coupling linear term. These results reveal that there is a limited effect of the catalyst annealing temperature on the catalyst activity for double bond hydrogenation within the range used in this study.

As shown in Table 3, the linear terms of KOH concentration and annealing temperature have insignificant effects on the TFAs content of hydrogenated palm oil. However, the coupling linear term is significant, which indicates a positive interaction between the two variables in the catalyst tendency to form the TFAs (Noshadi *et al.*, 2012). Furthermore, the quadratic terms for both variables are significant and have a noticeable effect on the TFAs content. The TFAs content decreased with decreasing KOH concentration and catalyst annealing temperature.

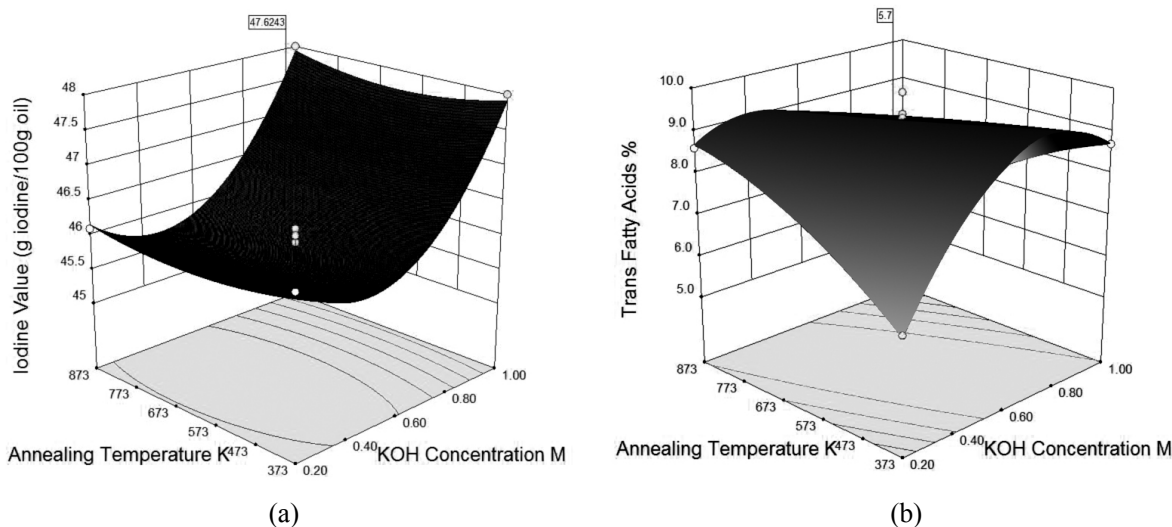


Figure 2: Response surface plot for the studied range of the variables for (a) predicted iodine value and (b) predicted trans fatty acids content.

Optimization of Catalyst Preparation Variables

Response surface methodology (RSM) was also used to determine the optimum conditions for Pd-B/ γ -Al₂O₃ preparation to achieve the best possible response (IV and TFAs content), which indicate the hydrogenation conversion and trans-isomerization selectivity, respectively. Table 6 shows the constraints for the variables and responses. Table 7 summarizes the values for the operating conditions to obtain lower values for both responses. In Table 6, the second of the four solutions was chosen because it had the highest desirability, 64.00%. Thus, the selected operating conditions for Pd-B/ γ -Al₂O₃ catalyst preparation are a KOH concentration of 0.96 M and annealing temperature of 873 K.

The Pd-B/ γ -Al₂O₃ catalyst sample was prepared under optimized conditions and then applied for palm oil hydrogenation. For the purpose of comparison, the Escat 1241 catalyst was also applied for hydrogenation of palm oil under similar conditions to

those mentioned above. The Pd-B/ γ -Al₂O₃ exhibited a 47% higher conversion and around 22% lower tendency to form TFAs than Escat 1241.

The activity of Pd-B/ γ -Al₂O₃ catalyst was compared with that of the Pd modified catalyst reported by Tonetto *et al.* (2009). Pd-B/ γ -Al₂O₃ catalyst activity in palm oil hydrogenation was 7.2×10^{-3} compared to 2×10^{-3} (Δ IV. min^{-1} . ppm^{-1}) for the Pd-Mg/ γ -Al₂O₃ in sunflower oil hydrogenation. The result for Pd-B/ γ -Al₂O₃ catalyst activity in this study is in agreement with those previously reported for the Pd-B/ γ -Al₂O₃ catalyst in the hydrogenation of different hydrocarbons (Ding *et al.*, 2003, Xiong *et al.*, 2007).

The distinctive performance of the Pd-B/ γ -Al₂O₃ catalyst in terms of activity and trans-isomerization selectivity can be attributed to the higher capability of hydrogen adsorption of the Pd-B alloy. The behavior of the boron metalloid as an electron donor gave the Pd-B/ γ -Al₂O₃ catalyst electronic properties different than those of Pd/ γ -Al₂O₃ (Ding *et al.*, 2003, Zou *et al.*, 2007).

Table 6: Constraints of design variables and responses.

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
KOH Concentration	In range	0.2	1.0	1	1	3
Annealing Temperature	In range	373	873	1	1	3
IV	Minimize	45.30	49.10	1	1	3
TFAs Content	Minimize	5.10	9.90	1	1	3

Table 7: Selected values obtained from response surface methodology.

No.	KOH Concentration M	Annealing Temperature K	IV (g iodine/100 g oil)	TFAs (wt. %)	Desirability
1	0.95	873	47.59	5.80	0.641
2	0.96	873	47.62	5.70	0.640
3	0.95	873	47.56	5.90	0.640
4	0.20	673	46.04	7.80	0.550

Characterization of the Optimized Pd-B/ γ -Al₂O₃ Catalyst

Characterization was performed for the Pd-B/ γ -Al₂O₃ catalyst sample prepared under optimized conditions. The BET surface area was found to be 135 m²/g, which was noticeably lower than the corresponding surface area of the alumina support. This decrease in the surface area can be attributed to the deposition of palladium and boron on the alumina support. The pore diameter of Pd-B/ γ -Al₂O₃ was found to be 7.4 nm. This diameter is considered suitable for oil hydrogenation according to the Coenen classification, because the triglyceride molecule can enter and exit a slot of the pore easily (Coenen 1976).

Figure 3 shows the XRD patterns of the optimized Pd-B/ γ -Al₂O₃. The diffraction peaks at $2\theta = 37^\circ$, 45.8° and 67.3° represent alumina (Gao *et al.*, 2008; Chen *et al.*, 2010), whereas, the peak at $2\theta = 33.8^\circ$ indicates the Pd₂B alloy. This alloy was a result of the chemical reduction of Pd/ γ -Al₂O₃ by KBH₄. It had a crystalline structure formed as a result of annealing at high temperature (Ma *et al.*, 2010).

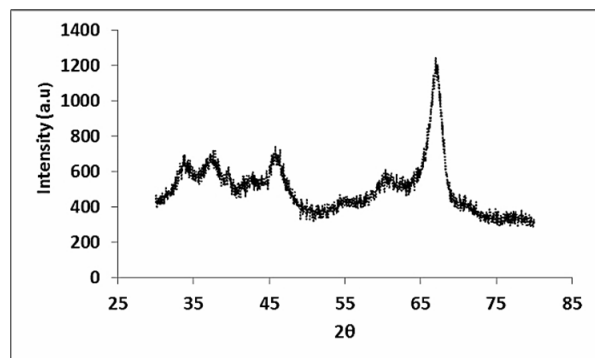
**Figure 3:** XRD diffraction pattern of Pd-B/ γ -Al₂O₃.

Figure 4 shows the surface morphology of Pd-B/ γ -Al₂O₃. It exhibited large cracked blocks at the surface, indicating a high degree of crystallization, which was attributed to the thermal treatment performed at 873 K.

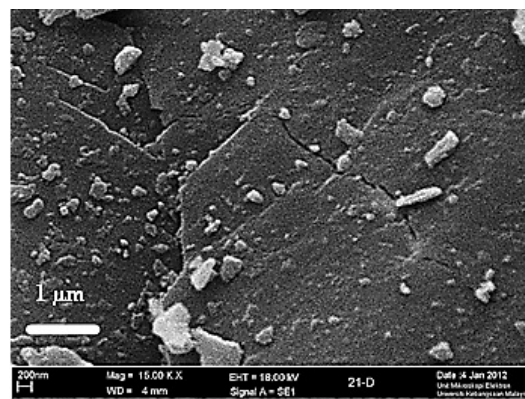
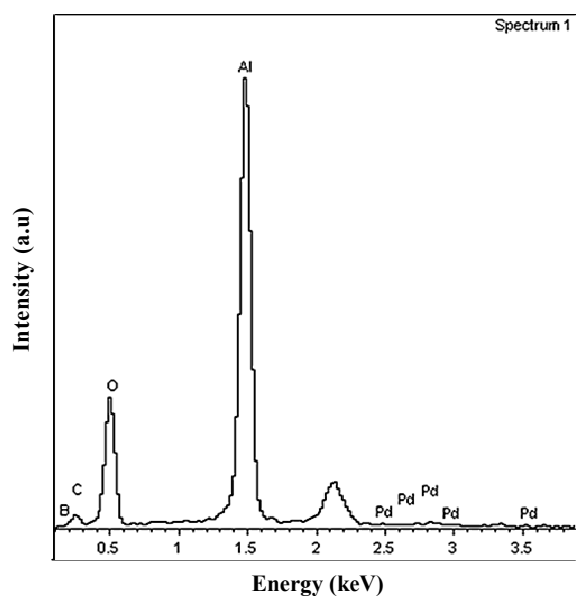
**Figure 4:** SEM images of Pd-B/ γ -Al₂O₃ prepared under the optimized condition.

Figure 5 depicts the EDX spectrum of Pd-B/ γ -Al₂O₃, which confirms the composition of the catalyst sample (Pd and B) and the support elements (Al and O₂). The average content of palladium and boron was 0.73% and 0.075% respectively.

**Figure 5:** Typical EDX spectrum of the Pd-B/ γ -Al₂O₃ catalysts.

The TEM image shown in Figure 6 depicts the optimized Pd-B/ γ -Al₂O₃. It reveals an average particle size of 8.2 nm. It is considered that this size is larger than that of the corresponding Pd/ γ -Al₂O₃ as a result of chemical reduction and thermal treatment (Alshaibani *et al.*, 2012).

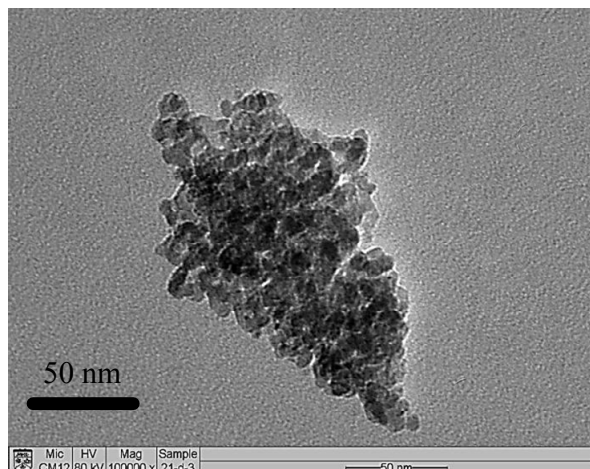


Figure 6: TEM image of the Pd-B/ γ -Al₂O₃ catalysts prepared under the optimized condition.

CONCLUSION

Models of iodine value and trans fatty acids prediction for palm oil hydrogenation were designed using response surface methodology. The models were evaluated and found to have sufficient capability to predict both responses under the condition of this study. The alkalinity of the Pd/ γ -Al₂O₃ catalyst reduction solution had a noticeable effect on the Pd-B/ γ -Al₂O₃ catalyst behavior, resulting in higher conversion and lower trans-isomerization selectivity during palm oil hydrogenation. Annealing temperature had a limited effect on the palm oil hydrogenation conversion, whereas an increase in the catalyst annealing temperature noticeably increased the catalyst's tendency to form TFAs. The Pd-B/ γ -Al₂O₃ catalyst prepared under optimized conditions exhibited higher conversion and lower trans-isomerization selectivity than the Escat 1241 commercial catalyst.

NOMENCLATURE

A	potassium hydroxide concentration
B	catalyst annealing temperature

C = C	carbon double bond
h	hour
K	Kelvin
KBH ₄	potassium borohydride
KOH	potassium hydroxide
kPa	kilopascal
M	molarity
Pd-B/ γ -Al ₂ O ₃	alumina-supported palladium boron catalyst
PdO	palladium oxide
R ²	coefficient of determination

Greek Symbols

α	distance from the center point
Δ	difference in value

Abbreviations

CCD	Central Composite Design
DOE	Design of Experiments
GC	Gas Chromatography
MPOB	Malaysian Palm Oil Board
IV	Iodine Value
rpm	rotations per minute
RSM	Response Surface Methodology
TFAs	Trans Fatty Acids

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