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# Optimised Biofuel Production via Catalytic Cracking of Residual Palm Oil Recovered from Spent Bleaching Earth (SBE) over Ni/HZSM-5 Zeolite

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| ARTICLE INFO | ABSTRACT |
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| | The concerns over the depletion of fossil fuel and security of energy supply have directed an increasing awareness about biomass or waste-derived energy. Fresh bleaching earth (BE) is used to remove colour, phospholipids, oxidised products, metals, and residual gums in the palm oil process refinery. Once the adsorption process ends, the spent bleaching earth (SBE) which contains approximately 20-40 wt% of the adsorbed oil, is usually disposed to landfills without any treatment. Thus, SBE as one of the major biomasses or wastes available in Malaysia is a potential source for hydrocarbon fuel production. Therefore, this study reported the employment of heterogeneous catalyst cracking of residual palm oil in SBE into liquid products by 15%Ni/HZSM-5 catalyst and the optimisation of the process. The experiments were designed using central composite design (CCD) approach via response surface methodology (RSM) to study the relationships of catalytic cracking temperature (400-500°C), heating time (60-180 min), and nitrogen flow rate (60-100 mL/min) on the liquid products yield. The experimental results were thoroughly analysed using analysis of variance (ANOVA). The optimum liquid products yield of catalytic cracking of residual palm oil in SBE was 12.91 wt% achieved at 452°C, 160 min of heating time, and 86 mL/min of nitrogen flow rate. On the basis of the obtained results, the heterogeneous catalyst of 15%Ni/HZSM-5 could be a potential catalyst for the conversion of residual palm oil in SBE into liquid products. |
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## 1. Introduction

Malaysia is one of the largest producers of palm oil. There has been a sustained interest in the utilisation of palm oil and oil palm biomass for the production of environmentally friendly biofuels [1]. In Malaysia, several studies focus on palm oil as the promising feedstocks for biofuel production such as palm oil, palm kernel oil, used or waste cooking oil, and palm oil-based waste fatty acid [2].

Spent bleaching earth is one of the palm oil solid wastes that can be utilised to synthesise bio-hydrocarbons.

SBE can be defined as an industrial waste that is mainly generated from the edible oil processing. SBE is commonly disposed in landfill without any pretreatment and usually contains 20-40 wt% of oil [3]. During the refining process, 0.5%-1.0% of activated clay or fresh bleaching earth (BE) is used where all BE will convert into waste as SBE and it is estimated that the production of SBE waste around the world is 600,000 tonne [4]. As the second largest producer of crude palm oil in the world, Malaysia alone produces more than 100,000 tonnes of SBE yearly which contains a high percentage of oil [5]. For this reason, it is potential to be used as a renewable raw material for the production of biofuel. From the environmental, safety, and regulatory points of view, it is suggested to restrict the landfill practice in the future. Additionally, SBE as bio-feed can be the best choice to solve the competition between the use of vegetable oil as the source of food and fuel.

Pyrolysis process is one of the most suitable technologies to convert biomass to bio-oil, char, and gases depending on the pyrolysis conditions [6]. It was reported that liquid mixtures with high percentages of hydrocarbons can be obtained by thermal cracking or pyrolysis, but in many of these studies, undesirable oxygenated compounds such as carboxylic acids and ketones still exist [7]. Besides, the major drawbacks of the bio-oil as fuel from pyrolysis is that it is highly oxygenated, viscous, corrosive, and thermally unstable [8,9], while its high concentration of water and oxygenated compounds reduces its calorific value and changes the combustion characteristics significantly. The presence of certain undesirable oxygenated compounds (organic acids and carbonyls) and polycyclic aromatic hydrocarbons (PAH) limits its potential for direct use in engines or turbines [10]. Boey *et al.,* [5] also reported that the yield of carboxylic acid was the major oxygenated compound found in SBE pyrolysis product as well as the process produced a low amount of high quality hydrocarbon. Due to this problem, to enhance and upgrade the liquid products or biofuel utilisation by applying catalytic technologies such as catalytic cracking and the introduction of bi-functional catalyst is found to be an interesting and promising solution. For that reason, catalytic cracking of palm oil residue in SBE using Ni/HZSM-5 zeolite as a catalyst was investigated to enhance the production of biofuel which is expected to increase the amount of aromatic hydrocarbon and decrease the amount of oxygenated compounds, focusing on the optimisation of SBE liquid products towards fuels and chemicals application.

Catalysis plays an important role in enhancing the yield of biofuel. In catalytic cracking processes, the large triglyceride molecules are subjected to de-oxygenation, converted into a relatively broad range of hydrocarbons following various reaction pathways, which are determined by the operating conditions and properties of the catalysts [11]. Among the different products that can be obtained, light olefins and aromatic hydrocarbons are particularly interesting due to their applications in the production of raw chemicals and fuels [10]. Zeolites HZSM-5 (Zeolite Socony Mobil-5) is a one-of-a-kind zeolite that can be used as a catalyst in catalytic cracking. HZSM-5 zeolites have advantages such as high thermal stability, high selectivity [11], and its highly ordered structure [12]. HZSM-5 also has strong acid site, high surface area, and appropriate pore diameter. Besides, the incorporation of metal active phases to HZSM-5 also provides bi-functional properties of acid and metal sites. Roesyadi *et al.,* [13] recommended Ni/HZSM-5 catalyst for the cracking of palm oil due to its high selectivity to produce gasoline. Moreover, the presence of some metals, such as nickel is expected to promote hydrogenation/dehydrogenation reactions, enhancing the production of high quality hydrocarbons without additional hydrogen consumption [14].

Statistical design of experiment (DOE) is an important tool to determine the optimum condition in any chemical or biochemical processes [15] and thus could be applied in the study of catalytic conversion of SBE to liquid products to determine the optimum operating parameters [11]. DOE has

been widely used in the studies on pollution control [16] and plant extraction recovery [17], as well as cracking of vegetable oil [11]. Central composite design (CCD) technique was adopted in this study. Response surface methodology (RSM) is governed by certain laws that can be approximated by deterministic relationship between the best conditions (levels) of the factors to optimise a desired output. The method was developed by Box–Wilson, Box–Hunter, Bradley, Davies, and Hunter [18]. The significant experimental results obtained are then thoroughly analysed using analysis of variance (ANOVA).

To the best of our knowledge, there is lack of study on the catalytic cracking of residue palm oil from SBE performances using the Ni/HZSM-5 heterogeneous catalyst for the conversion into liquid products, therefore studies in this area are highly desired. The objectives of this work were to investigate the interaction effects among process variables for the production of liquid products from catalytic cracking of residual palm oil in SBE and to optimise the process conditions for maximum liquid yield in the presence of 15%Ni/HZSM-5 catalyst. The effects of cracking temperature, heating time, and nitrogen flow rate on liquid products yield were reported. RSM was utilised to optimise the principle variables which affected the conversion of SBE into liquid products (biofuel).

## 2. Materials

The spent bleaching earth (SBE) containing up to 20 wt% of crude palm oil was obtained from a palm oil refinery (Sime Darby Sdn. Bhd., Pasir Gudang, Johor, Malaysia). Zeolite HZSM-5 ($SiO_2/nAl_2O_3$ = 30) was obtained from Zeolyst, USA in solid powder form. Nickel nitrate was purchased from Sigma Aldrich (M) Sdn. Bhd.

The SBE was directly used for catalytic cracking without any pretreatment. The triglyceride residues palm oil composition in SBE were palmitic acid (hexadecanoic acid, 44.8%), oleic acid (cis-9-octadecenoic acid, 38.6%), and linoleic acid (cis, cis-9,12-octadecadienoic acid, 10.6%) [19,20]. The insignificant difference in the fatty acids composition between crude palm oil and the residual oil in SBE confirms that the refining process has no effect on the fatty acid or triglyceride composition of the oil and the bleaching earth does not alter the chemical properties of the oil.

## 3. Experiment
### 3.1 Catalyst Preparation

Nickel (Ni) metal loaded into HZSM-5 catalyst was prepared according to the wet-impregnation method. Initially, the parent HZSM-5 zeolite was added into 100 mL of distilled water. Solid nickel nitrate was then added in to the solution, mixed and stirred at 60-70°C for 1 h to make up 15 wt% of Ni composition loaded on HZSM-5 catalyst. The solution was then dried at 100°C for 12 h and finally calcined at 550°C for 5 h The calcined catalyst was then crushed and sieved between 40 and 50 meshes (0.420 and 0.297 mm) for a uniform catalyst size [21].

### 3.2 Catalyst Characterisation

The textural properties of the catalyst were measured using nitrogen adsorption–desorption isotherm at −196 °C using Micromeritics Autochem II Chemisorption Analyzer. Prior to the analyses, the samples were treated at 300°C for 5 h under nitrogen flow to remove adsorbed compounds [12]. The Brunauer–Emmet–Teller (BET) equation was used for specific surface area calculation, whereas the micropore volume was determined using the Barrett–Joyner–Halenda (BJH) adsorption–desorption method [3].

The acidity of the catalyst was determined using temperature-programmed desorption of ammonia (TPD-NH$_3$) in a fixed-bed continuous flow microreactor at the atmospheric pressure equipped with a thermal conductive detector (TCD). The samples (0.1 g) were dried at 200°C for 1 h, and then were purged with 10% ammonia/90% helium in an NH$_3$ stream at 60°C for 30 min. After purging with ammonia/helium (30 mL/min) at 60°C for 30 min to remove the physically adsorbed NH$_3$, the samples were heated at a linear heating rate of 20°C/min up to 650°C. To determine the acidity from the NH$_3$ desorption profiles, the areas under the curves were integrated by Gaussian deconvolution of the peaks and the acidity was expressed as micromoles of ammonia per gram of catalyst.

### 3.3 Evaluation of SBE Catalytic Cracking Activity

The catalytic cracking of residual palm oil in SBE was investigated using a reactor as shown in Figure 1. Firstly about 100 g of SBE was heated from room temperature to 500°C for 60-180 min in an electric ceramic furnace to vaporise the organic compound in SBE. Then the volatile organic compounds passed through a catalytic bed at 400-500°C and atmospheric pressure under nitrogen gas flow (60-100 mL/min). About 1 g of catalyst was loaded over 0.2 g of quartz wool supported by a stainless steel mesh in the fixed bed reactor for each run. The volatiles and fine particles, carried by purging gas, passed through quartz wool filter and at this point the fine particles were removed. The volatile condensable products were quenched when the volatile organic compounds passed through a condenser then passed through the separating funnel to collect the organic liquid product.
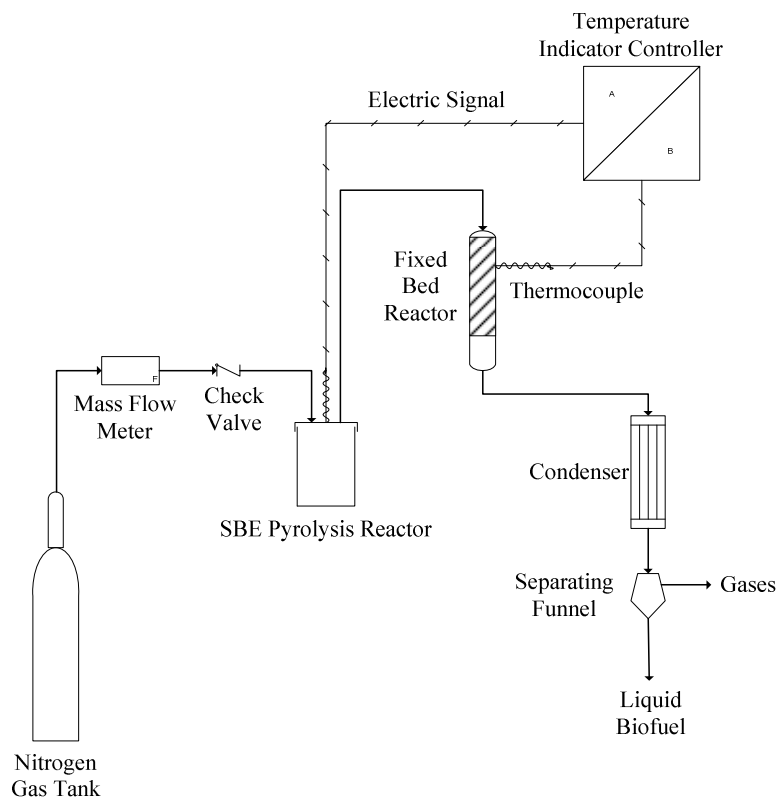


**Fig. 1.** Schematic diagram of catalytic cracking of SBE

The pyrolytic oil obtained was dissolved in dichloromethane and analysed using gas chromatography-mass spectrometry (GC-MS). The condenser and separating funnel were weighed and the weight difference before and after the experiment was recorded as the liquid yield. The total incondensable gases yield (wt.%) was calculated based on the difference in mass balance of the fed SBE in a specific period with the liquid yield product (wt.%). After every experiment, the SBE residues remained inside the SBE pyrolysis reactor was recorded as SBE solid waste. The condenser and all connection tubes were then washed using acetone and the liquid was also collected for further analysis. The liquid yield is calculated using Equation (1).

$$Liquid\ yield\ (wt.\%) = \frac{Desired\ product\ (g)}{SBE\ (g)} \times 100\ \% \qquad (1)$$

### 3.4 Design of Experiment (DOE) using Statistica

Full factorial design ($2^k$) as described by Montgomery [15] was used and statistical analysis of liquid product yield and SBE conversion in biofuel production was performed using Statsoft Statistica 8.0 software. The experimental design technique was employed to allow the gathering of maximum process information with a reduced number of experiments. Therefore, the reaction parameters in this study were optimised using a statistical technique called CCD which consumed short duration of experimental works to optimise the reaction conditions. RSM was used to describe the interaction of process variables and to predict the optimum process condition for liquid product yield.

The range and coded level of the catalytic cracking process variables studied are listed in Table 1. The three variables were catalytic cracking temperature ($X_1$), heating time ($X_2$), and nitrogen flow rate ($X_3$). Each variable consisted of three different levels of low (−1), medium (0), and high (+1). A full $2^3$ factorial design with six star points and two centre points was employed. The total number of experiments was 16, among which 14 experiments were augmented with two replications at centre point to evaluate the error. The complete experiment design matrix of CCD is given in Table 2. The percentage of the liquid products yield (Y) was taken as the response of the experiment. The full quadratic models for liquid yield were established by using the method of least squares shown in Equation (2) [18].

$$Y = \beta o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \qquad (2)$$

where,
$\beta_0$ = intercept coefficient (offset)
$\beta_1$, $\beta_2$, and $\beta_3$ = linear terms
$\beta_{11}$, $\beta_{22}$, and $\beta_{33}$ = quadratic terms
$\beta_{12}$, $\beta_{13}$, and $\beta_{23}$ = interaction terms
$X_1$, $X_2$, and $X_3$ = encoded independent variables

**Table 1**
Experimental range and level of independent variables

| Factors | Symbols | Range and levels | | |
|---|---|---|---|---|
| | | −1 | 0 | +1 |
| Catalytic cracking temperature (°C) | $X_1$ | 400 | 450 | 500 |
| Heating time (min) | $X_2$ | 60 | 120 | 180 |
| Nitrogen flow rate (mL/min) | $X_3$ | 60 | 80 | 100 |

The empirical mathematical model was tested using the analysis of variance (ANOVA) at 5% level of significance. ANOVA was used for checking the significance of the second-order models. The validity of the statistical model was performed via three analyses. The first analysis was to check the adequacy of the fitted model by ANOVA using Fisher's $F$-test or determined by the $F$-value. In general, the calculated $F$-value should be greater than the tabulated $F$-value to reject the null hypothesis, where all the regression coefficients are zero. Meanwhile, the tabulated $F$-values are obtained from $F$ distribution tables based on the degree of freedom (DF) for regression and residual at a specified level of significance which is defined as $\alpha$-value [18]. The significances of the models were determined by the experimental $F$-value derived from ANOVA, which is defined in Equation (3) [18,22].

$$F\text{-value} = (SSR/DF_{SSR})/(SSE/DF_{SSE}) \tag{3}$$

where,
SSR = sum of squares regression,
SSE = sum of squares errors,
$DF_{SSR}$ = degree of freedom for SSR, and
$DF_{SSE}$ = degree of freedom for SSE.

For the second analysis, either coefficient of correlation ($R$) or coefficient of determination ($R^2$) was determined to check the fit quality of the model. The last analysis was to analyse the significance of the model parameters using $p$-value and $t$-value.

## 4. Results and Discussion

### 4.1 RSM Study using Statistica

The experimental values for SBE conversion and yield of liquid products from statistical model for 16 runs are presented in Table 2. The range of the experimental values for the yield of liquid products was 10.3 to 12.98 wt%. The second-order polynomial equations that provide the empirical model for the dependent variable was obtained by using multiple regression analysis of the experimental data.

**Table 2**
Experimental design matrix and experimental results for SBE conversion and yield of liquid products

| Run No. | Factors | | | Experimental results |
|---|---|---|---|---|
| | Catalytic cracking temperature (°C), $X_1$ | Heating time (min), $X_2$ | Nitrogen flow rate (mL/min), $X_3$ | Yield of liquid products (wt%), Y |
| 1 | 450.00 | 120.00 | 44.72 | 11.27 |
| 2 | 400.00 | 180.00 | 60.00 | 11.89 |
| 3 | 400.00 | 60.00 | 60.00 | 11.32 |
| 4 | 450.00 | 120.00 | 80.00 | 12.47 |
| 5 | 361.81 | 120.00 | 80.00 | 10.33 |
| 6 | 450.00 | 120.00 | 115.28 | 12.59 |
| 7 | 400.00 | 180.00 | 100.00 | 11.52 |
| 8 | 450.00 | 225.83 | 80.00 | 12.77 |
| 9 | 450.00 | 120.00 | 80.00 | 12.98 |
| 10 | 500.00 | 180.00 | 100.00 | 11.78 |
| 11 | 500.00 | 60.00 | 100.00 | 11.06 |
| 12 | 500.00 | 180.00 | 60.00 | 11.56 |
| 13 | 500.00 | 60.00 | 60.00 | 10.56 |
| 14 | 400.00 | 60.00 | 100.00 | 10.95 |
| 15 | 538.19 | 120.00 | 80.00 | 10.46 |
| 16 | 450.00 | 14.17 | 80.00 | 10.38 |

*4.1.1 Analysis of variance (ANOVA)*

The full quadratic models were established using the method of least squares. The predicted of liquid products yield (Y) model is shown in Equations (4).

$$Y = 12.72367 - 0.069X_1 + 0.99500X_2 + 0.32460X_3 - 1.50469X_1^2 - 0.74612X_2^2 - 0.51791X_3^2 - 0.14500X_1X_2 - 0.36500X_1X_3 - 0.07000X_2X_3 \quad (4)$$

ANOVA was used for verifying the significance of the second-order model as well as demonstrating the total, residual, and regression of sum of squares as shown in Table 3. From Table 3, the $F_{value}$ indicates a ratio between the mean square of regression and the mean square of residual. The calculated $F_{value}$ was then compared to the tabulated $F$ (0.05, 9, 6) or $F_{0.05}$. If the calculated $F_{value}$ is greater than $F_{0.05}$ (4.10), the empirical model gives good prediction at high confidence level of 95%. The statistical model of liquid products yield in this study is 7.61 and it shows that the empirical model gives good prediction.

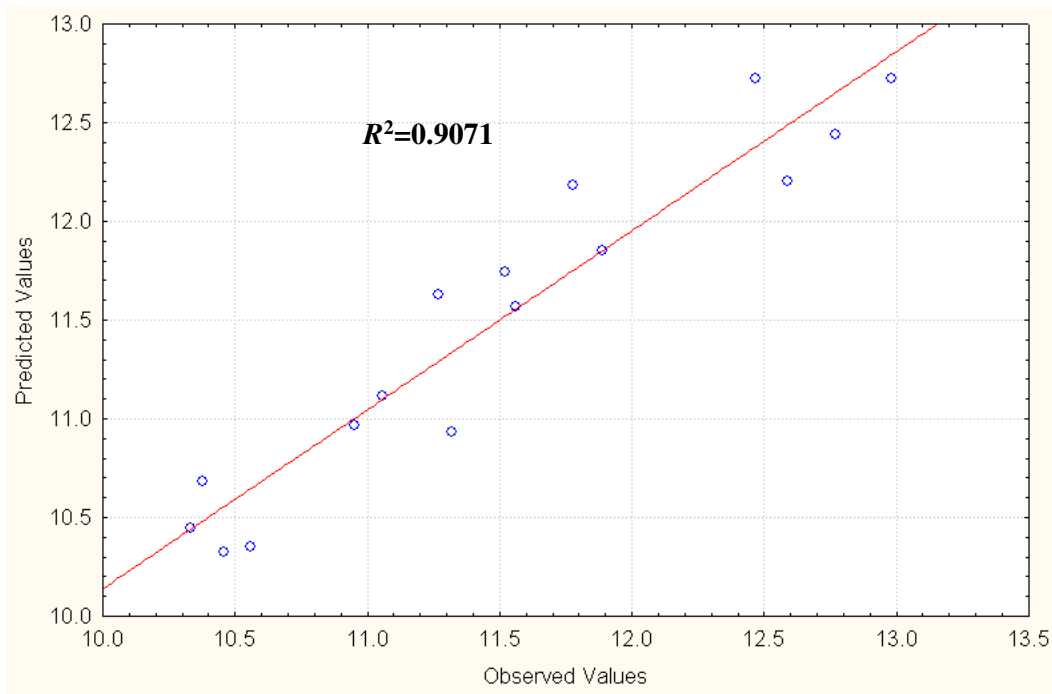**Table 3**
ANOVA for quadratic model of liquid products yield

| Source | Sum of Squares, (SS) | Degree of Freedom,(DF) | Mean Squares, (MS) | $F_{Value}$ | $F_{0.05}$ |
|---|---|---|---|---|---|
| S. S. Regression (SSR) | 12.29 | 9 | 1.37 | 7.61 | 4.10 |
| S. S. Errors (SSE) | 1.05 | 6 | 0.18 | | |
| S. S. Total (SST) | 11.34 | 15 | | | |

The numerical illustration of the observed and predicted values for the liquid products yield is demonstrated in Figure 2. The figure shows a parity plot of a straight line relationship between the observed and predicted values. The value for the coefficient of determination ($R^2$) is a measurement of the total variation for the observed values that described by the fitted model. The higher value of $R^2$ or $R^2 = 1$ indicates the statistical model considers the variability in the data while lower value of $R^2$ or $R^2 = 0$ indicates that none of the variability in the response can be described by the observed experimental data.

The coefficient of determination ($R^2$) value for SBE conversion is 0.9071 indicating 90.71% of the variability in the data is accounted to the model. Haaland [23] stated that the values of $R^2$ should be at least 0.75 to show that the empirical model is adequate to explain the variability of the observed data. Therefore, the values of $R^2$ in this study shows a good empirical model between the experimental data and predicted values.

The significance of each coefficient in the empirical model for the liquid products yield expressed by Equation 4 was determined using the student *t*-test distribution value and *p*-value shown in Table 4. The larger magnitude of *t*-test value and smaller *p*-value represent higher significance towards the model [18].

As illustrated in Table 4, the largest effect on liquid products yield was the quadratic (Q) term of the catalytic cracking temperature, followed by the linear (L) term of heating time and quadratic (Q) term of heating time with the largest *t*-value (−5.80288, 4.47910, −2.87744) and smallest *p*-value (0.001148, 0.004196, 0.028152), respectively.

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**Fig. 2.** Parity plot between observed and predicted values for the liquid products yield

**Table 4**
Significance of regression coefficients for liquid products yield

| Factor | Regression coefficient | $t$-test value | $p$-value |
|---|---|---|---|
| Mean/Intercept | 12.72367 | 43.00657 | 0.000000 |
| (1) Catalytic cracking temperature (°C) (L) | −0.06900 | −0.31063 | 0.766588 |
| Catalytic cracking temperature (°C) (Q) | −1.50469 | −5.80288 | 0.001148 |
| (2) Heating time (min) (L) | 0.99500 | 4.47910 | 0.004196 |
| Heating time (min) (Q) | −0.74612 | −2.87744 | 0.028152 |
| (3) Nitrogen flow rate (mL/min) (L) | 0.32460 | 1.46122 | 0.194263 |
| Nitrogen flow rate (mL/min) (Q) | −0.51791 | −1.99732 | 0.092770 |
| 1L by 2L | 0.14500 | 0.48955 | 0.641835 |
| 1L by 3L | 0.36500 | 1.23231 | 0.263928 |
| 2L by 3L | −0.07000 | −0.23633 | 0.821035 |

L: Linear term of quadratic models.
Q: Quadratic term of quadratic models.

### 4.1.2 The interaction effect of variables on liquid products yield

The correlation between the variables involved in this study were observed via three-dimensional (3D) and contour surface plots. The optimal conditions for optimum liquid products yield were clearly observed from the contour plots.

### 4.1.2.1 Effect of catalytic cracking temperature and heating time on liquid products yield

The effect of catalytic cracking temperature and heating time rate on liquid products yield is shown in Figure 3 which illustrates that the best ranges for cracking temperature and heating time rate were 450-480°C and 120-180 min, respectively. A higher catalytic cracking temperature and heating time will reduce liquid products yield. Meanwhile, a temperature below than 380°C was also identified as unsuitable for catalytic cracking process as the oil yield less than 10 wt.% was produced.
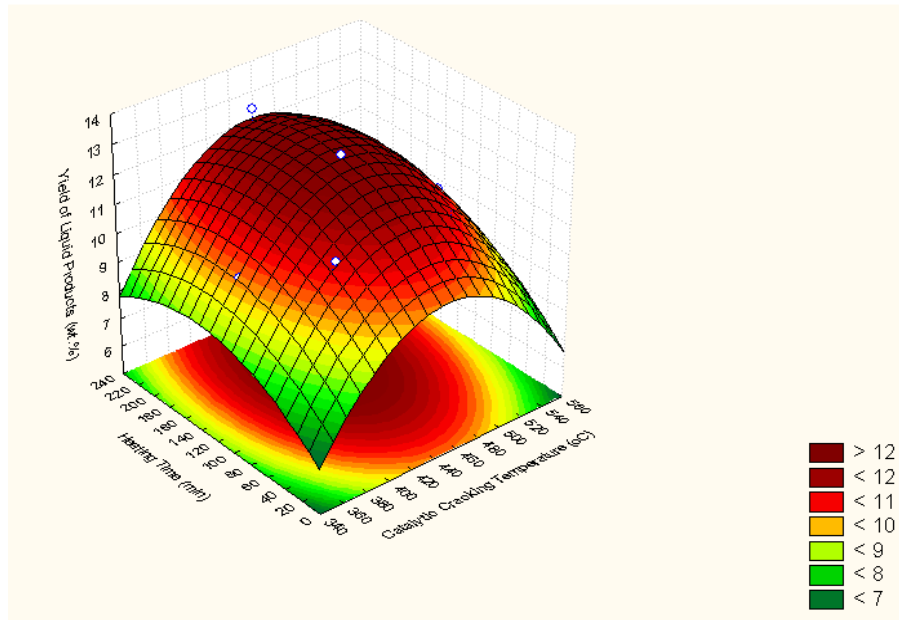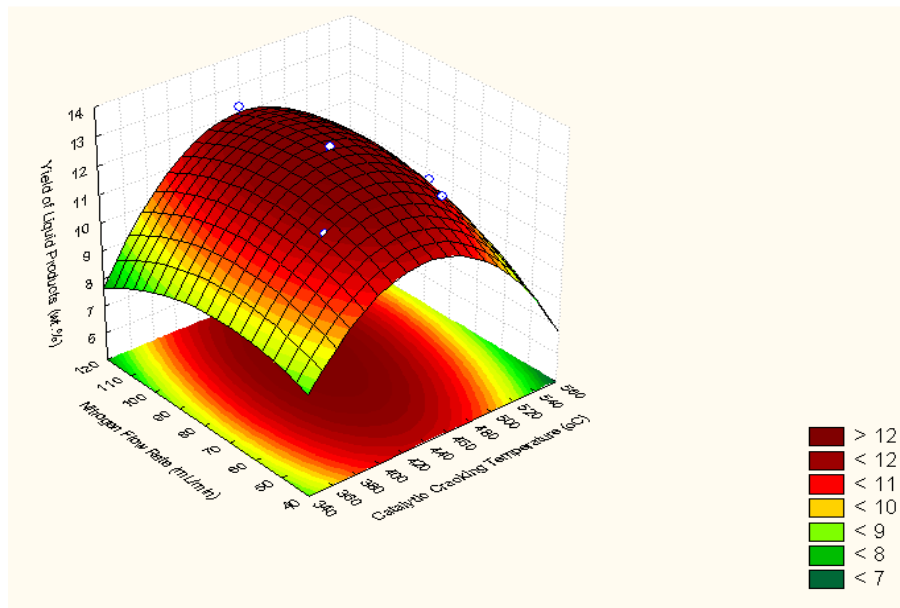


**Fig. 3.** Response surface plot for the effect of catalytic cracking temperature and heating time on liquid products yield

### 4.1.2.2 Effect of catalytic cracking temperature and nitrogen flow rate on liquid products yield
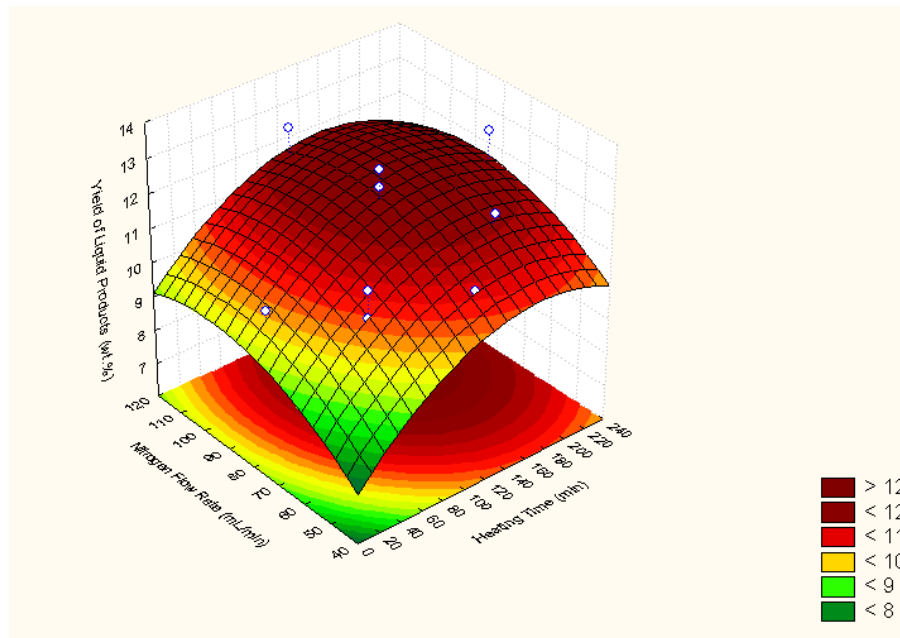
Figure 4 shows the response surface plot for the effect of catalytic cracking temperature and nitrogen flow rate towards liquid products yield. It can be observed that the catalytic cracking temperature and nitrogen flow rate at the range of 450-480°C and 80–100 mL/min, respectively can give the maximum liquid product yield more than 12 wt.%.

### 4.1.2.3 *Effect of heating time and nitrogen flow rate on liquid products yield*

Figure 5 represents the effect of heating time and nitrogen flow rate. A maximum liquid products yield can be achieved within the range studied, which were 120-160 min and 80-90 mL/min for heating time and nitrogen flow rate, respectively. Meanwhile, the heating time of higher than 160 min and the nitrogen flow rate of higher than 90 mL/min produced liquid products yield below 12.0 wt.%.

**Fig. 4.** Response surface plot for the effect of catalytic cracking temperature and nitrogen flow rate on liquid products yield



**Fig. 5.** Response surface plot for the effect of heating time and nitrogen flow rate on liquid products yield

### 4.1.3 Optimisation of liquid products yield

The optimum parameters for liquid products yield was obtained from the RSM using Statistica Stat Software as shown in Table 5. The predicted optimum liquid products yield from the catalytic cracking of residual palm oil in SBE was 12.91 wt.% achieved at 452°C, 160 min of heating time, and 86 mL/min of nitrogen flow rate.

Further experiment was performed at the suggested optimum condition to validate the modelling result. Based on Table 5, the observed value for liquid products yield obtained was 12.56 wt% which differed only 2.71% compared with the predicted results. The error was considered small as the observed values are within the 5% level of significance. Hence, the statistical model is valid to predict an approximate result due to the small percentages of error.

**Table 5**
The critical, observed (minimum and maximum), predicted, and observed values of catalytic cracking process parameters

| Factor | Observed Minimum | Critical Values | Observed Maximum |
|---|---|---|---|
| Catalytic cracking temperature (°C) | 361.81 | 452.16 | 538.19 |
| Heating time (min) | 14.17 | 159.46 | 225.83 |
| Nitrogen flow rate (mL/min) | 44.72 | 85.68 | 115.27 |
| Predicted value of liquid product yield (wt%) | | 12.91 | |
| Response | Predicted Value | Observed value | Error (%) |
| Liquid product yield (wt%) | 12.91 | 12.56 | 2.71 |

## 4.2 Physicochemical Properties of 15%Ni/HZSM5

The results of BET from nitrogen adsorption–desorption analysis for the parent HZSM-5 and 15%Ni/HZSM5 catalysts are presented in Table 6 alongside with the TPD–$NH_3$ results. The surface area and pore volume of the 15%Ni/HZSM5 catalyst decreased compared with those of the parent HZSM-5 catalyst. The result obtained was supported by the study done by Zakaria *et al.,* [21] which claimed that metal loading has significantly reduced the surface area and pore volume of the parent HZSM-5 zeolite. The decreases clearly indicate that Ni cluster might be located inside the zeolite channels and partially blocks the zeolite channels [14].

**Table 6**
Nitrogen adsorption–desorption and TPD–$NH_3$ method of catalysts

| Catalysts | Surface area (m$^2$/g)[a] | Micropore volume (cm$^3$/g)[b] | Total of acidity, (mmol/g)[c] | Distribution of acid sites | | |
|---|---|---|---|---|---|---|
| | | | | Weak | Moderate | Strong |
| HZSM-5 | 424.6482 | 0.1795 | 0.71973 | 0.20627 | 0.51346 | - |
| 15%Ni/HZSM-5 | 351.2613 | 0.1761 | 2.7376 | 2.1339 | 0.6037 | - |

[a]Obtained from BET method.
[b]Obtained from BJH method.
[c]Obtained from TPD–$NH_3$ analysis.

From the TPD-$NH_3$ test, it can be inferred that the impregnation of Ni induced new weak, moderate, and strong acid sites differently. The surface acidity was calculated as total acidity and expressed in terms of mmol of $NH_3$ desorbed per gram of catalyst, between 100 and 650°C [21]. The various acidic properties of catalysts are caused by the availability of crystallography of the catalyst due to the different atoms dwelling framework in diverse environments of the catalyst sites [24]. Table 6 shows the total acidity of each catalyst. It can be observed that the 15%Ni/HZSM-5 catalyst has the highest total acidity.

## 4.3 Liquid Products Analysis

The observed value for liquid products yield obtained was 12.56 wt%. The result obtained in this study was almost similar with our previous study [25] of 8.0-11.0 wt% of the cracking oil yield obtained from 100 g of SBE catalytic cracking. Table 7 shows the components of liquid products produced via the noncatalytic process, using the parent HZSM-5 and 15%Ni/HZSM5 catalysts. The liquid products yield was calculated on the basis of the condensed liquid in the separating funnel. The compounds in the liquid products that were identified using GC–MS were grouped into monoaromatic compounds, alkenes, alkanes, alcohols, ketones, aldehydes, carboxylic acids, esters, nitrogenated compounds, and polycyclic aromatic hydrocarbons (PAHs). The compounds found were almost similar to the catalytic cracking oil compounds reported in a previous study [5]. On the basis of area under curve, the carboxylic acid group was the major group of compounds found in the samples which covered 39.45%-42.80% of the total area followed by the ester group which covered 34.08%-37.02% of the total area.

The presence of small aliphatic products such such as alkenes and alkanes was also noticed in all samples. Compared with the products from the noncatalytic process and using the parent HZSM-5 catalyst, the area percentages of alkenes and alkanes content in the liquid products from the catalytic cracking using the 15%Ni/HZSM5 catalyst increased to a maximum of 5.48% and 3.15%, respectively, indicating that the Ni-modified HZSM-5 catalyst had good catalytic selectivity for the conversion of the residual palm oil in SBE into hydrocarbons. These results indicate that the incorporation of Ni over HZSM-5 zeolite promoted the cracking activity on catalyst. Nickel-doped HZSM-5 catalyst has a good catalytic behaviour due to the changes in total acid sites compared with that of the parent zeolite. A similar observation was reported by Maia *et al.,* [14] in the catalytic activity of Ni-HZSM-5 zeolites in the isobutane and n-butane cracking reaction. They found that the increasing percentage of Ni doped in HZSM-5 led to the increasing molar ratio of alkenes/alkanes in isobutane catalytic cracking compared with that of the parent HZSM-5 zeolite. They also suggested that the dehydrogenation products formed at the nickel sites sequentially reacted on the acidic sites.

According to Ong and Bhatia [26], palm oil first undergoes thermal and catalytic cracking on the external surface of the catalysts to produce heavy hydrocarbons and oxygenated compounds, and then these products are further cracked into light alkenes and alkanes, water, carbon dioxide, and carbon monoxide. Also, primary cracking occurs within the internal pore structure of zeolite catalysts. Furthermore, the palm oil containing triglycerides with long chain fatty acids are converted into short chain molecules by deoxygenation, cracking, oligomerisation, alkylation, isomerisation, and aromatisation [26].

The results in Table 7 show that the SBE cracking produced oxygenated group compounds such as alcohols, ketones and aldehydes. However, referring to the area percentage, not much different is observed. Some oxygenated hydrocarbon such as alcohols, ketones, aldehydes, and esters were detected in hydrocarbon biofuel due to the similar boiling points of the small molecules compared with those of the hydrocarbons [27].

The liquid products containing the highest monoaromatic compound was obtained via the catalytic cracking process using the 15%Ni/HZSM-5 catalyst of about 1.81%. Using the parent HZSM-5 catalyst, the monoramotic compound was only 0.79% and only 0.41% of monoaromatic compound was obtained from the noncatalytic process. The impregnation of HZSM-5 catalyst with nickel strongly increased the production of monoaromatic compound, roughly twice as much that that of the parent HZSM-5 zeolite. These results indicate that the Ni/HZSM-5 exhibited hydrogenation and ring opening of polyaromatics, which transformed polyaromatic compounds to monoaromatic compounds. Similar results were also reported on the catalytic cracking of waste tyre derived oil using

Ni/HZSM-5 where the introduction of nickel on the HZSM-5 zeolite might promote the cyclisation and dehydrogenation of olefins and aromatisation of naphthenes, leading to the high formation of mono-aromatics [28]. Katikaneni *et al.,* [29] also stated that aromatic hydrocarbons were produced through oligomerisation, acid catalysed cyclisation, and H-transfer reactions on the hydrocarbon molecules.

The area percentage of polycyclic aromatic hydrocarbons (PAHs) for the liquid products produced via the catalytic cracking with the presence of the parent HZSM-5 catalyst was the highest (10.92%) compared with those of the liquid products produced via the catalytic cracking using 15%Ni/HZSM-5 zeolite (6.62%) and noncatalytic process (7.75%). Namchot and Jitkarnka [28] reported that, for the parent HZSM-5 catalyst, the concentrations of monoaromatic compounds and naphthenes significantly decreased, whereas the concentration of polyaromatic compounds drastically increased when they used the catalyst in the waste tyre catalytic cracking reaction. They revealed that the formation of polyaromatic compounds possibly occurred at the acid sites located at the external surface of the HZSM-5 zeolite and it might promote the combination of naphthenes and/or monoaromatic compounds via oligomerisation/aromatisation reactions, resulting in the high formation of polyaromatic compounds.

**Table 7**
The total area percentage of hydrocarbon groups in the liquid products from the catalytic cracking of SBE using 15%Ni/HZSM-5 catalyst

| Compounds | % Area | | |
|---|---|---|---|
| | Thermal cracking (Noncatalytic) | HZSM-5 | 15%Ni/HZSM-5 |
| Alkenes | 0.86 | 1.047 | 5.48 |
| Alkanes | 1.85 | 2.55 | 3.15 |
| Monoaromatic compounds | 0.41 | 0.79 | 1.81 |
| Polycyclic aromatic hydrocarbons (PAH) | 7.75 | 10.92 | 6.62 |
| Alcohols | 0.16 | 0.14 | 0.06 |
| Ketones | 6.97 | 6.41 | 7.80 |
| Aldehydes | 0.67 | 0.21 | 0.31 |
| Carboxylic Acids | 42.80 | 41.21 | 39.45 |
| Esters | 37.02 | 36.59 | 34.08 |
| Nitrogenated compounds | 0.63 | 0.62 | 0.60 |
| Others | 0.93 | 0.15 | 0.19 |

Table 8 displays the percentages of quantified area for every identified peak (higher proportion). The results were obtained via the optimum reaction conditions at 452°C, 160 min of heating time, and 86 mL/min of nitrogen flow rate. The major compound found in all the samples in the catalytic cracking product of residual palm oil in SBE was dodecanoic acid with a mixture of aliphatic and aromatic hydrocarbons composed of oxygenated components. The presence of small alkenes and alkanes compounds was also detected. These compounds were mostly unsaturated, due to the lack of intermolecular hydrogen transfer to the cracked intermediates [22]. As mentioned in Section 2, the main triglyceride composition of the crude palm oil and residual oil in the bleaching earth is similar. From this result, it shows that the main palm oil residue in SBE containing the long-chain heavy fraction of triglyceride fatty acid such as palmitic acid, oleic acid, and linonelic acid were cracked into several short-chain molecules. These results indicate that the Ni-loaded HZSM-5 catalyst can promote the cracking of heavy fractions contained in SBE to lighter hydrocarbons. The product could be used as an alternative liquid fuel, hence future works regarding the modification of the liquid product as the fuel source are needed.

**Table 8**
Typical composition of the liquid products obtained via the optimum
catalytic cracking process of SBE with 15%Ni/HZSM-5 catalyst

| Chemical component | Area percentage |
|---|---|
| **Alkenes** | |
| 5-Dodecene, (E)- | 0.54 |
| 1-Undecene | 0.73 |
| 1-Decene | 0.37 |
| **Alkanes** | |
| Undecane | 1.11 |
| Tridecane | 0.84 |
| Hexadecane, 1-chloro- | 0.46 |
| **Alcohols** | |
| 1-Hexanol, 2-ethyl- | 0.06 |
| **Ketones** | |
| 2-Undecanone | 1.64 |
| 2-Tridecanone | 1.56 |
| 2-Dodecanone | 1.67 |
| 12-Tricosanone | 1.22 |
| **Aldehydes** | |
| Tridecanal | 0.23 |
| **Carboxylic Acids** | |
| Dodecanoic acid | 27.38 |
| Tetradecanoic acid | 11.79 |
| **Esters** | |
| 1,2-Benzenedicarboxylic acid, diisooctyl ester | 23.29 |
| **Nitrogenated Compounds** | |
| Dodecanenitrile | 0.60 |
| **Mono Aromatic Compounds** | |
| Benzene,1-methyl-1,2-propadienyl- | 0.36 |
| Benzene, 2-butenyl- | 0.23 |
| **Polycyclic Aromatic Hydrocarbons** | |
| Anthracene, 1-methyl- | 0.49 |
| Naphthalene | 0.40 |
| Naphthalene, 1-methyl- | 0.37 |

## 5. Conclusion

On the basis of the experimental results obtained, it can be concluded that the 15%Ni/HZSM-5 catalyst could be used as an effective heterogeneous catalyst for the conversion of residual palm oil in SBE into liquid products. All the variables such as catalytic cracking temperature, heating time, and nitrogen flow rate gave a significant effect on the catalytic cracking. The catalytic cracking temperature gave the largest effect on the liquid products yield. The results indicate that RSM can be used to find the relationships among the process variables and responses in an efficient manner using a minimum number of experiment. The optimum liquid products yield from the catalytic cracking of residual palm oil in SBE was 12.91 wt% achieved at 452°C, 160 min of heating time, and 86 mL/min of nitrogen flow rate. The liquid product can be used as a fuel with suitable modification. This study has highlighted the potentials of this approach to reduce the menace of SBE waste from the palm oil industry and to produce fuel as the value-added benefit.

## Acknowledgement

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