Optimization Process of Carbon Mono Oxide (CO) Gas Emission Adsorption using Activated Carbon from Rice Husk

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Abstract. This study aims to investigate the optimum conditions of CO emission adsorption by activated carbon from rice husk and to select the process conditions from combination of activated carbon mass, activator concentration, and the exit gas velocity to adsorption time and CO adsorption. Rice husk was carbonized in the tube furnace at 400 °C for 1.5 hours followed chemically activated using citric acid as an activator. The activated carbon formed was further tested for its ability to adsorb CO emissions on the adsorption tube connected to the motorcycle exhaust. CO emissions from motorcycles were analysed using E-Instrument E8500 while the optimum adsorption of CO gas emission was analysed using Design Expert 6.0.8 software with Box-Behnken Design. The results concluded that variables of activated carbon mass, activator concentration, and exit gas velocity influence to the adsorption time and CO gas adsorption. Based on the optimization analysis using regression quadratic model obtained that optimum condition of the CO emission adsorption process will be achieved at 30 g of activated carbon, activator concentration (citric acid) of 0.47 M, and at a flow rate of 20 m/s. In this optimum condition, the adsorbed CO gas obtained was 55.02 ppm which occurred for 1266 seconds.

1. Introduction
The increasing number of people, followed by an increase in motor vehicles, has led to vehicle exhaust emissions which could lead to accumulation and a negative impact on the lives and the environment. Exhaust gases in motor vehicles are a source of air pollution because contain many harmful substances such as NO2, SO2, Cl2, O3, CO, hydrocarbons (HC), dust particles and even lead (Pb) [1]. The exhaust gases generated from the combustion residue on motorcycle consist of various gases, some are toxic and some are non-toxic. Toxic gases are CO, HC, and NOx [2].

Among these toxic gases, CO emissions have the highest percentage (reach to 60%) compared to other exhaust gases [3]. CO gas is colourless and odourless so difficult to recognize. CO gas that affects to health of living beings needs to get a special study, because CO gas emission is toxic to humans, can cause eye pain, respiratory and lung problems. CO gas is one of the main causes of most common gas poisoning to human health. It should be realized and understood by the public that air pollution from the motor vehicle (spark ignition engine) produces 70% of CO, 100% of Pb, 60% of HC, and 60% of NOx. Diesel motor vehicle (compression ignition engines) produces fine particles that will settle longer in the lungs and become cancer-triggering factors [3,4].

In order for exhaust gas emission levels to meet the quality standard, various control measures are carried out such as modification of combustion engine and the development of exhaust system reactor.
Others innovative emission control measures are substitution of fuel for gasoline, the addition of glass wool, activated carbon, water or other materials that serve as motor vehicle exhaust adsorbents [5]. Agricultural wastes such as rice husk, corn, banana and others have good prospects used as adsorbent of flue gas. Among these organic wastes is the prospect of rice husk that has low nutritional value with high ash content, resistant to weathering, resembles wood content, and has a high enough carbon content. Rice husks are easy to find in any rice processing from paddy fields in tropical countries can be used as alternative adsorbents to reduce agricultural waste from rice husks. Rice husk is one of the dominant agricultural waste in Indonesia which is produced 22% annually and potentially as biosorbent [6,7,8]. Therefore, this research utilizes rice husk as an active carbon material to reduce CO gas emission level in motor vehicle as an effort to find solution of air pollution problem due to CO gas emission. The rice husk was activated by the addition of citric acid as activator material which can increase the adsorbent efficiency, and the output of this research obtained alternative adsorbent from rice husk that can adsorb CO emission from motor vehicle.

This research used Design Expert (DX 6.0.8) Response Surface Method (RSM) Box-Behnken Design (BBD) program to investigate and select the process conditions from the combination of activated carbon mass, activator concentration, and the exit gas velocity to adsorption time and adsorbed CO concentration. The advantages of this program can be used for analysis and modelling of a problem with one or more research treatments. RSM is a collection of statistics and mathematical techniques that are useful for developing, improving and optimizing processes, where responses are influenced by several factors (independent variables). RSM not only defines the influence of independent variables, but also produces mathematical models that explain chemical and biochemical processes. The main idea of this method is to know the effect of the independent variable on the response, to get the model of relationship between the independent variable and the response and to get the process condition that produces the best response. In addition, the advantages of this method are not requiring trial data in large numbers and does not require a long time [9]. BBD program is a good design for surface response methodology because it allows estimating parameters of quadratic models, making designs sequentially and can detect a lack of model matching [10].

Comparison between BBD and other surface response designs (Centre Composite Design, Doehlert matrix, and factorial design level three) has shown that the design of BBD and Doehlert matrices is slightly more efficient than Centre Composite Design but much more efficient than the full three-level factorial design [11].

2. Materials and Method

2.1. Materials
The main material used in this research was rice husk from Cot Yang rice mill, Tungkop village, Aceh Besar District, Aceh Indonesia. Citric Acid used was obtained commercially from Sigma LTD. Gas emission used as the object of this research was the emission of Honda motor vehicle production in 2007.

2.2. Equipment
Equipment used were Tube Furnace (LabHouse), Oven Dryer (ISUZU DSL-1000), Shaker (SLM-OS-250-Digital), Buchner Funnel (Pyrex), Digital Scales (ACIS, BC-500), Filter Paper 3M), Desiccators (Pyrex), and Flue Gas Analyser (E Instruments E8500). In addition, supporting tools for testing were 250 mL Erlenmeyer (Pyrex), 1000 mL (Pyrex) flask, thermometer (Yenaco), 100 mL (Pyrex), pH meter (Ohaus), and dropper (Pyrex).

2.3. Active Carbon Preparation
This research was conducted in three stages, consisting of preparation, activation, and adsorption. Rice husk was washed with aquaedest to remove impurities, furthermore, the pyrolysis reaction was performed in tube furnace (Line Thermolyne, model: FB1410M-33) at 400 °C for 1.5 hours to obtain the rice husk carbon that used for the activation process. Activation process was carried out by using
citric acid to improve the adsorption ability of rice husk carbon, with variation of citric acid concentration of 0.2 M; 0.3 M; and 0.6 M; respectively.

2.4. CO Gas Emission Adsorption Preparation and Analysis
The adsorption of CO gas emissions was carried out on the adsorption tube as shown in Figure 1 and the installation of the adsorbent medium was shown in Figure 2. The measured vehicle was placed in a flat position, the vehicle was powered on a steady idle engine for 10 minutes. The exit gas flow rate was adjusted at a speed of 10 m/s. To measure the emissions of the outgoing CO, the E-instruments E8500 probe was inserted into the motorcycle exhaust pipe. Measurements were carried out for 20 minutes to determine the initial gas concentration before the adsorption tube was installed. Furthermore, the adsorption tube containing 10 g of activated carbon was connected to the vehicle exhaust and then measured as the above steps. Measurements were conducted every one minute and then the measured gas concentration was recorded until it reaches a constant concentration. The treatments were repeated for a variation of 20 g and 30 g adsorbent mass for activated and non-activated carbon at an exit gas rate of 15 m/s and 20 m/s, respectively. This research used a BBD consisting of three response variables: active carbon mass (g), activator concentration (M), and exit gas velocity (m/s) as shown in Table 1.

![Figure 1](image1.png)
![Figure 2](image2.png)

### Table 1. Experimental Design of CO Gas Emission Adsorption based on RSM-BBD Approach

| Run | Activated Carbon mass (g) | Activator Concentration (M) | exit gas velocity (m/s) |
|-----|---------------------------|----------------------------|------------------------|
| 1   | 10                        | 0                          | 15                     |
| 2   | 20                        | 0.3                       | 15                     |
| 3   | 30                        | 0.6                       | 15                     |
| 4   | 30                        | 0.3                       | 20                     |
| 5   | 10                        | 0.6                       | 15                     |
| 6   | 20                        | 0.6                       | 10                     |
| 7   | 20                        | 0.3                       | 15                     |
| 8   | 10                        | 0.3                       | 10                     |
| 9   | 20                        | 0.3                       | 15                     |
| 10  | 30                        | 0.3                       | 10                     |
| 11  | 20                        | 0                          | 10                     |
| 12  | 30                        | 0                          | 15                     |
| 13  | 20                        | 0.6                       | 20                     |
| 14  | 20                        | 0.3                       | 15                     |
| 15  | 20                        | 0.3                       | 15                     |
| 16  | 10                        | 0.3                       | 20                     |
| 17  | 20                        | 0                          | 20                     |
3. Results and Discussion

3.1. Analysis of CO Gas Emission Adsorption Response Based on Design Expert RSM-BBD Approach

Results of CO gas adsorption based on RSM-BBD approach were tabulated in Table 1. Results showed that the largest CO gas adsorption time occurred at 1260 seconds in the run-4 treatment (activated carbon mass 30 g, activator concentration 0.3 M with 20 m/s exit gas velocity). Meanwhile, the lowest adsorption time was found in 420 seconds occurring on the run-1 (10 g of active carbon, without activation at an exit gas velocity of 15 m/s). Furthermore, the highest concentration of CO gas adsorbed was obtained at 58 ppm in the run-3 (activated carbon mass 30 g, 0.6 N activator concentration with 15 m/s exit gas velocity). Meanwhile, the lowest CO gas adsorbed was obtained at 30 ppm in the run-11 (20 g of active carbon mass, without activation at an exit gas velocity of 10 m/s).

### Table 2. CO Gas Adsorption based on the treatment conditions

| Run | Activated Carbon mass (g) | Activator Concentration (M) | exit gas velocity (m/s) | adsorption time (s) | CO gas adsorbed (ppm) |
|-----|---------------------------|-----------------------------|-------------------------|--------------------|-----------------------|
| 1   | 10                        | 0                           | 15                      | 420                | 36                    |
| 2   | 20                        | 0.3                         | 15                      | 1080               | 45                    |
| 3   | 30                        | 0.6                         | 15                      | 1020               | 58                    |
| 4   | 30                        | 0.3                         | 20                      | 1260               | 53                    |
| 5   | 10                        | 0.6                         | 15                      | 840                | 52                    |
| 6   | 20                        | 0.6                         | 10                      | 720                | 38                    |
| 7   | 20                        | 0.3                         | 15                      | 1080               | 45                    |
| 8   | 10                        | 0.3                         | 10                      | 780                | 34                    |
| 9   | 20                        | 0.3                         | 15                      | 1080               | 45                    |
| 10  | 30                        | 0.3                         | 10                      | 900                | 42                    |
| 11  | 20                        | 0                           | 10                      | 600                | 30                    |
| 12  | 30                        | 0                           | 15                      | 600                | 40                    |
| 13  | 20                        | 0.6                         | 20                      | 1020               | 49                    |
| 14  | 20                        | 0.3                         | 15                      | 1080               | 45                    |
| 15  | 20                        | 0.3                         | 15                      | 1080               | 45                    |
| 16  | 20                        | 0.3                         | 20                      | 1080               | 50                    |
| 17  | 20                        | 0                           | 20                      | 840                | 40                    |

Designed BBD has found an actual mathematical model that can be used to predict adsorption time and concentration of CO gas adsorbed based on the suggested model, and the suggested model was quadratic. Both design models have R² values close to 1, where the model design for adsorption time has a value of 0.9525 for R² and 0.8915 for Adj-R², respectively, while for concentration of CO gas adsorbed had a value of 0.9514 for R² and 0.889 for Adj-R², respectively. If the value of R² was close to 1, it identifies that there was a high correlation between the observed value and the predicted value \[12\]. Based on the quadratic model, the mathematical model equations generated for CO gas adsorption time were as follows.

\[
Y = -127.5 + 33.75X_1 + 2225X_2 + 21X_3 - 0.75000(X_1)^2 - 3166.66667 (X_2)^2
+2.52089E - 014(X_3)^2 + 2.07242E - 014X_1X_2 + 0.3X_1X_3 + 10X_2X_3
\]  

(1)

Whereas for the adsorbed CO gas concentration obtained the equation model were as follows.

\[
Y = -12.12500 - 0.81250X_1 + 28.75000X_2 + 6.15000X_1 + 0.035000(X_1)^2
-22.22 (X_2)^2 - 0.15 (X_1)^2 + 0.166X_1X_2 - 0.025X_1X_3 + 0.16X_2X_3
\]  

(2)

Based on the equation models (1) and (2) generated above, each variable was the mass of the activated carbon \((X_1)\), the activator concentration \((X_2)\), and the exit gas velocity \((X_3)\). These three
variables had a very important influence where the use of these three variables will increase the adsorption time and the concentration of CO gas adsorbed. Figure 3 shows the relationship of the predicted value of the adsorption time and the adsorbed CO gas concentration based on equation proposed by the response surface design and actual value generated from the experiment. This graph showed location of points spread evenly on a straight line. This condition can support the extent of accuracy of the model obtained.

![Figure 3](image)

**Figure 3.** Experimental design results and predictions for adsorption time (A) and adsorbed CO gas concentration (B)

Comparison between actual data and prediction data was shown in Figure 3. Figure 3(A) showed that for adsorption time, the centre point condition was looped 5 times at 20 g of activated carbon mass, 0.3 M of activator concentration with the exit gas velocity was 15 m/s and occurred the CO gas adsorption time of 1080 seconds. While in Figure 3 (B) for the adsorbed CO gas concentration showed that the centre point condition was also performed 5 times that occurred at 20 g of activated carbon mass, 0.3 M of activator concentration with the exit gas velocity was 15 m/s and adsorb CO gas at 45 ppm. ANOVA is one factorial of BBD which is useful to generate interaction between process variables with response variable. The components in ANOVA will be used to calculate the F-ratio that serves to determine the effectiveness of a model. ANOVA results for the analysis of CO gas emission adsorption in this study were shown in Tables 3 and 4.

### Table 3. ANOVA results for surface quadratic model of CO adsorption time

| Source | Sum of Squares | DF | Mean Square | F       | Prob. > F |
|--------|----------------|----|-------------|---------|-----------|
| Model  | 7.766E+005     | 9  | 86288.24    | 15.61   | **0.0008** Significant |
| A      | 54450.00       | 1  | 54450.00    | 9.85    | **0.0164**     |
| B      | 1.625E+005     | 1  | 1.625E+005  | 29.38   | **0.0010**     |
| C      | 1.800E+005     | 1  | 1.800E+005  | 32.56   | **0.0007**     |
| A²     | 23684.21       | 1  | 23684.21    | 4.28    | 0.0772       |
| B²     | 3.420E+005     | 1  | 3.420E+005  | 61.86   | **0.0001**     |
| C²     | 0.000          | 1  | 0.000       | 0.000   | 1.0000       |
| AB     | 0.000          | 1  | 0.000       | 0.000   | 1.0000       |
| AC     | 900.00         | 1  | 900.00      | 0.16    | 0.6986       |
| BC     | 900.00         | 1  | 900.00      | 0.16    | 0.6986       |
| Residual | 38700.00     | 7  | 5528.57     |         |            |
| Lack of Fit | 38700.00    | 3  | 12900.00    |         |            |
| Pure Error  | 0.000       | 4  | 0.000       |         |            |
| Cor. Total | 8.153E+005   | 16 |             |         |            |
Table 4. ANOVA results for surface quadratic model of adsorbed CO gas concentration

| Source | Sum of Squares | DF | Mean Square | F Value | Prob. > F |
|--------|----------------|----|-------------|---------|-----------|
| Model  | 798.19         | 9  | 88.69       | 15.23   | **0.0008** Significant |
| A      | 55.13          | 1  | 55.13       | 9.47    | **0.0179** |
| B      | 325.13         | 1  | 325.13      | 55.85   | **0.0001** |
| C      | 288.00         | 1  | 288.00      | 49.47   | **0.0002** |
| A²     | 51.58          | 1  | 51.58       | 8.86    | **0.0206** |
| B²     | 16.84          | 1  | 16.84       | 2.89    | 0.1328    |
| C²     | 59.21          | 1  | 59.21       | 10.17   | **0.0153** |
| AB     | 1.00           | 1  | 1.00        | 0.17    | 0.6909    |
| AC     | 6.25           | 1  | 6.25        | 1.07    | 0.3346    |
| BC     | 0.25           | 1  | 0.25        | 0.034   | 0.8417    |
| Residual | 40.75        | 7  | 5.82        |         |           |
| Lack of Fit | 40.75    | 3  | 13.58       |         |           |
| Pure Error | 0.000        | 4  | 0.000       |         |           |

Table 3 shows the F value in the model was 15.61, it indicates that the resulting model was significant. However, there was a possibility of 0.08% that this "F value model" can be generated larger. Prob. value > F <0.05 indicated a significant model term. In this case A, B, C, B² were significant models. Table 4 shows ANOVA for the adsorbed CO gas concentration, this result indicates that F value in this model was 15.23, it indicates that the resulting model was significant. However there was a possibility of 0.08% that this "F value model" can be generated larger. Prob. value >F<0.05 indicated a significant model term. In this case A, B, C, A² and C² were significant models. A value greater than 0.1 indicated an in-significant model. If there were many in-significant models (not including those needed to support the hierarchy), model reductions can improve the model.

3.2. Effect of Activated Carbon Mass and Activator Concentration on the Time of Adsorption and CO Gas Adsorbed

The model suggested to calculate the adsorption time and the concentration of CO gas adsorbed in this study was the quadratic equation. Model selection was based on several factors, such as the value of R². From the model, we can find the influence of both response variables by using response surface analysis through two types of plot, contour plot and 3D plot. Contour plots are useful for analysing the interaction effects among factors on the response. The 3D plot shows the effect of two variables on the response to which the variable is made in a fixed state. The relationship between the three independent variables to the response was shown in Figure 4 and Figure 5.

Figure 4 shows the effect of activated carbon mass and activator concentration on the duration of CO gas emission adsorption. At an exit gas velocity of 15 m/s with an activated carbon mass of 30 g and an activator concentration of 0.6 M, the required adsorption time reached to 1020 second, at the same mass flow rate with 10 g carbon without activation, the adsorption time was 420 second, while the optimum adsorption time was obtained for 1080 seconds which occured at 20 g activated carbon with activator concentration of 0.3 M.

Figure 5 shows the effect of activated carbon mass and activator concentration (citric acid) on the amount of CO gas emission adsorption. At an exit gas velocity of 15 m/s with an activated carbon mass of 30 g and an activator concentration of 0.6 M, the CO gas adsorption reached to 58 ppm, at the same mass flow rate with 10 g carbon without activation, the CO gas adsorption was 36 ppm, while the optimum CO gas adsorption was obtained 45 ppm which occured at 20 g activated carbon with activator concentration of 0.3 M.
3.3. Optimization of CO Gas Emission Adsorption

The optimum conditions of adsorption time and the concentration of CO gas adsorbed using activated carbon from husk rice obtained from the optimization function of Design Expert 6.0.8 Software. The purpose of this optimization process are as follows:

1. to learn the effects of statistically designed combinations;
2. to estimate coefficients by adjusting them to mathematical models that provide the best fit for the conditions of study;
3. to predict the influence of the appropriate model; and
4. to check the accuracy of the model.

In this research, the optimization process was conducted by adjusting the mass of activated carbon, activator concentration, and the exit gas velocity corresponding to its level range. The response variable was the adsorption time and the adsorbed CO gas that was adjusted maximum to obtain the highest yield. The optimization solution of adsorption time and CO gas adsorption calculated by Design Expert 6.0.8 Software in this study was shown in Table 5.
Table 5. Optimization solution of adsorption time and CO gas adsorption

| No. | Activated Carbon mass (g) | Activator Concentration (M) | exit gas velocity (m/s) | adsorption time (s) | CO gas adsorbed (ppm) | Desirability |
|-----|---------------------------|-----------------------------|-------------------------|--------------------|-----------------------|--------------|
| 1   | 30.00                     | 0.47                        | 20                      | 1266.21            | 55.0272               | 1.000        |

Figure 6. Optimization model of time and CO gas adsorption, (A) Plot contour and (B) 3D plot

Figure 6 shows the optimization of time and CO gas adsorption. This results showed that the optimum conditions of the process will be achieved at 30 g of activated carbon, activator concentration (citric acid) of 0.47 M, and at a flow rate of 20 m/s.

4. Conclusion
The analysis results using RSM concluded that variables of activated carbon mass, activator concentration, and exit gas velocity influence to the adsorption time and CO gas adsorption. The RSM with the BBD can be used to predict and determine the desired process conditions. Result of process optimization analysis using regression quadratic model obtained that optimum conditions of the process will be achieved at 30 g of activated carbon, activator concentration (citric acid) of 0.47 M, and at a the flow rate of 20 m/s. In this optimum condition, the adsorbed CO gas obtained was 55.02 ppm which occurred for 1266 seconds.

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