The Use of Response Surface Methodology in Ammonia Oxidation Reaction Study

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The design of experiments (DoEs) with response surface methodology (RSM) were used to investigate the effect of operating parameters on the ammonia oxidation process. In this paper, the influence of reactor’s load and temperature of reaction as independent variables was investigated. The efficiency of NH₃ oxidation to NO and N₂O concentration in nitrous gases gas was identified as response variables. As a result of these studies, statistically significant models for two responses variables were developed.

1. Introduction

At the industrial scale, nitric acid is obtained in the Ostwald process which is composed of three major stages: the catalytic oxidation of NH₃ to NO, oxidation of NO to NO₂, and NO₂ absorption in water with the formation of HNO₃ [1].

Overall, the nitric acid production process is described with the following equation:

\[ \text{NH}_3 + 2\text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 421.2 \text{kJ} \]  

(1)

For producing nitrogen oxides and then nitric acid, only nitrogen derived from ammonia is used, whereas nitrogen coming from air does not take part in the reaction. Theoretically, the specific consumption of ammonia is 269 kg NH₃/t HNO₃.

Depending on the process conditions, NO, N₂O, and N₂ are obtained in varying proportions as a result of ammonia oxidation according to the following reactions:

\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} + 907.3 \text{kJ} \]  

(2)

\[ 4\text{NH}_3 + 4\text{O}_2 \rightarrow 2\text{N}_2\text{O} + 6\text{H}_2\text{O} + 1104.9 \text{kJ} \]  

(3)

\[ 4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} + 1369.1 \text{kJ} \]  

(4)

Additionally, for the determination of real specific consumption of ammonia, a number of factors should be taken into account including absorption capacity and ammonia demand for the selective catalytic reduction of NOₓ (if present in the process) and the degree of ammonia conversion to the main product (NO), that is, ammonia oxidation efficiency. Apart from reactions (2)–(4), depending on the process conditions, the other parallel and sequential reactions can occur, but their nitrogen products are N₂ and N₂O. The real specific consumption of ammonia is higher by dozens or kilograms than a theoretical one, and the value of this depends on the formation of by-products in the ammonia oxidation process. The efficiency of reaction depends mainly not only on the type of the catalyst but also on process parameters such as pressure, temperature, the residence time, or reactor’s load and ammonia concentration in inlet mixture. Reactor’s load is described as the amount of oxidized ammonia per gauze surface and time unit, kg NH₃/(m²h).

Due to the binding legal provisions, the other important parameter when regarding the ammonia oxidation reaction is the amount of nitrous oxide which is a greenhouse gas being formed as a by-product. A measure of the amount of nitrous oxide being formed is its concentration in nitrous gases.

Nowadays, commonly applied catalysts for ammonia oxidation are catalytic gauzes made of the platinum alloy with rhodium. Usually, additional gauzes made of palladium, nickel, or gold alloy are placed under the gauze package, the function of which is to “catch” platinum diminishing from the
catalytic gauzes. Catalytic gauzes are made of wire with a diameter of 0.060–0.092 mm [1–5].

An alternative solution involves the application of the oxide catalyst containing no noble metals among which different catalysts were studied, e.g., perovskite-type oxides with different metals, monolith, and the hybrid one combined with the monolith catalyst and catalytic gauzes [6–10].

Oxidation pressure has an inversely proportional effect on ammonia oxidation efficiency. A maximum efficiency (equilibrium) in reactors operating under atmospheric pressure is 97%–98%, whereas in plants operating under higher pressure, it is 95%–97% at medium pressure (3–6 bar) and 92–94% at high pressure (10 bar). In order to compensate the effect of oxidation pressure, the temperature of reaction should be risen. During exploitation, the catalyst for ammonia oxidation undergoes the process of aging and ammonia efficiency is steadily decreasing because of the loss of platinum. In modern dual pressure nitric acid plants, ammonia is oxidized under the medium pressure of 3.5–5 bar. The remaining parameters such as the reactor’s load, temperature of reaction, and the number of catalyst gauzes are subject to optimization.

Optimization of process variables is based on the mathematical modeling. In order to obtain a reliable process model, it is necessary to know the bases of the process and the effect of the process variables on its course. Very often, carrying out tedious studies is necessary to optimize the process variables. For example, in conventional research, the method of “one factor at a time” technique is applied, i.e., the effect of only one parameter on the experiment result is observed with maintaining other parameters at the stable level. This time-consuming and costly method is more frequently replaced with statistical-mathematical methods which involve design of experiments and analysis of the obtained results using response surface methodology (RSM). This makes it possible to study the effect of a few process variables (independent variables) on one or a few final results of the process (response variable). The choice of experiment plan depends mainly on the issue being the subject matter of studies as well as on the set objectives. Among different available experiment plans, most frequently applied are as follows: full factorial design, fractional factorial design, Plackett–Burman, central composite, Box–Behnken, or Taguchi design [11].

The design of experiments (DoEs) are often used for study of the effect of parameters on the course of various chemical processes and the process optimization. The examples of those are research on optimization of anaerobic ammonium oxidation [12], CO hydrogenation [13], ammonia photocatalytic degradation by Zn/Oak charcoal composite [14], steam methane reforming [15, 16], water-gas shift reaction [17], and methanol synthesis [18, 19].

Central composite design (CCD) is widely applied in research due to its flexibility [11]. CCD contains a factorial or fractional factorial design with center points and an additional axial point (star points). Exemplary types of central composite design are presented in Figure 1.

In the present work, the face-centered central composite design (CCD) method was used to study the influence of temperature of nitrous gases directly under catalytic gauzes meaning the effect of the temperature of reaction and reactor’s load on ammonia oxidation efficiency and N2O concentration in nitrous gases. Based on results obtained in experiments of the ammonia oxidation process under medium pressure carried out in accordance with the selected plan, the mathematical model, its statistical significance evaluation, and result analysis with response surface methodology (RSM) were developed.

2. Experimental

2.1. Materials. The package of five standard knitted gauzes made of the platinum alloy with the addition of 10 wt.% Rh made of 0.076 mm wire and a specific weight of 600 g/m² was applied in studies of the ammonia oxidation process. The catalyst applied in studies constitutes the part of the catalyst package usually used in industrial nitric acid plants.

2.2. Equipment. Studies were carried out in the pilot plant, the scheme of which is presented in Figure 2. The ammonia-air mixture with the stable ratio is directed to the reactor with a diameter of 100 mm where the catalytic gauzes are placed. The ammonia concentration in air-ammonia mixture determined on the basis of flow measurements of these two gases was 10.9 vol.% During measurements, the temperature of air-ammonia mixture was changed in such a manner as to obtain the temperature of nitrous gases as assumed in the experiment plan at approximately constant air-ammonia ratio. Temperatures of air-ammonia mixture were shown with research results in Table 1. The flow of air ammonia was also controlled in order to obtain the accurate reactor’s load. All the parameters were recorded. All the measurements were carried out under the pressure of 5 bar. The air-ammonia mixture flow rate at the inlet of the reactor was selected in such a manner so that the linear velocity of the gas flow through the catalytic gauzes was in the range of 1–2.5 m/s, as typical for the medium-pressure reactor.

2.3. Analytical Methods. Ammonia oxidation efficiency was determined by a titration method. The air-ammonia mixture and nitrous gases after reaction samples at claimed parameters were collected at the same time in the vacuum flasks containing appropriate absorbent solutions.

Ammonia from air-ammonia mixture samples was absorbed in water with the formation of ammonia-water solution which was then titrated with sulphuric acid.

In case of nitrous gases samples, 3% water solution of hydrogen peroxide was used. After conditioning the sample for a sufficient period of time, NO oxidized completely to NO2 and next it reacted with water to form HNO3. The formed nitric acid was titrated with the sodium hydroxide solution in the presence of an indicator.

Ammonia oxidation efficiency η was calculated according to the following formula:

\[ \eta = \left( \frac{X_2}{X_1} \right) \cdot 100\% \]  

where \( X_1 \) is the ammonia concentration in ammonia-air mixture, % w/w, and \( X_2 \) is the concentration of oxidized
ammonia, % w/w. The result of each measurement is an average value, calculated from 7 independent samplings. The difference in the extreme individual values was not greater than ±0.3% in comparison with the average one.

Nitrous oxide (N2O) concentration in nitrous gases was determined by the gas chromatography method. Gaseous samples were collected in the vacuum flasks containing 3% water solution of hydrogen peroxide. After the absorption of nitrous gases and water vapor condensation, exhaust gas from the flasks was injected to the gas chromatograph through 1 ml sample loop. The nitrous oxide concentration was determined by the Unicam 610 gas chromatograph equipped with a discharge ionization detector (DID) and the Haye Sep Q column. Filament current was 6.36 mA, whereas helium carrier gas flowed at the rate of 47 mL/min. The result of each measurement was an average value calculated from 3 independent samplings. The difference in the extreme

Figure 1: Star points locations in three types of CCD plans [20]: (a) circumscribed; (b) inscribed; (c) face-centered.

Figure 2: Scheme of the pilot plant. C1, absorption column; C2, bleaching column; E1–E6, heat exchangers; M1, air-ammonia mixer; R1, ammonia oxidation reactor; R2, selective catalytic reduction reactor.

<table>
<thead>
<tr>
<th>Run</th>
<th>Air-ammonia mixture temperature (°C)</th>
<th>Ammonia oxidation efficiency (%)</th>
<th>N2O concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>165</td>
<td>92.2</td>
<td>1499</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
<td>92.0</td>
<td>1762</td>
</tr>
<tr>
<td>3</td>
<td>195</td>
<td>93.5</td>
<td>1079</td>
</tr>
<tr>
<td>4</td>
<td>190</td>
<td>92.7</td>
<td>1207</td>
</tr>
<tr>
<td>5</td>
<td>165</td>
<td>92.4</td>
<td>1460</td>
</tr>
<tr>
<td>6</td>
<td>135</td>
<td>90.8</td>
<td>1968</td>
</tr>
<tr>
<td>7</td>
<td>165</td>
<td>92.5</td>
<td>1451</td>
</tr>
<tr>
<td>8</td>
<td>170</td>
<td>93.7</td>
<td>1348</td>
</tr>
<tr>
<td>9</td>
<td>180</td>
<td>90.9</td>
<td>1443</td>
</tr>
<tr>
<td>10</td>
<td>158</td>
<td>91.4</td>
<td>1620</td>
</tr>
<tr>
<td>11</td>
<td>145</td>
<td>94.1</td>
<td>1536</td>
</tr>
</tbody>
</table>
individual values was not greater than ±35 ppm in comparison with the average one.

2.4. Design of Experiment. Face-centred central composite design (CCD) was used to determine the influence of the independent reaction variables on the ammonia oxidation process. The Design Expert 11.0.6.0 version (Stat-Ease, Inc., Minneapolis, MN, USA) software was used for the experimental design and regression analysis of experimental data.

The reactor’s load and (X1) and temperature (X2) were selected as independent variables. For statistical calculations, the levels of independent variables were normalized (coded) according to the following equation:

\[ X_i = \frac{x_i - x_0}{\Delta x_i} \]  

where \( X_i \) is the coded level of the independent variable (−1, 0, or 1), \( x_i \) is the actual value of variable, \( x_0 \) is the value of \( x_i \) at the centre point, \( \Delta x_i \) is the step change in \( x_i \), and \( i \) is the independent variable (1, 2). The minimum and maximum ranges for both parameters are presented in terms of coded and uncoded symbols in Table 2.

The response variables were ammonia oxidation efficiency (\( R_1 \)) and N\(_2\)O concentration in nitrous gases (\( R_2 \)). In order to describe the effect of independent variables, the polynomial second-degree model given by the following equation was initially assumed:

\[ R = b_0 + b_1 X_1 + b_2 X_2 + b_{12} X_1 X_2 + b_{11} X_1^2 + b_{22} X_2^2 \]  

where \( R \) is the measured response variable, \( b_0 \) is the constant, \( b_1 \) and \( b_2 \) are the linear coefficients, \( b_{11} \) and \( b_{22} \) are the quadratic coefficients, and \( b_{12} \) is the interaction coefficient.

A total of 11 experiments including three replicates at the centre point were necessary to estimate the coefficients of the model using multiple linear regression analysis.

The experiments were conducted in a random order to minimise the effects of uncontrolled factors. The experimental design matrix of the independent variables (coded) is presented in Table 3.

The effect of each variable and their interactions on response variables was studied. The validity of the model equation was checked with analysis of variance (ANOVA) and with the correlation coefficient \( R^2 \). The significance was checked with the F-test.

3. Results and Discussion

In the studied scope of independent variables \( X_1 \) and \( X_2 \), ammonia oxidation efficiency (\( R_1 \)) ranged from 90.8% to 94.1%, whereas N\(_2\)O concentration (\( R_2 \)) ranged from 1079 to 1978 ppm. The air-ammonia mixture temperature during sampling and individual results of experiments is presented in Table 1.

Results of ANOVA for the response variables \( R_1 \) and \( R_2 \) are presented in Tables 4 and 5, respectively.

The model F value of 20.90 implies that the model is significant. There is only a 0.23% chance that an F value this large could occur due to noise. \( p \) values less than 0.0500 indicate that model terms are significant. In this case, only \( X_1 \) meets this requirement. The lack-of-fit F value of 4.67 implies that lack-of-fit is not significantly relative to the pure error. There is 18.15% chance that a lack-of-fit F value this large could occur due to noise.
The model $F$ value of 73.40 implies that the model is significant. There is only a 0.01% chance that $F$ value this large could occur due to noise. $p$ values less than 0.0500 indicate that model terms are significant. In this case, $X_1$ and $X_2$ are significant model terms. The lack-of-fit $F$ value of 3.37 implies the lack-of-fit is not significant relative to the pure error. There is a 23.74% chance that a lack-of-fit $F$ value this large could occur due to noise.

In accordance with the proposed equation (7), regression coefficients for two response variables ($R_1$ and $R_2$) were calculated. For both these responses, good adjustment of experimental data with 95% confidence interval was achieved. The calculation results are presented in Table 6.

Figures 3 and 4 present response surface developed based on calculation results.

The calculated correlation coefficients $R^2$ for both response surfaces are shown in Table 7.

In case of oxidation efficiency, the predicted $R^2$ of 0.5725 is not as close to the adjusted $R^2$ of 0.9087 (the difference is more than 0.2). This may indicate a large block effect or a possible problem with this model and/or data. In the case of N$_2$O concentration, the predicted $R^2$ of 0.8772 is in reasonable agreement with the adjusted $R^2$ of 0.9731.

Bearing in mind the statistical significance of particular elements of equation (7) specified with the value of $p$ parameter ($p$ value $< 0.05$) and low value of the predicted $R^2$ coefficient, the base equation (7) was modified by reducing the elements with no statistical significance.

Finally, equations are as follows (7):

$$R_1 = 92.39 - 1.37X_1,$$
$$R_2 = 1488 + 178X_1 - 256X_2.$$

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**Table 6:** Regression coefficients of the second-order polynomials models for ammonia oxidation efficiency ($R_1$) and N$_2$O concentration ($R_2$).

<table>
<thead>
<tr>
<th>Regression coefficients</th>
<th>Value</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_0$</td>
<td>92.43</td>
<td>0.1694</td>
</tr>
<tr>
<td>$b_1$</td>
<td>-1.37</td>
<td>0.1348</td>
</tr>
<tr>
<td>$b_2$</td>
<td>0.0295</td>
<td>0.1348</td>
</tr>
<tr>
<td>$b_{12}$</td>
<td>0.1535</td>
<td>0.1651</td>
</tr>
<tr>
<td>$b_{11}$</td>
<td>0.0490</td>
<td>0.2075</td>
</tr>
<tr>
<td>$b_{22}$</td>
<td>-0.1210</td>
<td>0.2075</td>
</tr>
<tr>
<td>$b_0$</td>
<td>1468.33</td>
<td>20.51</td>
</tr>
<tr>
<td>$b_1$</td>
<td>178.06</td>
<td>16.33</td>
</tr>
<tr>
<td>$b_2$</td>
<td>-256.00</td>
<td>16.33</td>
</tr>
<tr>
<td>$b_{12}$</td>
<td>-16.83</td>
<td>19.99</td>
</tr>
<tr>
<td>$b_{11}$</td>
<td>18.17</td>
<td>25.12</td>
</tr>
<tr>
<td>$b_{22}$</td>
<td>18.67</td>
<td>25.12</td>
</tr>
</tbody>
</table>

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Figure 3: Response surface plot and contour plot showing the effect of independent variables $X_1$ and $X_2$ on the response variable $R_1$ (%).
Results of ANOVA for the modified models and values of correlation coefficients were presented in Tables 8–10. After reducing the base model to statistically important elements, it turned out that the model was simplified to the linear one without interaction. In case of ammonia oxidation efficiency within the studied scope of variability, the temperature had no effect on the achieved ammonia oxidation efficiency, but it had the impact on the reactor’s load. The model adequacy was confirmed by the analysis of variance (ANOVA) with $F$-test. The model $F$ values of 148.48 and 203.41 imply that models are significant. In those cases, there is only a 0.01% chance that $F$ values this large could occur due to noise. The $p$ values for both cases (less than 0.0500) indicate that models terms are significant.

The models accuracy was checked by comparing the experimental and predicted results. The difference between the adjusted $R^2$ and predicted $R^2$ for two response surfaces was less than 0.2 (Table 10). Figure 5 shows this dependency for both response variables graphically.

Based on simplified models, the effect of two independent parameters on the values of response variables was determined, which is presented in Figure 6.

### 4. Conclusions

Ammonia oxidation process was regarded as a “black box” with no reference to reaction mechanism and no kinetic stables being specified.

This paper presents studies of the effect of reactor’s load and temperature of reaction on ammonia oxidation efficiency and the amount of by-product N$_2$O. For the quantitative indication of this issue, the face-centered central composite design (CCD) was applied.
Based on the results of experiments, the empirical equation was obtained which describes the quantitative effect of independent variables (reactor’s load and temperature of nitrous gases) on response variables (ammonia oxidation efficiency and N\textsubscript{2}O concentration). Findings of these studies show that the effect of these parameters can be shown with statistically significant linear function with a 95% confidence interval, for which regression coefficients were calculated.

For this experiment, the number of gauzes was selected in such a manner as to ensure that the obtained ammonia oxidation efficiency was lower than the possible maximum efficiency than can be achieved under such a pressure. The obtained values of ammonia oxidation efficiency ranged from 90.8% to 94.1%, whereas under such a pressure, ammonia oxidation efficiency can reach 97%. These experiment conditions allowed specifying variability of response variables with the changed independent variables. Within the studied scope of variables, ammonia oxidation efficiency is reversely proportional to the reactor’s load for the applied catalytic package. Lowering the catalyst’s load below the studied scope and/or increasing the number of gauzes in the catalyst package would allow obtaining oxidation efficiency similar to equilibrium efficiency achieved under this pressure.

According to dependency known in the literature \cite{1} the optimum temperature of ammonia oxidation is 890°C under...
5 bar. The choice of reaction temperature variability (±20°C) allowed specifying the variability sensitivity of this parameter to ammonia oxidation results. Based on the achieved results, it was found that the change of temperature in the regarded variability scope has no effect on ammonia oxidation efficiency. The extension of this scope would lead to studying this dependency under conditions inapplicable in industrial practice.

In the case of N₂O concentration, both these variables have a linear effect on the achieved value of this response variable. Increasing the temperature with a simultaneous decrease in reactor’s load reduces the amount of N₂O being formed with the temperature having a greater effect. However, higher temperature causes higher losses of platinum during catalyst exploitation which has also a significant impact on the catalyst industrial exploitation.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

References
