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Screening the Important Factors Affecting the Process of Ammonia Synthesized by the Plackett-Burman Method and the Process Optimization with RSM

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ABSTRACT

The optimization of the ammonia synthesis plant to increase the production of ammonia is studied in this line of research. In this paper, the steady-state ammonia synthesis is simulated using the Aspen HysysV.11 software. By comparing the simulation results with the industrial information, a mean relative error of 7.71 % was obtained, which indicated the high accuracy of the simulation. Then, four effective variables were selected from among 11 independent variables by the Plackett-Burman method. The effects of the Hydrogen flow in the feed stream, Recycle stream pressure, Feed stream temperature, and input temperature of the third reactor were investigated, and the response surface design method of the central composite design was performed to plant optimize. It is obtained that the Hydrogen flow in the feed stream is equal to 6255 $\frac{kmol}{h}$*, the feed stream pressure is equal to 205 bar, the temperature of the excess stream inlet in the first reactor is equal to 663 K, and the temperature of the stream inlet of the second reactor is 677.5 K which increased the ammonia production by 7.5 %.*

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1. Introduction

Ammonia is one of the most important petrochemical products, which is the most widely used chemical in the chemical industry after sulfuric acid and is used for the production of nitrogen fertilizers. In 1909, Fischer Haber first executed a laboratory-scale ammonia production project. In 1912, Haber and Bush introduced the commercial process of producing ammonia through syngas. The first commercial ammonia production unit started its activity with a daily capacity of 30 tons in 1913 in Germany under the license of BASF, and in 1916 its capacity increased to

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250 tons per day. In 1945 there were about 125 factories with a total capacity of 4.5 million tons. The emergence of ammonia units based on methane steam reforming, which was founded by Kellogg Company, was an important development in the ammonia industry. This technology has reduced production costs and increased the ammonia production capacity [1]. In recent years, the ammonia production has reached 146 million tons per year in the world, of which China has the largest share [2].

Babu and Angira [3], simulated and optimized an auto-thermal ammonia synthesis reactor. Estimating the length of the optimal reactor, for various high temperatures and under the constraints caused by the energy and mass balance of the reaction feed gas temperature, and the nitrogen mass flow rate for the ammonia production, is the key objective of the optimal design of an auto-thermal ammonia synthesis reactor. There are countless combinations that may be made with the feed gas temperature, nitrogen mass flow rate, reacting gas temperature, and reactor length. The contradictory results, using the gear package of the old NAG subroutine (D02EBF), which is now replaced with D02EJF, in combination with simple GA, that have been reported in earlier literatures, are verified using the NAG subroutine (D02EJF) in MATLAB (with analytical Jacobian) for the simulation in combination with the Quasi-Newton (QN) method for the optimization purpose. Additionally, the new NAG subroutine contrasts with the features of multimodal objective function identified in the earlier studies with a unimodal one. It was discovered that even at the high peak temperature of 800 K, the new routine (D02EJF) did not exhibit any spikes, reverse reaction effects, or the equation instability.

Farivar and Ale Ebrahim [4], developed one-dimensional heterogeneous model for an intercooled horizontal ammonia synthesis reactor (HASR) of the Khorasan petrochemical plant. In order to replicate the HASR with two quench streams, the model is further expanded. To produce concentration, temperature, and pressure profiles along the reactor beds, the fourth-order Runge-Kutta method has been used to simultaneously solve the mass balance, energy balance, and pressure drop equations in MATLAB. Two-point boundary value differential equations have been solved using a modified shooting method for the purpose of calculating the effectiveness factor. When the simulation findings and plant data are compared, a good level of agreement is found. A new setup for HASR is suggested in the paragraphs that follow. Intercooled and two quench flow HASRs are combined in the suggested design. Therefore, it has a better nitrogen conversion and, as a result, a higher rate of the ammonia production as compared to the standard HASR with two quench flows and intercooled HASR. The simulation results contrasted with those from the conventional HASRs and showed how the suggested reactor performs better.

Azarhoosh et al. [5] presented two scenarios for the simulation and optimization of a horizontal ammonia synthesis reactor: the first involves an intercooled reactor, and the second involves a reactor with two quench flows. For the catalyst pellets that were employed in the simulations, the one-dimensional heterogeneous mathematical model consisted of two point boundary value differential equations. The impact of variables, including the operating pressure, total feed flow rate, and intake temperature, on the ammonia production then investigated. Finally, a genetic algorithm is used to select the best solutions for

the highest mass flow rate of the production of ammonia. The results of the optimization show that the maximum ammonia mass fluxes of 52433 $kg.hr^{-1}$ and 73979 $kg.hr^{-1}$ were produced in the two cases, in which the inlet temperature, feed flow rate, and operating pressure were524 °C, 217005 $kg.hr^{-1}$ and 167 atm for the first case and 437 °C, 354986 $kg.hr^{-1}$ and 237 atm for the second one.

Tripodi et al. [6], carried out a modelled ammonia synthesis over different iron- and ruthenium-based catalysts with appropriate rate models, used for the simulation of the process under different configurations and conditions. Simulated kinetic models have been validated using experimental data. The design of a scaled-up reactor began with a once-through configuration. We carried out a sensitivity study on this model reactor to improve the reaction conditions. Then, by sizing an ammonia separation unit and optimizing the recycling loop, we were able to contrast several design options. Then, in order to maximize the ammonia production, a multibed catalytic reactor with intercooling was built, using either the same catalyst or different types of catalysts. In particular, Fe-based catalysts were followed by the Ru/C one, to push the ammonia productivity towards the equilibrium value. The aim of the initiative is to design an ammonia synthesis loop that combines various catalysts to maximize productivity and reduce installation and operating costs.

Shamiri and Aliabadinia [7] used a heterogeneous model to improve three adiabatic catalyst beds in an industrial ammonia synthesis reactor. The diffusion-reaction equation was taken into account when calculating the effectiveness factor in this model. Regarding the component mole fraction and temperature of the reactor, there was a respectable level of agreement between simulation findings and industrial data. This mathematical model was modified to improve the performance of the ammonia converter and predict the effectiveness factors, fractional nitrogen conversion, temperature, and hydrogen and ammonia mole fraction profiles. By altering the operational parameters of the reactor and observing their impacts on the reactor output, the competency of the updated model has been studied for the industrial use. The results showed the reliability of the produced model. On the basis of the equilibrium curve for the ammonia synthesis reaction, the model is used to determine the ideal temperature profiles for each catalyst bed in the reactor. By adjusting the reactor quench valves, the operating conditions of the reactor were altered to provide the optimal temperature profile in accordance with the results of the model. After implementing changes in the reactor, the reactor performance and its efficiency have improved by increasing the ammonia conversion from 15.26 % to 15.45 %, which increases the ammonia production by 3t/d, and the energy saving by 1.66 Gj/h. The differential temperature of the first catalyst bed increased dramatically by 6 °C, and the overall differential temperature through the ammonia converter increased by around 4 °C. This increases the steam production by 2t/h through the loop boiler.

Mirvakili et al. [8] have investigated a three-bed ammonia reactor with the radial-axial flow and two heat exchangers in the center. This reactor differs from the previous generation in terms of the fluid regime type which had a two-dimensional axial-radial flow and intercooler. The fluid flow, concentration, and temperature profiles through the reactor can be predicted using two-dimensional mathematical modeling. The Navier-Stokes, mass, and heat

partial differential equations are solved simultaneously via orthogonal collocation on the finite element. When the results were compared to industrial data, a good agreement was found.

Matos et al. [9] proposed a reactor for the synthesis of the ammonia optimization model. Nitrogen and hydrogen are the reactants in the reversible exothermic reaction, which is occurring at high temperatures and pressures with an iron catalyst. The maximizing of the economic return and the maximization of nitrogen conversion were two different single-objective optimization issues that were taken into consideration. The partial pressures of the components were used to define the reaction rate of the model. The problem was coded and solved in MATLAB using a derivative-free method after reformulating a constrained optimization problem into an unconstrained one, by penalizing the infeasibilities of the constraints in the objective functions (barrier function). The evaluation of the maximal ammonia production, the temperature profile, and the combination of direct-search methods in solving the optimization problem are the primary contributions of this research.

Farsi et al. [10], investigated ammonia synthesis reactors, methanation reactors, low and high temperature shift converters, steam and autothermal reforming reactors, and hydrogen purification section.. Based on the mass and energy balance equations and taking into account the heat and mass transfer resistances in the gas and catalyst phases, the catalytic reactors are heterogeneously modeled. The absorption column is additionally simulated using an equilibrium model. The accuracy of the proposed framework is then assessed using plant data. The results show that the internal mass transfer resistance in the commercial catalyst limits the syngas production in the reforming section. The second phase involves formulating an optimization problem to increase the ammonia production while taking operating and safety constraints into account. The formulated optimization problem is handled by employing the genetic algorithm. The results show that more syngas production in the optimized hydrogen unit is one of the main reasons for more ammonia synthesis in the considered plant. Applying optimal conditions to the process increases the ammonia production from 1890 to 2179 mol/s.

Burrows and Bollas [11] modelled a cutting-edge, massive ammonia production system in Aspen Plus that was transformed into a flow-driven model in Aspen Dynamics to serve as a guide. Using consistent length to diameter ratios for the reactors, the reference model was then scaled down to 10 % of its original capacity. Both models were then subjected to disturbances in the temperature, flow rate, and natural gas input of the reactors. In the small-scale model, a 5 % pulse in the natural gas flow rate is shown to cause 100 °C swings in reactor temperature and 550 kmol/h swings in reactor flow rate, while the reference model remains stable. The need for decoupled ammonia synthesis pathways that enable the independent control of the extent of reactions and, consequently, their heat generation or consumption, is discussed in our conclusion. Nikzad et al. [12] used computational fluid dynamics to simulate the two-dimensional ammonia tubular and three configurations of spherical radial flow reactors. To support the accuracy of the indicated model, the tubular reactor findings are validated using experimental data under the same conditions. The ability to use a higher flow rate and reduced pressure drop compared to the tubular configuration is one of the advantages of the

proposed topologies. The three proposed configurations include spherical reactors with four feed inputs (Config. 4F), six feed inputs (Config 6F), and eight feed inputs (Config. 8F). The simulation results also show that the nitrogen conversion rates in the recommended configurations have improved by 20.96 %, 20.28 %, and 19.66 %, respectively. The spherical radial flow reactor with four feed inlets has the best performance among the provided configurations. Furthermore, the effect of process parameters, including the flow scale-up ratio and outlet temperature of intermediate coolers, on the conversion of nitrogen has been investigated.

The amount of the energy consumption in the ammonia production unit is very high, so that to produce one ton of ammonia, 50-53 Gj energy is required [13].

Panjeshahi et al. [14] simulated the ammonia synthesis unit and optimized the unit energy. Providing correction plans in the unit is leading to storage of 6076 kW energy in the unit.

Sunny et al. [15] simulated the synthesis part of the ammonia production process, of which the feed was changed from naphtha to the R-LNG fuel that is cleaner and cheaper, and slightly reduces the energy consumption.

Sahafzadeh et al. [16] integrated a gas turbine with the process of the ammonia production to generate electricity and reduce the exergy loss associated with the synthesis unit, reduced the amount of exergy loss of the heat exchange process significantly from 9027.43 kW to 3433.14 kW.

Flórez-Orrego and de Oliveira Junior [17] presented an exergy modeling and optimized an industrial ammonia unit based on the steam methane reforming (SMR) process. The base-case unit produces about 1000 t NH_3/day. Some critical parameters of the operation are analyzed, and the base-case and optimal operating conditions of the major components are compared. Since the ammonia synthesis process is highly exothermic, higher per-pass conversions in industrial adiabatic reactors are often achieved using various sequential catalyst beds, where a near-optimum profile of the reaction rate vs. temperature can be attained by regulating the inlet temperature of each bed. This is performed via internal heat recovery, either by preheating the reactor feed gas or by using waste heat boilers, which results in an increase of the steam production and a smaller fuel consumption. But, although such near-optimum operation conditions may lead to higher reaction rates and, thus, lower the volume of catalysts that to be required, it is found that the optimal design of the ammonia loop is instead determined by the performance of each component and their interdependencies. Moreover, since the proposed objective function (exergy destruction minimization) is susceptible to specific process variables, the convergence of the solution algorithm is sometimes hindered. The exergy destruction breakdown shows that the ammonia converter and the refrigeration system are together responsible for more than 71-82 % of the total exergy destruction in the ammonia loop, which in turn varies between 25.6 and 38.8 MW for optimal and base-case operation conditions respectively.

Chen et al. [18] proposed a design for the first time for an entire ammonia synthesis system consisting of a heat recovery reactor to heat supercritical steam and a preconditioning system to preheat the feed gas at a sufficiently high temperature. The structural (wall) material cost of the system may be relatively high due to the use of a high-temperature creep-resistant material. Thus, the focus of this study is on minimizing the volume of the wall

material. A parametric analysis has been performed to investigate the effects of the diameter, mass flow rate, and inlet temperature on the reactor wall volume for each component of the system The results show that a smaller tube diameter is preferred because it enhances the heat transfer and thereby reduces the reactor size. The results also show the necessity of optimizing the entire system simultaneously because of the interactions between different components. An optimization algorithm is used to design the whole synthesis system with the minimum volume of the wall material per the power delivered to the steam. The results show that preconditioning the system plays a vital role in the required volume of the wall. A modular system design, which subdivides the heat recovery reactor into different sections, is also proposed to tailor the plan to local conditions. The modular design is shown to reduce the volume of the wall material.

Chen et al. [19] proposed an autothermal heat recovery reactor (AHRR), which can not only heat the working fluid but preheat the feed gas simultaneously with the ammonia synthesis. A model is proposed to simulate the heating of the working fluid, e.g., CO_2, and the feed gas in an AHRR. Based on the model results, the AHRR not only requires a less volume of catalysts but has the potential to cause lower heat losses than the previous system. The research shows the model is the most sensitive one to the activation energy of the catalyst E_a. A parametric study has been performed to investigate the effects of diameters, mass flow rates, and inlet gas temperature for reaction on the volume of the reactor wall of the AHRR. The results show that smaller diameters of the centeral tube and outer annulus are preferred for reducing the reactor size due to the enhanced heat transfer for the secondary flows. But the thiner catalyst bed is not selected because of the more significant pressure drop. Increasing the CO_2 mass flow rate also reduces the reactor size by enhancing the heat transfer. Although increasing the inlet gas temperature for the reaction decreases the reactor size as well as the required pumping power, there is a trade-off between reducing the reactor size and increasing the size of the heat exchanger for preheating the feed gas. The study provides a baseline for the further optimization, including the economic analysis.

Ishaq and Dincer [20] proposed a new configuration for synthesizing pure ammonia using clean hydrogen produced by renewables. The proposed system mainly consists of a proton exchange membrane electrolyzer, pressure swing adsorption unit, compressor, ammonia synthesis reactors, and condenser. The designed configuration uses a cascaded approach for the ammonia synthesis by employing two reactors in series to achieve high conversion ratios and reduce the recycle loops. The proposed system is simulated using the industrial software of Aspen Plus V11 and Aspen adsorption V11 and the obtained results are discussed in detail. The designed system is investigated under different operating conditions. In the Aspen Plus simulation, both stoichiometric and Gibbs reactors are installed alternatively to investigate the ammonia synthesis process in depths and to establish the effect of temperature and pressure on the ammonia production capacities. The maximum exergy destruction rate of 65.43 kW is delivered by the primary ammonia synthesis reactor.

In this study, first the ammonia synthesis unit was simulated in the AspenHysys. V11 software, then with the help of the design of the experiments method, which has received a

lot of attention in recent years [21-26], a statistical relationship between independent variables and the amount of the ammonia production was obtained. Finally, the optimal values of the independent variables to produce the maximum amount of ammonia were finally obtained under optimum conditions.

2. Methodology

2.1. Simulation

We, in here, consider the ammonia synthesis process as given in Figure 1, which is a simplified version of an actual industrial plant. Hydrogen and nitrogen are fed to the process at the molar ratio of 3:1, along with a small concentration of inerts (methane and argon). In the synthesis reactor, the following exothermic equilibrium reaction 1 takes place [27]:

$$N_2 + 3H_2 \Leftrightarrow 2NH_3 \qquad (1)$$

The catalysts used commercially are Fe based, formerly obtained from magnetite oxide (Fe_3O_4) [28-31] and later from wustite ($Fe_{1-x}O$) [32] or Fe-Co [33]. Different Ru/C based materials are exploited in the Kellogg advanced ammonia process (KAAP) [34-42]. For the equilibrium of ammonia synthesis reaction, obtained the coefficients of Equation (2) which show the equilibrium constant of the reaction [43].

$$\mathrm{LnK} = 8.790 + \frac{4682}{\mathrm{T}} - 3.218\ln \mathrm{T} + 1.288 \times 10^{-3}\mathrm{T} \qquad (2)$$

where T is the temperature in K. The simplified reactor model is shown in Figure 1. It consists of three adiabatic catalytic reactors (beds) in sequence, with the preheating of the feed with the reactor effluent between stages, and the interstage cooling. The direct mixing of the cold reactor feed with the appropriate input flow with each bed provides the interstage cooling. Three heat exchangers, of which the first (H-501) uses the hot reactor gases to produce low pressure steam, are used to quench the reactor effluent.. The third heat exchanger (H-583) cools the ammonia condensation stage in the separator while the second heat exchanger (H-502) pre-heats the reactor feed (V-502). About 97 % (w/w) of the ammonia product (the end product) exits the process as a liquid stream through the separator bottom. To prevent the buildup of inerts (methane and argon) in the system, a small flow is purged from the separator, and any leftover exhaust gas flow from the separator is recycled to the unit [27].

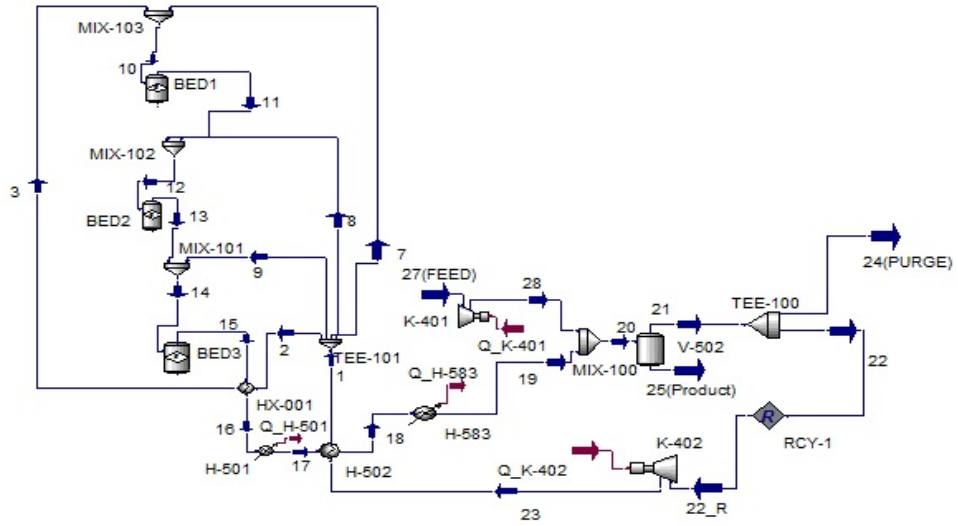

Figure 1. Ammonia synthesis flowsheet.

2.2. Design of experiments

The design of experiments includes an experiment or a series of experiments that consciously make changes in process input variables to observe and identify the extent of changes in the process output response. In this research, the central composite design (CCD) method has been used on five levels. The advantage of this method over other methods is that it is an economical method and does not require much data for modeling. To express a mathematical relationship between dependent and independent variables, data must first be collected using experiments or precise simulations, and then the regression analysis is used to examine the relationship between the response variable and the factors affecting the response. To analyze the regression and determine the regression model and estimate the model parameters, the least squares method, according to Equation (3), can be used [44]:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad (3)$$

In Eq (3), β is the matrix of coefficients, ε is the error value, x is the independent variable, y is the dependent variable, and i, j and k are the numerators of the independent variables.

3. Results and discussion

3.1. Simulation

The steady-state ammonia synthesis is simulated using Aspen Hysys V.11 software. The SRK equation is used to calculate the physical properties [45]. The simulation results in Table (1) have been compared and validated with industrial data.

Table 1
Validation of the liquid streaming the separator bottom.

Parameters	Design	Simulation	Deviation (%)
T (°C)	40.4	40.8	1
P (bar)	195.3	195.0	0.14
$\mathbf{N_2}\ (\frac{\mathbf{kmol}}{\mathbf{h}})$	21.26	19.28	9.3
$\mathbf{H_2}\ (\frac{\mathbf{kmol}}{\mathbf{h}})$	57.71	42.32	27
$\mathbf{NH_3}\ (\frac{\mathbf{kmol}}{\mathbf{h}})$	4041.66	3997.54	1.1

3.2. Design of experiments

In order to enable and justify flexible regulatory paths for manufacturing and innovations, multivariate mathematical approaches like the statistical design of experiments, response surface methodologies, process simulations, and pattern recognition tools are used. Researcher can find the important components of a large-scale simulation with a relatively short number of runs by using screening designs that are commonly utilized in the early stages of researches and developments. In order to create a model with an emphasis on finding the active main effects and the interaction between factors, researchers must first screen the inputs in an experimental design of the least resolution. The Plackett-Burman method

enables the simultaneous consideration of many parameters. The number of model scenarios needed to do the analysis is roughly twice as many as the number of parameters [46-53]. In this paper, four effective variables were selected from 11 independent variables by the Plackett-Burman method. In this study, the Plackett-Burman method was performed once in the presence of factor A (the Hydrogen flow in the feed stream) and once without considering factor A (the Hydrogen flow in the feed stream), of which the results are given in Table (2). One of the common methods for designing experiments is the central composite method (CCD). This method is performed in 5 levels +α, +1, 0, -1 and -α, which are designed for +1 and -1 points on the surfaces, 0 central points and +α and -α axial points respectively [54]. In this work, the Design-Expert V.10 software has been used to design experiments. Table (3) shows the levels selected for the independent variables in the CCD method. Table (4) also shows the experiments performed and the resulted amount of the ammonia production for each test.

Table 2
Result of the Plackett-Burman method.

Factor	Contribution with A (%)	Contribution without A (%)
Hydrogen flow in the feed stream (A)	76.69	0
Feed stream pressure (B)	6.84	18.632
Recycle stream pressure (C)	1.61	3.012
Feed stream temperature (D)	1.36	7.932
Temperature of excess stream inlet the first reactor (E)	0.36	14.942
Pressure of stream inlet the first reactor(F)	1.99	5.782
Pressure of stream inlet the second reactor(G)	0.67	0.632
Pressure of stream inlet the third reactor(H)	2.73	0.912
Temperature of stream inlet the second reactor(J)	4.42	35.062
Temperature of stream inlet the third reactor(K)	0.21	12.702
Waste stream to recycle stream ratio(L)	3.13	0.38571

Table 3
Levels and experiments ranges of a factor or independent variable.

Factor	Range and levels				
	−α	-1	0	1	+α
A	6120	6165	6210	6255	6300
B	190	195	200	205	210
E	612	629	646	663	680
J	670	677.5	685	692.5	700

Table 4
The natural values and outcomes of the experiments design matrix.

Run	A ($\frac{\text{kmol}}{\text{h}}$)	B (bar)	E (K)	J (K)	Y ($\frac{\text{kmol}}{\text{h}}$)
1	6255	205	629	692.5	10881.3
2	6210	200	646	685	10761.8
3	6210	210	646	685	10948.7
4	6210	200	680	685	10929.9
5	6255	205	663	692.5	11045.5
6	6210	200	646	685	10761.8
7	6165	195	629	677.5	10607.9
8	6210	200	646	685	10761.8
9	6210	200	646	685	10761.8
10	6255	195	663	692.5	10818.2
11	6210	200	646	685	10761.8
12	6165	195	629	692.5	10433.6
13	6165	195	663	692.5	10587.8
14	6210	200	646	685	10761.8
15	6300	200	646	685	11357.4
16	6210	200	646	670	10941.1
17	6255	195	663	677.5	10998.6
18	6165	205	663	692.5	10609.4
19	6165	205	663	677.5	10788
20	6255	195	629	692.5	10646.8
21	6210	200	612	685	10468.1
22	6165	205	629	677.5	10749.5
23	6255	205	629	677.5	11058.5
24	6165	205	629	692.5	10572.9
25	6255	195	629	677.5	10822.7
26	6120	200	646	685	10537.7
27	6210	190	646	685	10738.4
28	6165	195	663	677.5	10766.1
29	6255	205	663	677.5	11227.2
30	6210	200	646	700	10699

3.3. Analysis of variance

Equation (6) show the production of ammonia:

$$Y = +1.07570 \times 10^{6} - 289.02996A - 1121.49550B - 2.29275E - 191.27611J + 0.16721AB + 0.023923AE - 1.39630 \times 10^{-3}AJ - 0.18512BE - 8.33333 \times 10^{-3}BJ - 7.31373 \times 10^{-3}EJ + 0.019711A^{2}0.55593B^{2} - 0.076901E^{2} + 0.14288J^{2} \quad (6)$$

In Equations (6), A is the Hydrogen flow in the feed stream ($\frac{\text{kmol}}{\text{h}}$), B is the feed stream pressure (bar), E is the temperature of the excess stream inlet in the first reactor (K), J is the temperature of the stream inlet in the second reactor (K) and Y is the ammonia

production ($\frac{\text{kmol}}{\text{h}}$). Figure (2) shows the correlation between the actual values and the predicted values. As you can see, the predicted values correspond very well to the actual values.

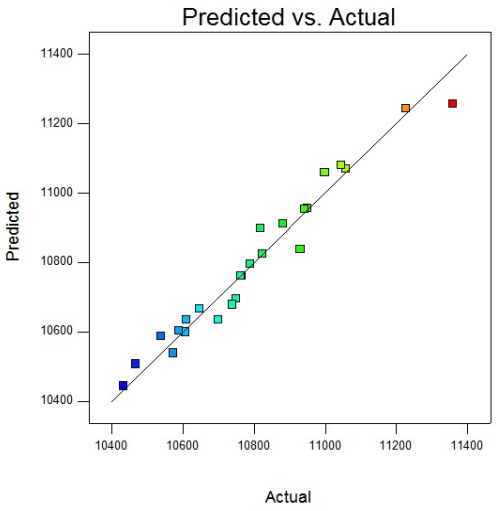

Figure 2. Plot of the predicted response vs. the ammonia production.

According to Equation (7), the F-Value used for the analysis of variance is defined as the ratio of the mean squares of the effect ($\text{MS}_{\text{effect}}$) to the mean squares of the error (MS_{error}) [55].

$$\text{F} = \frac{\text{MS}_{\text{effect}}}{\text{MS}_{\text{error}}} \tag{7}$$

According to Fisher calculations, a parameter is, which has a value of less than 0.05 for effective factors, is defined as P-Value. [55]. Tables (5) show the F-Values and P-Values for the obtained model. The simplified model (equation 6) was presented based on Table 5.

$$\begin{aligned}\text{Y} = {} & +8.68527 \times 10^{5} - 257.71520\text{A} - \\ & 1024.41983\text{B} + 116.49471\text{E} - \\ & 10.59589\text{J} + 0.16721\text{AB} + \\ & 0.018357\text{A}^2 - 0.086388\text{E}^2\end{aligned} \tag{8}$$

3.4. Analysis of the dependence of the ammonia production on independent variables

As shown in Figure 3 and Figure 4, according to the results obtained in the reference [56] by increasing the injection of fresh hydrogen feed, increasing the feed stream pressure, increasing the temperature of the excess stream inlet in the first reactor and decreasing the temperature of the stream inlet in the second reactor, the ammonia production increases.

Table 5

The effectiveness of the selected variables on the amount of the ammonia production.

Variable	F-Value	P-Value
Model	26.75	< 0.0001
A	208.77	< 0.0001
B	36.03	< 0.0001
E	51.16	< 0.0001
J	46.93	< 0.0001
AB	7.01	0.0183
AE	1.66	0.2172
AJ	1.1×10^{-3}	0.9740
BE	1.23	0.2855
BJ	4.838×10^{-4}	0.9827
EJ	4.307×10^{-3}	0.9485
$\mathbf{A^2}$	13.53	0.0022

$\mathbf{B^2}$	1.64	0.2197
$\mathbf{E^2}$	4.19	0.0585
$\mathbf{J^2}$	0.55	0.4704

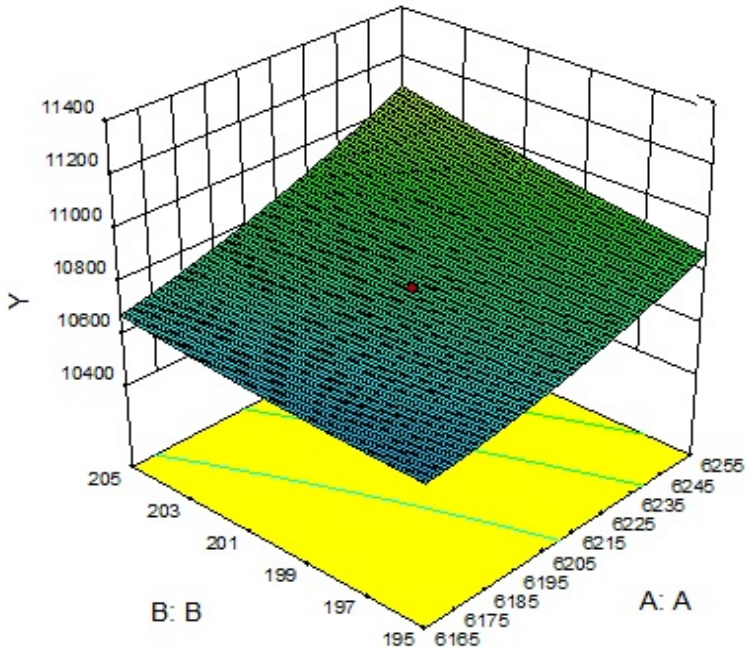

Figure 3. Effect of the hydrogen feed flow and the feed stream pressure on the ammonia production.

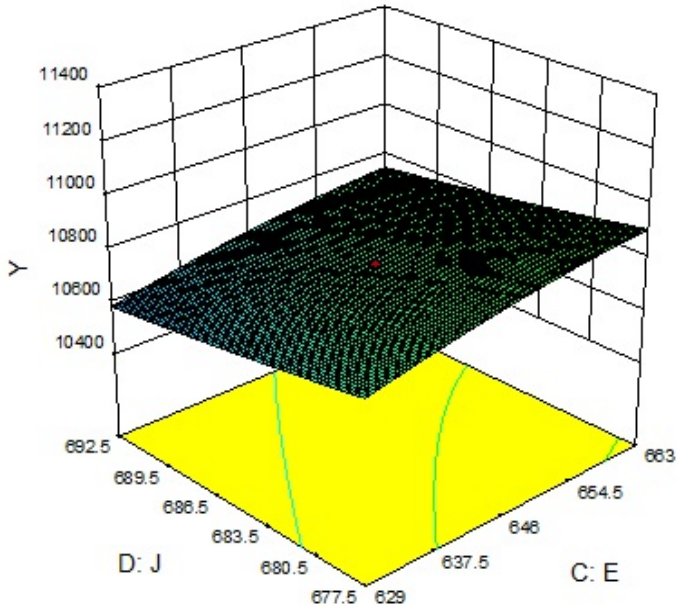

Figure 4. Effect of the temperature of the excess stream inlet in the first reactor and the temperature of the stream inlet in the second reactor on the ammonia production.

3.5. Optimization

In the present study, the optimal feed pressure was increased to 205 bar. According to the results obtained in the reference [56-57],

increasing the pressure also increases the equilibrium conversion rate and increases the ammonia production. In the ammonia production reaction, the H_2/N_2 ratio should not be less than 2.5. Also, increasing the amount of hydrogen leads to the movement of the equilibrium reaction towards the production of ammonia [57-58]. The optimal hydrogen flow in the feed stream in this study is 6255 $\frac{\text{kmol}}{\text{h}}$. According to the study done by Khademi et al., when the temperature of the feed gas in the first reactor is equal to 635 K, the maximum conversion for nitrogen is achieved [59]. In this study the optimal temperature of the stream inlet in the first reactor is 614 K (The temperature of the excess stream inlet in the first reactor is 663 K and the temperature of the mix stream inlet in the first reactor is 505 K). Table (6) shows the optimal values of the operating parameters for maximizing the amount of the ammonia production (the objective function of Equation (6)).

As shown in Figure 5, with the optimal value, the ammonia production increased from 10231 $\frac{\text{kmol}}{\text{h}}$ to 10998 $\frac{\text{kmol}}{\text{h}}$.

Table 6
Optimal operating parameters of the ammonia synthesis.

Parameters	Lower bound	Upper bound	Current value	Optimal value
$A\ (\frac{kmol}{h})$	6120	6300	6123.66	6255
B (bar)	190	210	196.3	205
E (K)	612	680	613.3	663
J (K)	670	700	674.3	677.5

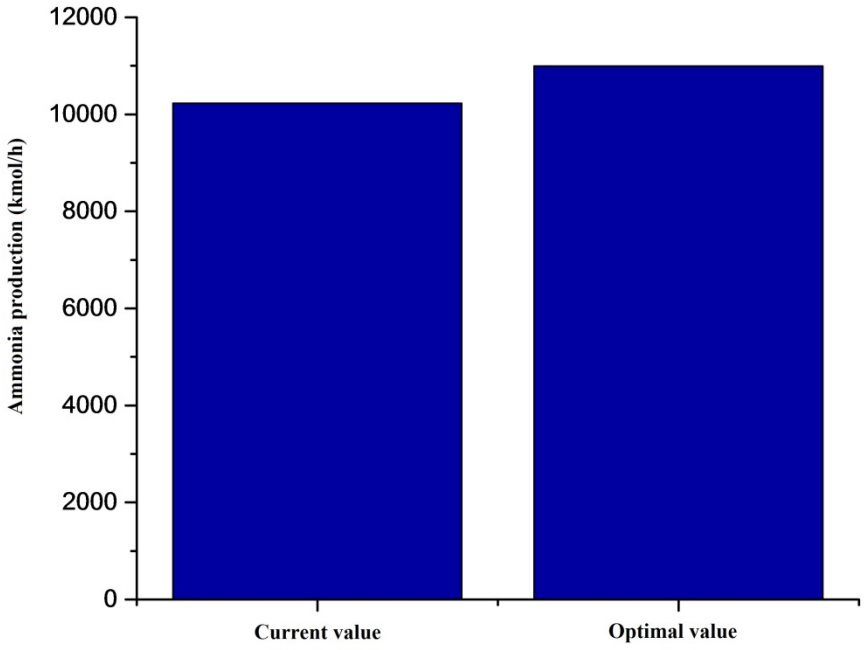

Figure 5. Compare the current value and optimal value for the ammonia production.

4. Conclusions

The simulation of the ammonia synthesis unit and the design of experiments by the response level design method of the central composite design using Design Expert software (v.10) and the analysis of the diagrams obtained high accuracy modeling and also the great effect of selected parameters showed the amount of the ammonia production. The results showed that 2.14 % increase in the Hydrogen flow in the feed stream, 4.43 % increase in the feed stream pressure, 8.10 % increase in the temperature of the excess stream inlet in the first reactor and 0.47 % increase in the temperature of stream inlet in the second reactor,consequently increased the production of ammonia by 7.5 %.

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Nomenclature

A	hydrogen flow in the feed stream $[\frac{\text{kmol}}{\text{h}}]$.
B	feed stream pressure [bar].
C	recycle stream pressure [bar].
D	feed stream temperature [K].
E	temperature of excess stream inlet the first reactor [K].
F	pressure of stream inlet the first reactor [bar].
G	pressure of stream inlet the second reactor [bar].
H	pressure of stream inlet the third reactor [bar].
i	numerators of the independent variables.
J	temperature of stream inlet the second reactor [K].
j	numerators of the independent variables.
K	temperature of stream inlet the third reactor [K].
L	waste stream to recycle stream ratio.
T	temperature [K].
x	independent variable.
Y	amount of ammonia production $[\frac{\text{kmol}}{\text{h}}]$.
y	dependent variable.
β	matrix of coefficients.
ε	error value.

References

[1] Aika, K. I., Christiansen, L. J., Dybkjaer, I., Hansen, J. B., Højlund Nielsen, P. E., Nielsen, A., Stoltze, P. and Tamaru, K., Ammonia: Catalysis and manufacture, Springer Science & Business Media, (2012).

[2] Yagmurlu, B., Dittrich, C. and Friedrich, B., "Effect of aqueous media on the recovery of scandium by selective precipitation", *Metals*, **8** (5), 314 (2018).

[3] Babu, B. V. and Angira, R., "Optimal design of an auto-thermal ammonia synthesis reactor", *Computers & Chemical Engineering*, **29** (5), 1041 (2005).

[4] Farivar, F. and Ebrahim, H. A., "Modeling, simulation, and configuration improvement of horizontal ammonia synthesis reactor", *Chemical Product and Process Modeling*, **9** (1), 89 (2014).

[5] Azarhoosh, M. J., Farivar, F. and Ebrahim, H. A., "Simulation and optimization of a horizontal ammonia synthesis reactor using genetic algorithm", *RSC Advances*, **4** (26), 13419 (2014).

[6] Tripodi, A., Compagnoni, M., Bahadori, E. and Rossetti, I., "Process simulation of ammonia synthesis over optimized Ru/C catalyst and multibed Fe+ Ru configurations", *Journal of Industrial and Engineering Chemistry*, **66**, 176 (2018).

[7] Shamiri, A. and Aliabadi, N., "Modeling and performance improvement of an industrial ammonia synthesis reactor", *Chemical Engineering Journal Advances*, **8**, 100177 (2021).

[8] Mirvakili, A., Eksiri, Z., Biniaz, P. and

Mohaghegh, N., "Two-dimensional mathematical modeling of an industrial ammonia synthesis reactor with CFD analysis", *Journal of the Taiwan Institute of Chemical Engineers*, **121**, 1 (2021).

[9] Matos, K. B., Carvalho, E. P. and Ravagnani, M. A. S. S., "Maximization of the profit and reactant conversion considering partial pressures in an ammonia synthesis reactor using a derivative-free method", *The Canadian Journal of Chemical Engineering*, **99**, S232 (2021).

[10] Farsi, M., Chabi, N. and Rahimpour, M. R., "Modeling and optimization of ammonia process: Effect of hydrogen unit performance on the ammonia yield", *International Journal of Hydrogen Energy*, **46** (79), 39011-39022 (2021).

[11] Burrows, L. and Bollas, G., "Comparison of ammonia synthesis plants of different scale with a dynamic model", Computer Aided Chemical Engineering, Elsevier, Vol. 49, p. 901 (2022).

[12] Nikzad, A., Iranshahi, D., Ranjbaran, M. and Bagherpour-Ardakani, E., "Conceptual comparison of three novel configurations in the spherical radial flow reactor for ammonia production", *Fuel*, **321**, 123945 (2022).

[13] Lababidi, H. M., Alatiqi, I. M. and Nayfeh, L. J., "Energy retrofit study of an ammonia plant", *Applied Thermal Engineering*, **20** (15-16), 1495 (2000).

[14] Panjeshahi, M. H., Langeroudi, E. G. and Tahouni, N., "Retrofit of ammonia plant for improving energy efficiency", *Energy*, **33** (1), 46 (2008).

[15] Sunny, A. and Solomon, P. A., "Revamping of ammonia plant with R-LNG and simulation of syngas production using Aspen HYSYS", *Proceedings of International Conference on Gas, Oil and Petroleum Engineering (GOPE 2016)*, Organized by United Scientific Group, Las Vegas, USA, (November 2016).

[16] Sahafzadeh, M., Ataei, A., Tahouni, N. and Panjeshahi, M. H., "Integration of a gas turbine with an ammonia process for improving energy efficiency", *Applied Thermal Engineering*, **58** (1-2), 594 (2013).

[17] Flórez-Orrego, D. and de Oliveira Junior, S., "Modeling and optimization of an industrial ammonia synthesis unit: An exergy approach", *Energy*, **137**, 234 (2017).

[18] Chen, C., Lovegrove, K. M., Sepulveda, A. and Lavine, A. S., "Design and optimization of an ammonia synthesis system for ammonia-based solar thermochemical energy storage", *Solar Energy*, **159**, 992 (2018).

[19] Chen, C., Zhao, L., Kong, M. and Lavine, A. S., "Heat recovery from an autothermal ammonia synthesis reactor for solar thermochemical energy storage", *Solar Energy*, **176**, 256 (2018).

[20] Ishaq, H. and Dincer, I., "Design and simulation of a new cascaded ammonia synthesis system driven by renewables", *Sustainable Energy Technologies and Assessments*, **40**, 100725 (2020).

[21] Kalantari, H., Nosrati, M., Shojaosadati, S. A. and Shavandi, M., "Optimization of factors affecting on sulfide oxidation from synthetic spent caustic by Haloalkaliphilic Thioalkalivibrio versutus by focus on sodium ion effect: Application of response surface methodology", *Iranian Journal of Chemical Engineering (IJChE)*, **14** (1), 74 (2017).

[22] Alihemati, Z. and Navarchian, A. H., "Response surface methodology for

investigating the effects of hydrolysis reaction parameters on molecular structure and performance of polyvinyl alcohol as primary suspending agent", *Iranian Journal of Chemical Engineering (IJChE)*, **14** (1), 52 (2017).

[23] Ahmadpour, A., Haghighiasl, A. and Fallah, N., "Investigation of spent caustic wastewater treatment through response surface methodology and artificial neural network in a photocatalytic reactor", *Iranian Journal of Chemical Engineering (IJChE)*, **15** (1), 46 (2018).

[24] Arinkoola, A., Salawudeen, T., Salam, K., Jimoh, M., Atitebi, Z. and Abidemi, G., "Optimization of water based drilling fluid produced using modified Nigerian bentonite and natural biopolymers: Reduced experiment and Response Surface Methodology", *Iranian Journal of Chemical Engineering (IJChE)*, **16** (1), 39 (2019).

[25] Abbasi, P., Shayesteh, K., Vahidfard, V. and Hosseini, M., "Optimization and comparison of Ni and Cd removal using zinc powder with the Response Surface Methodology", *Iranian Journal of Chemical Engineering (IJChE)*, **17** (4), 3 (2020).

[26] Panahadeh, A., Parvareh, A. and Moraveji, M., "Optimization of the adsorption of Pb(II) and Zn(II) onto the EDTA-modified MnO_2/Chitosan/Fe_3O_4 nanocomposite from an aqueous solution using RSM according to the CCD method", *Iranian Journal of Chemical Engineering (IJChE)*, **18** (3), 33 (2021).

[27] Araújo, A. and Skogestad, S., "Control structure design for the ammonia synthesis process", *Computers & Chemical Engineering*, **32** (12), 2920 (2008).

[28] Gaube, J., Fertilizer science and technology series, Vol. 2, Ammonia, part III, Slack, A. V. and James, G. R. Eds., Marcel Dekker Inc., New York, Basel 1977, 459 Seiten, Preis: SFr 222, (1980).

[29] Jennings, J. R., Catalytic ammonia synthesis: Fundamentals and practice, Springer, (1991).

[30] Nielsen, A., Ammonia: Catalysis and manufacture", Springer, Heidelberg, Berlin, (1995).

[31] Liu, H., Ammonia synthesis catalysts: Innovation and practice, World Scientific, (2013).

[32] Pernicone, N., Ferrero, F., Rossetti, I., Forni, L., Canton, P., Riello, P. and Pinna, F., "Wustite as a new precursor of industrial ammonia synthesis catalysts", *Applied Catalysis A: General*, **251** (1), 121 (2003).

[33] Liu, H., "Ammonia synthesis catalyst 100 years: Practice, enlightenment and challenge", *Chinese Journal of Catalysis*, **35** (10), 1619 (2014).

[34] Rossetti, I., Pernicone, N. and Forni, L., "Promoters effect in Ru/C ammonia synthesis catalyst", *Applied Catalysis A: General*, **208** (1-2), 271 (2001).

[35] Liang, C., Wei, Z., Xin, Q. and Li, C., "Ammonia synthesis over Ru/C catalysts with different carbon supports promoted by barium and potassium compounds", *Applied Catalysis A: General*, **208** (1-2), 193 (2001).

[36] Rossetti, I., Pernicone, N. and Forni, L., "Characterisation of Ru/C catalysts for ammonia synthesis by oxygen chemisorption", *Applied Catalysis A: General*, **248** (1-2), 97 (2003).

[37] Rossetti, I. and Forni, L., "Effect of Ru loading and of Ru precursor in Ru/C catalysts for ammonia synthesis", *Applied*

Catalysis A: General, **282** (1-2), 315 (2005).

[38] Rossetti, I., Pernicone, N. and Forni, L., "Graphitised carbon as support for Ru/C ammonia synthesis catalyst", *Catalysis Today*, **102**, 219 (2005).

[39] Rossetti, I., Pernicone, N., Ferrero, F. and Forni, L., "Kinetic study of ammonia synthesis on a promoted Ru/C catalyst", *Industrial & Engineering Chemistry Research*, **45** (12), 4150 (2006).

[40] Rossetti, I., Mangiarini, F. and Forni, L., "Promoters state and catalyst activation during ammonia synthesis over Ru/C", *Applied Catalysis A: General*, **323**, 219 (2007).

[41] Truszkiewicz, E., Raróg-Pilecka, W., Schmidt-Szałowski, K., Jodzis, S., Wilczkowska, E., Łomot, D. and Kowalczyk, Z., "Barium-promoted Ru/carbon catalyst for ammonia synthesis: State of the system when operating", *Journal of Catalysis*, **265** (2), 181 (2009).

[42] Tripodi, A., Conte, F. and Rossetti, I., "Process intensification for ammonia synthesis in multibed reactors with Fe-wustite and Ru/C catalysts", *Industrial & Engineering Chemistry Research*, **60** (2), 908 (2021).

[43] Pakzad, P., "Integration of a novel ammonia synthesis process with ORC cycle as a waste heat recovery unit: Energy and exergy analysis", Proceedings of *8th International Conference on Chemistry, Chemical Engineering and Petroleum*, Tehran, Iran, (2021).

[44] Davoodbeygi, Y. and Irankhah, A., "Nanostructured CeCu mixed oxide synthesized by solid state reaction for medium temperature shift reaction: Optimization using response surface method", *International Journal of Hydrogen Energy*, **43** (49), 22281 (2018).

[45] Shacham, M. and Brauner, N., "A hundred years of chemical equilibrium calculations–The case of ammonia synthesis", *Education for Chemical Engineers*, **13**, 17 (2015).

[46] Beres, D. L. and Hawkins, D. M., "Plackett–Burman technique for sensitivity analysis of many-parametered models", *Ecological Modelling*, **141** (1-3), 171 (2001).

[47] Vanaja, K. and Shobha Rani, R. H., "Design of experiments: Concept and applications of Plackett Burman design", *Clinical Research and Regulatory Affairs*, **24** (1), 1 (2007).

[48] Bakonyi, P., Nemestóthy, N., Lövitusz, É. and Bélafi-Bakó, K., "Application of Plackett–Burman experimental design to optimize biohydrogen fermentation by E. coli (XL1-BLUE)", *International Journal of Hydrogen Energy*, **36** (21), 13949 (2011).

[49] Vani, S., Binod, P., Kuttiraja, M., Sindhu, R., Sandhya, S. V., Preeti, V. E. and Pandey, A., "Energy requirement for alkali assisted microwave and high pressure reactor pretreatments of cotton plant residue and its hydrolysis for fermentable sugar production for biofuel application", *Bioresource Technology*, **112**, 300 (2012).

[50] Lochmatter, S. and Holliger, C., "Optimization of operation conditions for the startup of aerobic granular sludge reactors biologically removing carbon, nitrogen, and phosphorous", *Water Research*, **59**, 58 (2014).

[51] Priyadharshini, S. D. and Bakthavatsalam, A. K., "Optimization of phenol degradation by the microalga Chlorella

pyrenoidosa using Plackett–Burman design and response surface methodology", *Bioresource Technology*, **207**, 150 (2016).

[52] Thirugnanasambandham, K., "Application of Plackett–Burman design to screen the effective process parameters for biodiesel production", *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, **40** (4), 453 (2018).

[53] da Silva, J. A., Braga, A. F., Fermoso, F. G., Zaiat, M. and Silva, G. H., "Evaluation of the influence of trace metals on methane production from domestic sewage, using the Plackett-Burman experimental design", *Journal of Environmental Management*, **294**, 113002 (2021).

[54] Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S. and Escaleira, L. A., "Response surface methodology (RSM) as a tool for optimization in analytical chemistry", *Talanta*, **76** (5), 965 (2008).

[55] Breig, S. J. M. and Luti, K. J. K., "Response surface methodology: A review on its applications and challenges in microbial cultures", *Materials Today: Proceedings*, **42**, 2277 (2021).

[56] Bolton, C. S., "Bermudagrass species response to microbial inoculants", Doctoral dissertation, University of Georgia, (2021).

[57] Hosseinzadeh, B. and Sadeghi, M. T., Optimization of ammonia synthesis reactor using genetic algorithm, (2008).

[58] Reddy, K. V. and Husain, A., "Modeling and simulation of an ammonia synthesis loop", *Industrial & Engineering Chemistry Process Design and Development*, **21** (3), 359 (1982).

[59] Khademi, M. H. and Sabbaghi, R. S., "Comparison between three types of ammonia synthesis reactor configurations in terms of cooling methods", *Chemical Engineering Research and Design*, **128**, 306 (2017).