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Statistical investigation of study the effects of different parameters on hexamine production using response surface methodology (RSM)

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Abstract

The current study was devoted to investigate experimentally and statistically the effects of different parameters on hexamine production in a bench-scale setup operating in a batch mode. The operating variables were varied in the range of (formaldehyde/ammonia) ratio =2 to 10; temperature = 20 to 80 ^{o}C; process time = 0 to 100 min). Experimental results revealed that a positive impact of (formaldehyde/ammonia) ratio on the production process was observed across the studied range, while temperature and time showed optimum values of 60 ^{o}C and 60 min, respectively for the optimum % yield of hexamine is 98%. Statistical analysis of the process showed that the Model F-value of 17.63 reveals the model's significance. While there is only a 0.01% chance that a "Model F-value" could come because of noise. Values of "Prob > F" less than 0.0500 point model codes are significant.

Keywords: Aqueous formaldehyde ; Central composite design ;Hexamine production; Liquid phase ;Statistical analysis.

1. Introduction

Hexamine is a white color crystal form powders, scentless with a slightly sugary savor **[1]**. It has a molecular formula: $(CH_2)_6N_4$ and a molecular weight of 140.19 g/mol **[2]**. Its chemical structure is shown in Figure 1**[3]**:

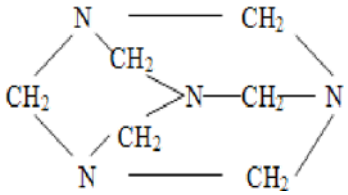


Fig. 1 Chemical structure of Hexamine [2, 3]

Hexamine has a highly steady framework making the molecule refractory to oxidation through methylotrophic mechanisms then few kinds of microorganisms in soil can degrade hexamine to use it as a starting origin of carbon, nitrogen, and energy **[4]**. As a result, hexamine is considered a resistible material for biodegradation **[5, 6]**, even when the sludge has been adapted for a long time **[7]** and it must be believed as an effective wastewater pollutant and should not be entered into the aquatic environment and soils **[8]**. Hexamine has a broad range of implementations in different areas. It is utilized as a stiffener in artificial resin, treating factor in phenolic plastic **[9]**, catalyst in amino plastic, vulcanization booster (H) in rubber manufacture and anti-retractability factor in textile production **[10]**. Moreover, it is utilized as a diuretic factor in medicines, antiseptic in food manufacture and raw substance for preparing numerous amino complexes, e.g., insecticide in cultivation. As well as, blended with sodium hydroxide and phenol naphthalene, it can be utilized as the assimilation factor of phosgene for anti- poisonous muzzle; when mixed with nitric acid, it can be employed to produce powerful explosives **[11, 12]**. Hexamine is produced by two pathways by liquid-phase method and by gas-phase one. Both methods utilize CH2O and NH3 as raw substances. In the liquid-phase procedure, 37% aqueous CH2O mixture is utilized to process with NH3 gas **[13]**. The prepared hexamine solution is demoistured by vaporizing, centrifuged, and dried to produce a rigid form output. Because of the quantity of steam expended in the vaporizing, intensification, and dehydrating operations, much energy is consumed **[14]**. This operation is outstanding in old-fashioned production methods and straightforward processes. Moreover, the particles diameter of the prepared hexamine is big due to the utilization of vaporizing gateway and long crystallization period. The chemical pathway liberates large quantity of energy and H_2O **[15, 16]**. Many published papers have been devoted to studying hexamine properties and the improvement of its production techniques. Anita Kovač

Kralj and Davorin Kralj **[17]** studied the kinetic determination of hexamine production in an aqueous solution of ammonia hydroxide and formaldehyde. Mahalakshmi and Selvaraju **[18]** studied the growth of a nonlinear optical crystal of hexamine by slow evaporation solution growth technique using deionized water at room temperature. The functional groups and vibrational frequencies were identified using the FTIR spectrum. The optical transmittance window and lower cutoff wavelength have been identified by double beam UV-absorption spectrum analysis **[19, 20]**. García et al. **[21]** revealed experimentally that hexamine can have various catalytic influences in the polycondensation of resorcinol furaldehyde to synthesize carbon cryogels. The producing carbons have a tunable framework that overrides what showed in the published data thanks to such decomposition reactions of hexamine when two solvent chemistries were used. Takayanagi et al. **[22]** determined experimentally the dissociation constant of hexamine by capillary Zone Electrophoresis. The present work was devoted to study experimentally and analytically the various operating parameters such as (temperature, reaction time, and the ratio of formaldehyde to ammonia) affecting the synthesis process of hexamine.

2. Material and Methods

2.1 Materials

The only chemicals needed are ammonium hydroxide (25%) and formaldehyde (37%) which were purchased from Sigma Aldrich, India. Distilled water supplied from the local market.

2.2 Experimental Setup

In this study, a 125 ml of ammonia (25%) is put in a separation funnel and 250 ml of formaldehyde (37%) is putted in a two holes bulb flask, the separation funnel that contains ammonia is allowed to drop a droplets of ammonia solution to the flask that contains formaldehyde (as shown in Figure 2), where the concentration, the volume of formaldehyde, rpm of the mixer and the pH value of the reaction are fixed. Different volume ratios of formaldehyde to the ammonia were taken (2:1 – 10:1) with a range of time and temperature (20-100 min), (20-100 ^{o}C) respectively. A heater is placed under the flask that contains formaldehyde solution to obtain the reaction temperature, one of the holes of the two holes bulb flask is connected to the separation funnel to allow the ammonia entrance (as shown in Figure 2), and the other hole is used to put a thermometer in it to determine the reaction temperature instantly. After the reaction is completed an evaporation process is started by using a heater (as shown in Figure 3) to get rid of water that is produced in the reaction and to obtain a saturated solution, a condenser is used in the other hole of the bulb flask to control the ammonia emissions to the environment during the evaporation process.

Fig. 2 Reactor setup

Fig. 2 Evaporation process

3. Experimental design method

The hexamine production process used RSM supplied via the "Design-Expert" version 7.00 software. A standard (RSM) design tool recognized as Central Composite Design (CCD) was employed for analyzing and getting a proper model for responses. Table 1 shows the experimental range and independent variable levels. A replicate of two was followed for each experimental run.

Table 1 Factors and their levels selected for the present study

Temperature ^{o}C	Ratio (formaldehyde to ammonia)	process time min
20	2	20
60	6	60

100	10	100

4. Results and Discussion

4.1 FTIR analysis

Figure 4 shows the FTIR spectra of formaldehyde (red line) and hexamine (blue line). These spectra have confirmed the production of Hexamine.

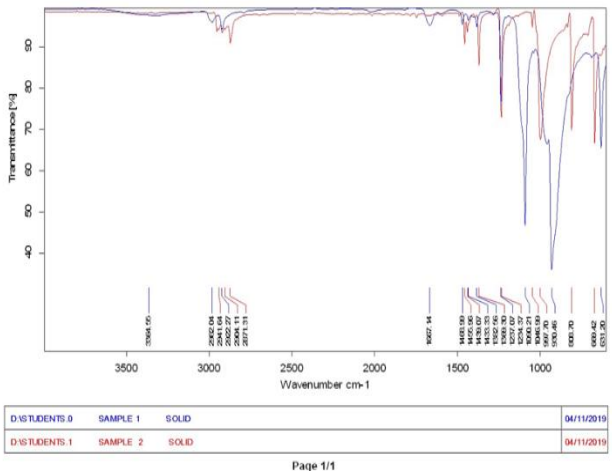


Fig. 4 FTIR spectra of formaldehyde (red line) and hexamine (blue line).

4.2 effect of operating variables on Hexamine Yield

The CCD technique has been used to explore the association between the process yield (Y %) and the process variables. Based on the regression analysis technique, the equations (1) and (2) below reveals the objective function (i.e., %Y) as a function of operating parameters. The three variables experiments with the objective function (%yield of hexamine) arranged according to the central composite design (CCD) is listed in Table 2.

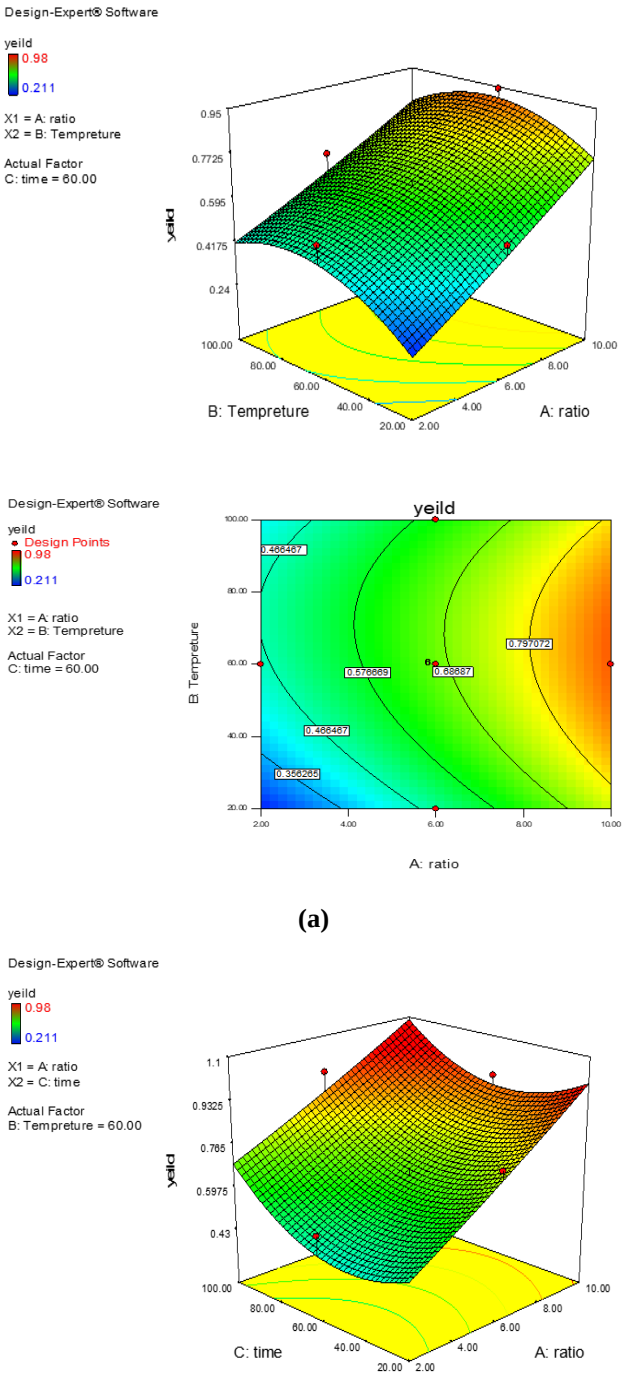
Table 2 The central composite design (CCD) with the response (percentage yield of hexamine)

Run No.	Operating parameter			Percentage Yield of Hexamine
	Ratio	Temperature (°C)	Time (min)	
1	10.00	20.00	20.00	0.854
2	6.00	60.00	60.00	0.633
3	2.00	100.00	100.00	0.551
4	2.00	60.00	60.00	0.53
5	10.00	100.00	20.00	0.887
6	10.00	100.00	100.00	0.98
7	2.00	100.00	20.00	0.51
8	10.00	60.00	60.00	0.943
9	2.00	20.00	20.00	0.211
10	6.00	60.00	60.00	0.633
11	6.00	60.00	60.00	0.633
12	6.00	60.00	20.00	0.775
13	6.00	100.00	60.00	0.672
14	10.00	20.00	100.00	0.921
15	6.00	60.00	100.00	0.956
16	6.00	60.00	60.00	0.633
17	6.00	20.00	60.00	0.53
18	6.00	60.00	60.00	0.633
19	6.00	60.00	60.00	0.633
20	2.00	20.00	100.00	0.53

3D response surface and a 2D contour plots were embedded in one graph (see Figure 5- a, b, and c) and used to provide a graphical explanation of the concept of the effects of different studied parameters on hexamine production. When the other variables stay constant, the 3D response surface plots the dependent variable, Hexamine Yield, against two independent variables. Furthermore, 2D contour plots are comparable to 3D response surface plots, and they can aid in explaining and analyzing the impact of independent coefficients on the objective function. The 2D contour figures depict the sort of influence between the independent parameters. It is clear in Figure 5(a) that a high yield of Hexamine was attained when increasing the (formaldehyde/ammonia) ratio and process temperature. This trend was attributed to the endothermic behavior of the reaction between formaldehyde and ammonia which increased in rate as the temperature was increased. Moreover, increasing the ammonia in the reaction mixture raised the alkalinity of the reaction mixture and pushes the reaction to more production of Hexamine. However, lowering the pH solution decreases the yield because hexamine is hydrolyzed to formaldehyde and ammonia under acidic conditions **[7, 23]**.

In Fig. 5(b), the results indicate that the Hexamine yield increases sharply during the first 60 min of the reaction. With the increase in contact time from 60-100 min, the residual formaldehyde concentration decreases gradually. The equilibrium is almost obtained at a time greater than 60 min, and it is enough to get proper formaldehyde removal. Furthermore, as shown earlier, the ratio of (formaldehyde/ammonia) has always a positive impact on Hexamine yield **[24]**. Thus one may conclude that the increase in contact time has a positive effect on the Hexamine yield process, but the ratio was more effective **[14, 25]**.

It is observed from Figure 5 (c) that both temperature and reaction time have optimum values (i.e., 60 ^{o}C, 60 min) at which hexamine attained the best yield.



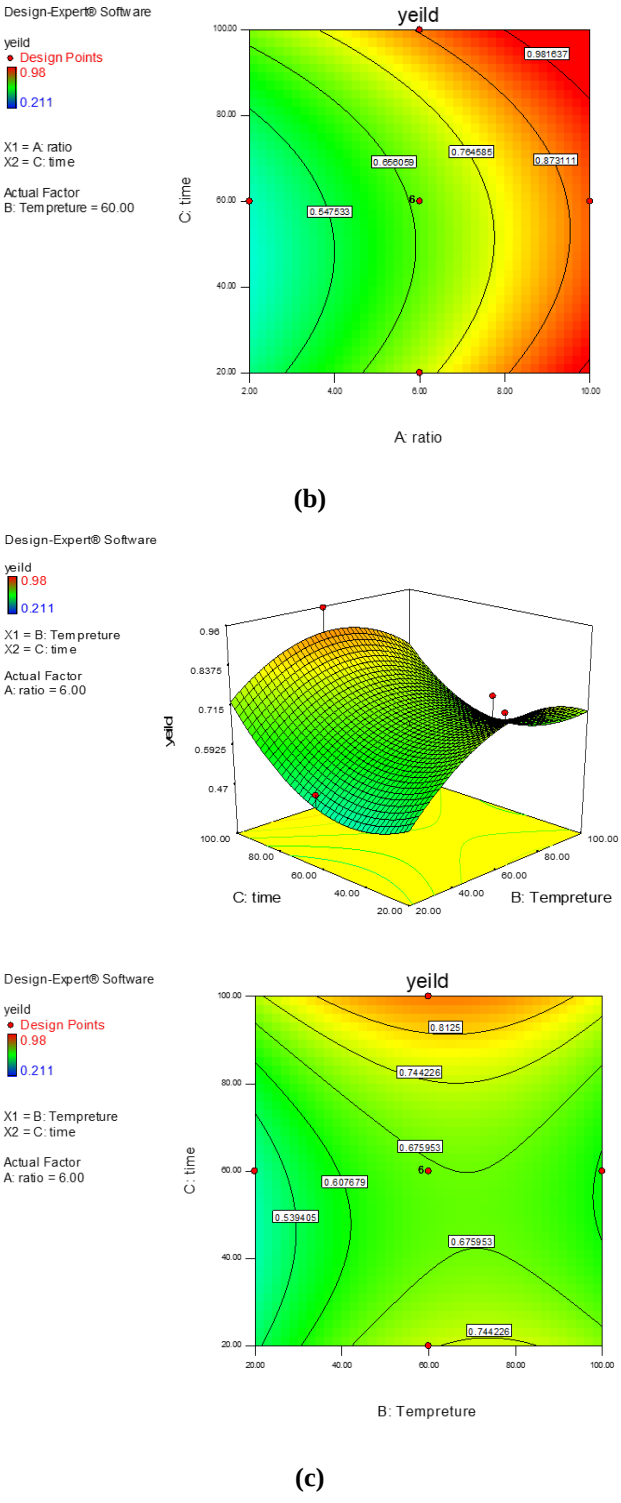


Fig. 5 3D and 2D plots of Hexamine Yield against (a) operating temperature and formaldehyde/ammonia ratio,(b) operating time and formaldehyde/ammonia ratio,(c) operating time and temperature

The regression analysis of experimental results resulted Equation (1) in terms of coded factors, while Equation (2) was in terms of the actual factors,

*Yield = 0.67 + 0.23 * A + 0.055 * B + 0.070 * C – 0.028 * A * B – 0.025 * A * C – 0.031 * B * C + 0.010 * A2 – 0.13 * B2 + 0.14 * C2.* (1)

*Yield = +7.26818*10-3 + 0.068717 * ratio + 0.013030 * Tempreture – 6.57080*10-3 * time -1.78125*10-4 * ratio * Tempreture -1.56250*10-4 * ratio * time -1.96875*10-5 * Tempreture * time + 6.39205*10-4 * ratio^2 - 7.82955*10-5 * Tempreture^2 +8.70170*10-5 * time^2.* (2)

A positive sign in the preceding equation implies that increasing the value of the variable leads to an increase in hexamine production. Concurrently, the negative sign depicts that the value of the variable results in a decrease in hexamine production. The interaction effect is represented by two variables, whereas the square effect is represented by the second-order term of the variables. The response surface method (RSM) was applied to define the significant factors that affect the reaction process [26, 27]. It was found that the effects of three variables take the following sequence: ratio > > time > temperature.

4.3 ANOVA Analysis

In the designed experimental technique, an ANOVA test was utilized to determine the relevance of each factor as in Table (3). The F statistic is essentially a two-variance ratio. Variances are a metric for dispersion, or how far the data deviates from the mean **[28]**. If the model is to be regarded as an ideal indication of the pilot program performance, F should be larger than the value set for F distribution. The P-value is often used to assess whether the F distribution is significant statistically when P becomes less than 0.05. The F–value denotes a substantial lack of fit. DF refers to the degree of freedom. F refers to the probability distribution, while P denotes the probability **[29]**. The R^2 and R (adj.): R^2 indicate whether or not the software is reliable in its outcome prediction **[30]**. Table (4) shows that R^2 and (adj.) R^2 in this case suggest an adequate degree of appropriateness (goodness-of-fit). The coefficient of determination (R^2) was used to estimate the models' fit, which is shown in Table (3). The R^2 value was high (nearly one), which is acceptable and reasonable with the empirical data's quadratic model. The standard error ratio about the mean value of the intercepted response is known as the coefficient of variance (CV), and it is also known as the model's reproducibility. A low value for the CV indicates that the model is accurate and reliable. The normal probability is calculated by examining the normal distribution of data.

Table 3 ANOVA for the hexamine production Process

Source	Sum of Squares	*DF	Mean Square	F-value	p-value Prob > F	
Model	0.68	9	0.075	17.63	< 0.0001	significant
A-ratio	0.51	1	0.51	118.62	<0.0001	
B-Tempreture	0.031	1	0.031	7.17	0.0232	
C-time	0.049	1	0.049	11.48	0.0069	
AB	6.498E-003	1	6.498 E-003	1.52	0.2460	
AC	5.000E-003	1	5.000 E-003	1.17	0.3051	
BC	7.938E-003	1	7.938 E-003	1.85	0.2031	
A^2	2.876E-004	1	2.876 E-004	0.067	0.8007	
B^2	0.043	1	0.043	10.08	0.0099	
C^2	0.053	1	0.053	12.46	0.0055	
Residual	0.043	10	4.279 E-003			
Lack of Fit	0.043	5	8.559 E-003			
Pure Error	0.000	5	0.000			
Cor Total	0.72	19				

The Model F-value of 17.63 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, B2, and C2 are important model codes. Quantities more than 0.1000 mark the model expressions are not important. When there are some lower-valued model codes, model curtailment may enhance your model.

From Table (4), the "Pred R-Squared" of 0.4325 is not as near to the "Adj R-Squared" of 0.8874 as one might usually anticipate. This may mark a major block influence of probable trouble with your model and/or information. Things to consider are model reduction, response tranformation, overshooting values, etc."Adeq Precision" estimates the (signal / noise) ratio. A ratio > 4 is preferable. A ratio of 15.366 marks a suitable index. This model can be utilized across the planning domain.

Table 4 Coefficient of determination (R^2) of production process

Std. Dev.	0.065	R-Squared	0.9407
Mean	0.68	Adj. R-Squared	0.8874
C.V. %	9.59	Pred. R-Squared	0.4325
PRESS	0.41	Adeq. Precision	15.366

Conclusions

The present work was devoted to study experimentally and statistically the effects of three different key process parameters e.g., (formaldehyde/ammonia) ratio, temperature, and time on hexamine production in a bench-scale setup operating in a batch mode. It was found that the effects of the three studied variables take the following sequence: ratio > time > temperature. However, time and temperature have

optimum values for the best yield of Hexamine. The Statistical analysis of the process using ANOVA technique showed that the Model F-value of 17.63 implies the model significance. The small value (i.e., 0. 959) for oefficient of variane indicted that the model was accurate and reliable. Values of "Prob > F" less than 0.0500 indicate model terms were significant.

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