APPLICATION OF EXPERIMENTAL DESIGN METHOD FOR COPYROLYSIS OF PVC WITH CATTLE MANURE

Chanatip Samart and Apinya Duangchan*

Department of Chemical Engineering, Kasetsart University
50 Paholyotin Rd., Ladyao Jatujak, Bangkok 10900, Thailand

ABSTRACT

Experimental design methods are practically used for screening factors and determining optimal conditions in chemical reaction. In this research, factorial design and Box-Behnken design were applied to copyrolysis reaction between polyvinyl chloride (PVC) and cattle manure for screening factors which had no effect on HCl reduction and optimizing the experimental conditions providing maximum HCl reduction. Experimental data was obtained from a fixed bed reactor heated by an electrical furnace. The furnace temperature was controlled by PID controller. The pyrolyzed products were carried by nitrogen gas and condensed by a condenser. The non-condensed products passed through sodium hydroxide solution where HCl was captured. The HCl removal efficiency was determined from the amount of the remaining sodium hydroxide. The reaction temperature, reaction time, heating rate and ratio of PVC:cattle manure was studied in the ranges of 250-450°C, 0-60 min, 1-5°C/min and 1:1 to 1:5, respectively. From statistical results, factorial design showed that heating rate and reaction temperature were significant factors due to very low P values ($P<0.05$). The other factors which had high P values showed effects on HCl reduction. Box-Behnken design was used to determine the optimum conditions. The highest efficiency of HCl reduction was obtained from the lowest heating rate of 1°C/min, the highest reaction temperature of 450°C, the PVC:cattle manure ratio of 1:5 and the reaction time of 60 min with reliability more than 90%.

KEYWORDS: experimental design, pyrolysis, PVC, cattle manure, dechlorination.

1. INTRODUCTION

In this decade, a large amount of PVC waste is discarded more than 7 billion pounds a year in the US. More than 2 billion pounds of PVC wastes are short life products which are disposed in municipal plastic wastes [1]. The conventional methods of destroying plastic wastes are incineration and landfilling. The incineration of PVC produces dioxin which is highly toxic. Landfilling of PVC is also problematic due to leaching of toxic additives into groundwater, dioxin formation and release of toxic emission in landfill gas. Pyrolysis is a challenge way for PVC reduction. It is thermal decomposition in the absence of oxygen which can reduce dioxin formation but the reactor is corroded by HCl formation. Miranda *et al.* [2] pyrolyzed PVC in vacuum conditions. The corrosion problem and amount of chlorinated hydrocarbon in liquid product can be reduced to nearly zero. Horikawa *et al.* [3] used metal oxide for dechlorination. The process has two steps, adsorption and desorption. Hydrogen chloride adsorbed on metal oxide which was then changed to metal chloride. The other step is the desorption of chloride to form chlorine gas. Cobalt oxide showed the highest dehydrochlorination efficiency (about 70%). Iron oxide compounds were used as chlorine sorbent in pyrolysis of plastic mixtures. The results indicated that Fe_2O_3 is not as effective as FeOOH and Fe_3O_4 [4]. The bifunctional catalyst such as Al-Zn which is active in both cracking and dechlorination reactions degraded PVC-containing plastic mixtures. Chlorine content in oil decreased from 13,500 to 3,300 ppm [5]. A new method of dehydrochlorination uses nitrogen compound in bio-waste. The application of bio-waste such as cattle manure to reduce corrosion problem by copyrolysis with PVC was studied in this work and the statistical method was used to design the optimum conditions.

* Corresponding Author: Tel: 662-9428555 ext 1211Fax:662-5614621
E-mail: fengapd@ku.ac.th

2. MATERIALS AND METHODS

2.1 Copyrolysis reaction.

Pyrolysis was operated in a tubular reactor which was made from stainless steel. It was placed in an electrical furnace (Lenton Thermal Designs). A mixture of PVC powder obtained from VinyThai public company limited and cattle manure at a specified ratio was placed in the reactor. Nitrogen was used as a carrier gas. The furnace was programmed to reaction temperatures of 250-450°C at various heating rates from 1 to 5°C/min and held at reaction times of 0 to 60 min. Nitrogen gas carried products from the reactor to a condenser where liquid was condensed and collected in a collector. The remaining HCl in gas product was absorbed in the sodium hydroxide solution and the amount of HCl absorbed in sodium hydroxide solution was investigated. The reduction in molarity of the solution was converted to number of moles of the HCl absorbed. The process diagram is shown in Figure 1.

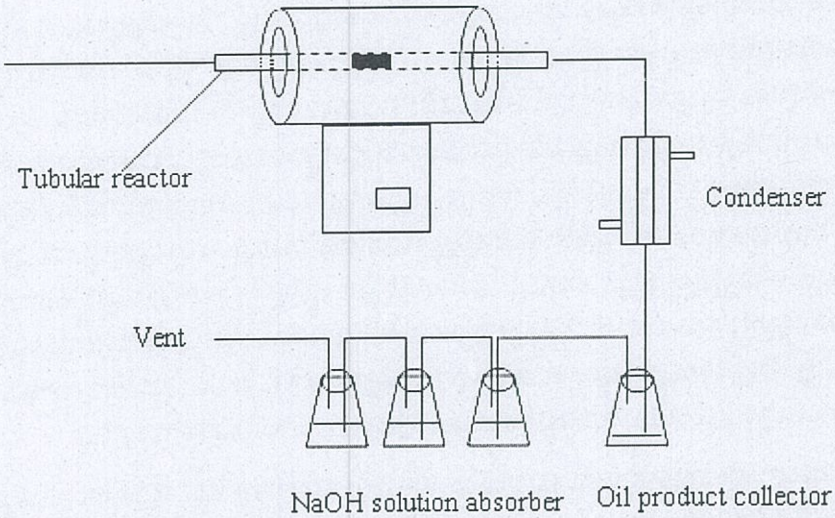

Figure 1 Process diagram of copyrolysis reaction.

2.2 Factorial design method

Table 1 Experimental conditions according to factorial design.

Standard order	Run order	PVC:cattle manure	Reaction temperature (°C)	Heating rate (°C/min)	Reaction time (min)
8	1	1:5	450	5	0
6	2	1:5	250	5	0
14	3	1:5	250	5	60
3	4	1:1	450	1	0
16	5	1:5	450	5	60
13	6	1:1	250	5	60
4	7	1:5	450	1	0
9	8	1:1	250	1	60
5	9	1:1	250	5	0
1	10	1:1	250	1	0
10	11	1:5	250	1	60
12	12	1:5	450	1	60
15	13	1:1	450	5	60
11	14	1:1	450	1	60
2	15	1:5	250	1	0
7	16	1:1	450	5	0

Four factors : heating rate, reaction temperature, reaction time, and PVC:cattle manure ratio, were considered by two level factorial design. The 16 experimental conditions were designed following 2^4 factorial design by Minitab program as shown in Table 1.

2.3 Box-Behnken design method

Box-Behnken statistical design method was used to determine the optimal conditions which provided high efficiency of HCl reduction. It was three-level design for fitting response surfaces. The statistical results were calculated by the Minitab program. Only three factors were studied: heating rate, reaction temperature, and the ratio of PVC:cattle manure because factorial design showed non-interaction between reaction time and other factors. The experimental conditions of Box-Behnken design is shown in Table 2.

Table 2 Experimental conditions according to Box-Behnken design.

Standard order	Run order	PVC:cattle manure	Heating rate (°C/min)	Reaction temperature (°C)
6	1	1:5	3	250
1	2	1:1	1	350
13	3	1:3	3	350
8	4	1:5	3	450
11	5	1:3	1	450
10	6	1:3	5	250
7	7	1:1	3	450
5	8	1:1	3	250
3	9	1:1	5	350
14	10	1:3	3	350
12	11	1:3	5	450
9	12	1:3	1	250
15	13	1:3	3	350
2	14	1:5	1	350
4	15	1:5	5	350

3. RESULTS AND DISCUSSION

3.1 Screening factors by two-level factorial design.

The experimental results of each condition from factorial design in Table 1 are shown in Table 3. These results are the percentages of HCl reduction when pyrolysis of PVC with cattle manure were compared with pyrolysis of PVC in the absence of manure as shown in equation 1. The negative value was obtained when the amount of HCl from pyrolysis of PVC with cattle manure was higher than that in the absence of manure.

$$\%HCl\ reduction = \frac{\left(HCl_{purePVC} - HCl_{purePVC+manure}\right)}{HCl_{purePVC}} \times 100 \qquad (1)$$

These results were analyzed by factorial method using Minitab program under hypothesis of average results of two conditions that are not different. Results of experiment from two conditions that are not different significantly will be rejected. From normal distribution curve, P value was area under the curve outside the area of reliability. Since the reliability area of 0.95 was chosen (or 95% of reliability), therefore P value of each factor must be less than 0.05. The statistical results are shown in Table 4. Screening factor method concerning P value of each factor is shown in Table 4. Heating rate and reaction temperature had significant effects on HCl reduction with reliability of 95% which P value showed less than 0.05. The other two factors, the ratio of PVC:cattle manure and reaction time had P values higher than 0.05 which were 0.81(23% reliability) and 0.19 (81% reliability). However, from the main effect plots in Figure 2, the percentage of HCl reduction varied with reaction time. Therefore, reaction time also affected the HCl reduction. Heating rate and reaction temperature affected HCl reduction. Only the ratio of PVC:cattle manure had a slight effect on HCl reduction. Table 5 is analysis of variance (ANOVA). It shows the P value of 0.004, therefore the model of factorial design has the reliability of more than 99%.

Table 3 Experimental results of HCl reduction following 2^4 factorial design.

Standard order	Run order	% HCl Reduction	Standard order	Run order	%HCl Reduction
8	1	2.59	5	9	-32.22
6	2	-33.58	1	10	10.32
14	3	-40.11	10	11	27.52
3	4	11.45	12	12	28.81
16	5	14.32	15	13	1.59
13	6	-5.50	11	14	18.44
4	7	15.98	2	15	17.01
9	8	19.22	7	16	0.58

Table 4 Fractional factorial fit: %HCl reduction versus ratio of PVC:cattle manure, temperature, reaction time, and heating rate.

Term	Effect	Coefficient	SE Coefficient	T	P
Constant		3.53	3.253	1.08	0.302
Ratio of PVC:cattle manure	1.09	0.54	3.253	0.17	0.871
Reaction temperature	16.39	8.19	3.253	2.52	0.029
Heating rate	-30.13	-15.07	3.253	-4.63	0.001
Reaction time	9.02	4.51	3.253	1.39	0.193

Note: SE- standard error

Table 5 Analysis of Variance

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main effect	4	5036	5036	1259.1	7.44	0.004
Residual error	11	1863	1863	169.3		
Total	15	6899				

Note: SS- sum of square, DF- degree of freedom, MS- mean square, Adj- Adjust

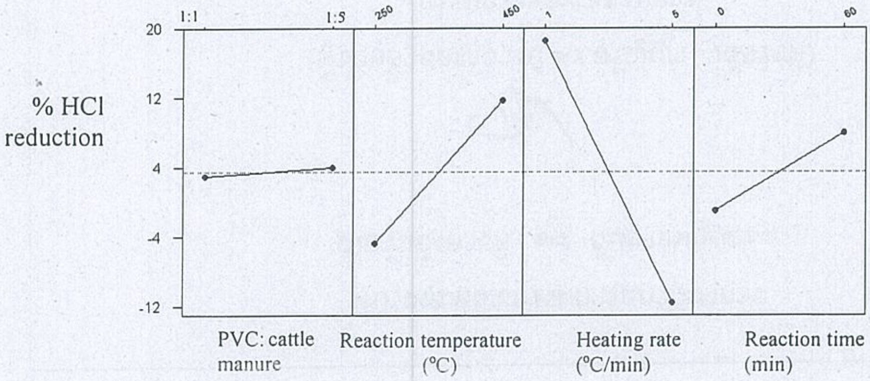

Figure 2 The main effect plot calculated by factorial design using Minitab program.

The interaction plot of each factor is shown in Figure 3. Three factors: ratio of PVC:cattle manure, reaction temperature, and heating rate had interaction among them because the lines crossed in the interaction plot. Reaction time did not interact with the other factors. From the results of the interaction plot, the ratio of PVC:cattle manure cannot be screened because it interacted with other factors. Reaction time which had no interaction with any other factors was kept constant and among the reaction times of 0-60 minutes the reaction time of 60 minutes provided the best result.

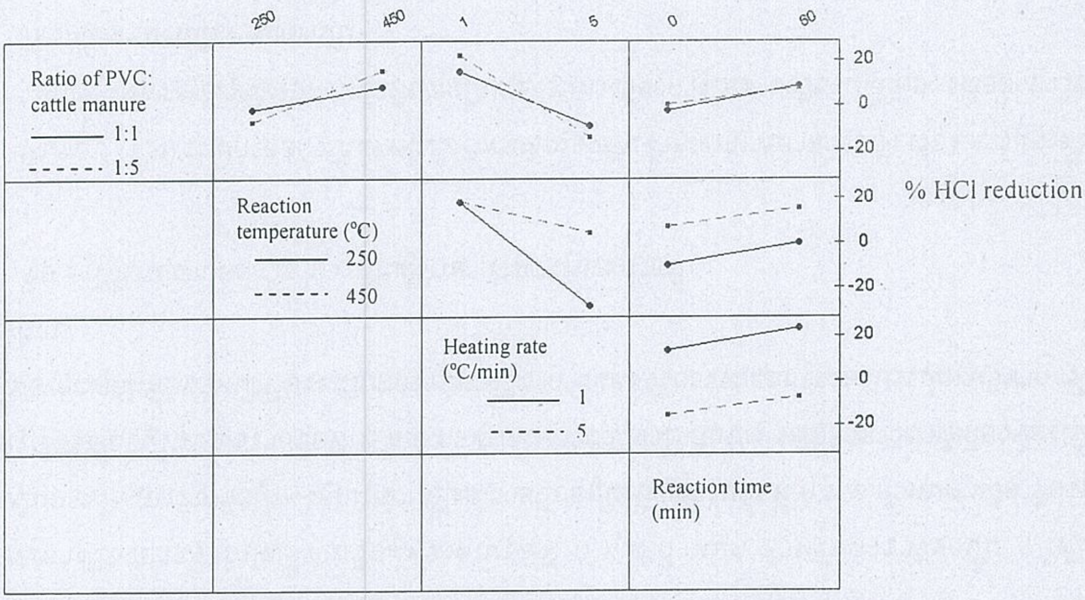

Figure 3 Interaction plot of factors: ratio of PVC:cattle manure, reaction temperature, heating rate, and reaction time.

3.2 Optimization of experimental conditions by Box-Behnken design.

From the results of factorial design, no factor was screened. Therefore, all four factors were optimized to determine the conditions of high HCl reduction efficiency. However, low reliability was obtained when more than three factors were optimized. Therefore, the reaction time was neglected because it did not interact with the other factors and the previous results showed longer reaction time provided higher HCl reduction efficiency.

Table 6 Experimental results of HCl reduction following Box-Behnken design conditions.

Standard order	Run order	%HCl reduction	Standard order	Run order	%HCl reduction
6	1	15.04	3.00	9	-2.13
1	2	4.41	14.00	10	8.78
13	3	12.97	12.00	11	3.46
8	4	-1.76	9.00	12	1.06
11	5	23.43	15.00	13	13.58
10	6	1.06	2.00	14	8.76
7	7	8.50	4.00	15	-7.49
5	8	-23.48			

The experimental results from Box-Behnken are shown in Table 6. These results were calculated statistically by Minitab program. Table 7 shows the coefficients of a statistical model. The statistical model was used to predict the profile of the percentages of HCl reduction with all three factors. They were presented in response surface plot and contour plot. Figure 4 shows the response surface plot and contour plot of the relation between HCl reduction efficiency, heating rate, and reaction temperature. The values in the contour plot were calculated from a model equation using the values of %HCl reduction at various reaction temperatures and heating rates with constant ratio of PVC:cattle manure of 1:3. The HCl reduction efficiency was about 22% at low heating rate of 1°C/min and high reaction temperature of 450°C.

Table 7 Estimated regression coefficient from Minitab program.

Term	Coefficient	SE Coefficient	T	P
Constant	-778.8	136.591	-5.702	0.002
Ratio of PVC: cattle manure	85.2	18.156	4.694	0.005
Heating rate	16.4	10.380	1.576	0.176
Reaction temperature	1.1	0.256	4.391	0.007
Ratio*Ratio	-2.3	0.671	-3.458	0.018
Heating rate*Heating rate	-0.4	0.671	-0.598	0.576
Reaction temperature*Reaction temperature	-0.0	0.000	-1.087	0.327
Ratio*Heating rate	-0.6	0.645	-0.941	0.390
Ratio*Reaction temperature	-0.1	0.013	-4.727	0.005
Heating rate*Reaction temperature	-0.0	0.013	-1.935	0.111

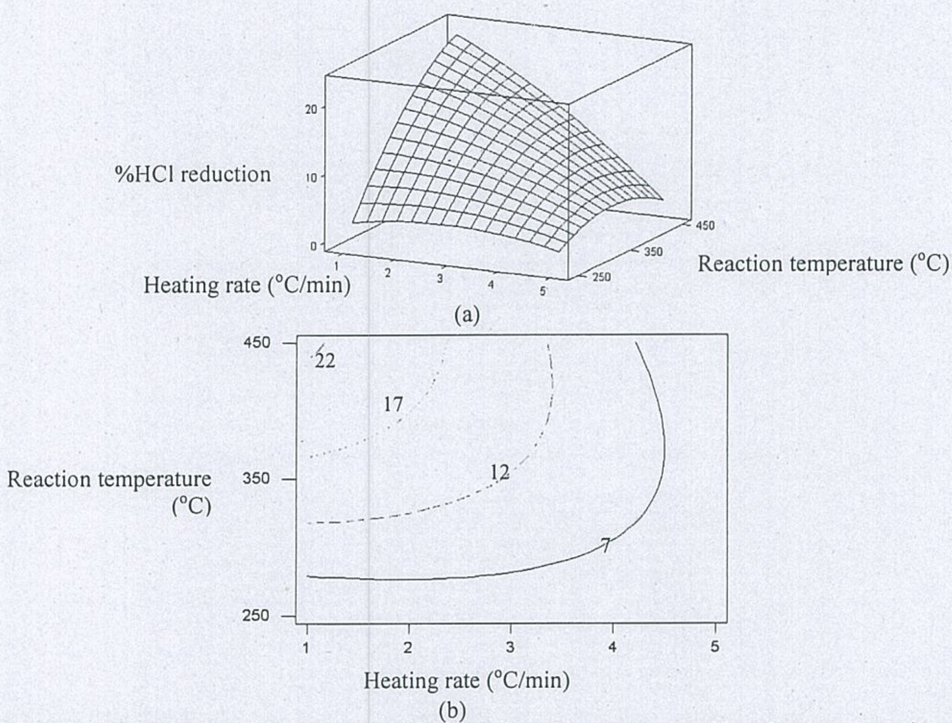

Figure 4 Relation between %HCl reduction, reaction temperature and heating rate at ratio of PVC:cattle manure of 1:3 (a) response surface plot and (b) contour plot.

The relation among HCl reduction, ratio of PVC:cattle manure, and reaction temperature at heating rate of 3°C/minis shown in Figure 5. It was calculated from a statistical model using the values of HCl reduction at various reaction temperatures and ratios of PVC:cattle manure with constant heating rate of 3°C/min. At low reaction temperature, the PVC:cattle manure ratio of 1:5 gave high HCl reduction efficiency but the curve of HCl reduction efficiency at high reaction temperature dropped when cattle manure was more than three times the amount of PVC.

The effect of ratio of PVC:cattle manure and heating rate on HCl reduction efficiency at reaction temperature of 350°C is shown in Figure 6. The values in this plot were calculated from a statistical model using the values of HCl reduction at various heating rates and ratios of PVC:cattle manure with constant reaction temperature of 350°C. Low heating rate of 1°C/min and cattle manure five times the amount of PVC provided high HCl reduction efficiency.

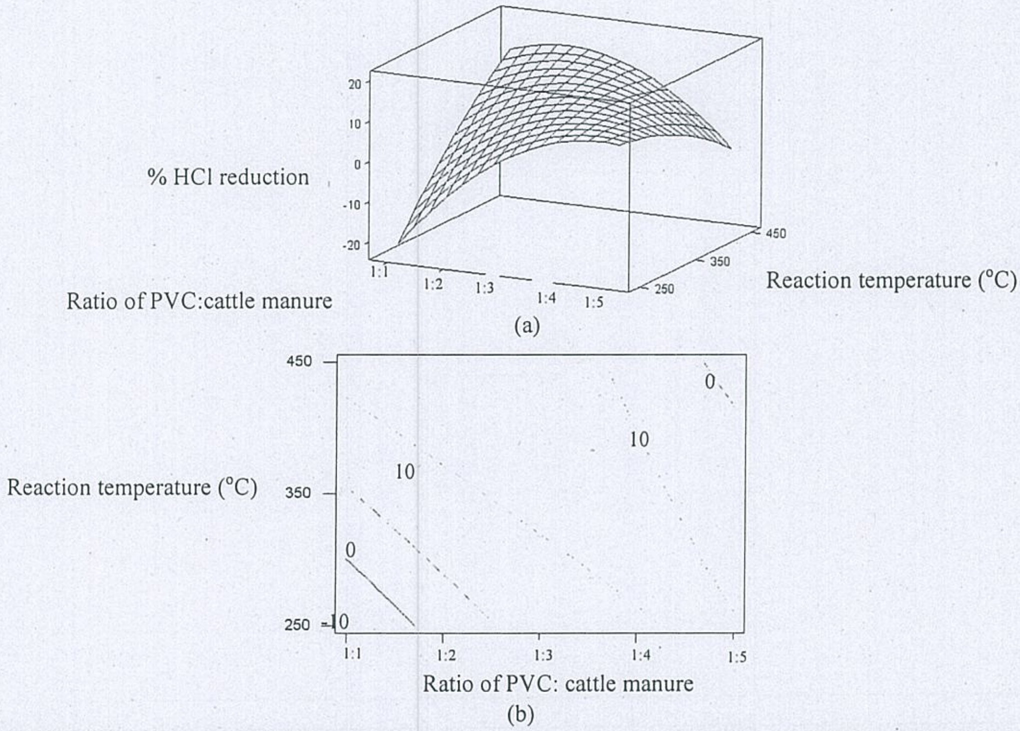

Figure 5 Relation between %HCl reduction, reaction temperature and ratio of PVC:cattle manure at heating rate of 3°C/min (a) response surface plot and (b) contour plot.

The Box-Behnken design showed the best conditions of HCl reduction at low heating rate of 1°C/min, high reaction temperature of 450°C and cattle manure:PVC of 5:1. In the statistical method, reliability of our model was R^2=92.2% and lack of fit gave reliability in the range of 85%, therefore, these results are acceptable.

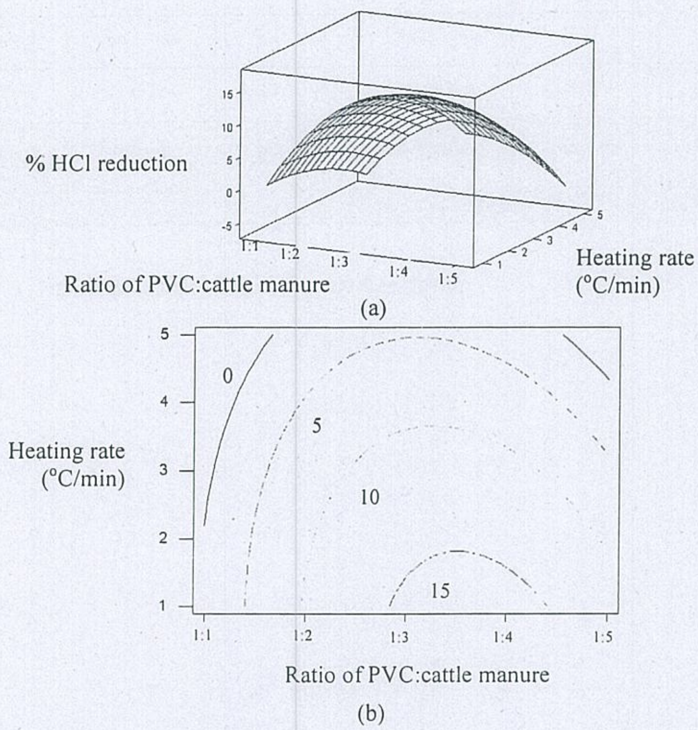

Figure 6 Relation between %HCl reduction, heating rate and the ratio of PVC:cattle manure at reaction temperature of 350°C (a) response surface plot and (b) contour plot.

4. CONCLUSION

Factorial design and Box-Behnken design were used to screen factors and to optimize experimental conditions, respectively. These statistical methods were applied to copyrolysis of PVC and cattle manure reaction. There are four factors: reaction temperature, reaction time, heating rate, and the ratio of PVC to cattle manure, which were concerned. Factorial design showed that heating rate and reaction temperature had significant effects on HCl reduction but factorial design could not screen the other factors since reaction time and PVC:cattle manure ratio had slight effects and interact with other factors, respectively. There are interactions among the three factors: heating rate, reaction temperature, and the ratio of PVC:cattle manure; reaction time did not interact with the other factors. The optimized conditions obtained by Box-Behnken design showed that high efficiency of HCl reduction was obtained from the lowest heating rate of $1^{\circ}C/min$, the highest reaction temperature of $450^{\circ}C$, a high amount of cattle manure at PVC:cattle manure ratio of 1:5 and the longest reaction time of 60 min. The model had $R^2 = 92.2\%$ and lack of fit had more than 90% reliability.

5. ACKNOWLEDGEMENTS

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