INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

Optimization of Ketene Production Using Computer Simulated Experimental Design

Abiye Aseminaso and Christopher Tubuyai Iriakuma - Federal Polytechnic of Oil and Gas, Bonny, Rivers State, Nigeria.

Abstract: The Box-Behnken Design was applied with Response Surface Methodology to investigate the influence of four process variables (Temperature, reaction volume, pressure and Acetone flow rate) on the production of Ketene. The percentage conversion of Acetone was used to measure the response of the influence of the variables on the production of Ketene. The results were analyzed with ANOVA and a second order polynomial was used to predict the effect of the process variables on the percentage Acetone conversion. Results show that temperature has the highest effect on the pyrolysis process. The percentage conversion of Acetone was shown to have a direct relationship with temperature, pressure and reactor volume and an inverse relationship with flowrate. Multi-objective optimization study showed that the optimum condition for acetone conversion was a temperature of 992.2°C, a pressure of 46.2 bar, a flowrate of 21kg/h and a reactor volume of 9.98m^3 with a desirability of 1.

Key words: Computer simulated experimental design, ketene production, optimization, response surface methodology

Introduction

The thermal decomposition of materials at elevated temperatures is called pyrolysis. The process involves breaking chemical bonds in molecules by heating the material to a temperature above its decomposition temperature. One of the most common pyrolysis experiments in Chemical Engineering is that of Acetone for the production Ketene. Also known as propanone, Acetone is a colourless liquid used as a solvent in the chemical industry for the manufacture of plastics and other chemical products. It is also found in the human body as a by-product of metabolism. The pyrogenic decomposition of acetone produces Ketene. Ketene can be synthesized from the thermolysis of acetone at 600-700°C in the presence of trace amounts of Carbon disulphide (CS_2) (Weissermel & Arpe, 2003). The process gives 25% acetone conversion with a ketene selectivity of 70-80%. Ketenes are highly unstable and as a result, they are consumed as soon as they are produced when used as reagents.

The market for Ketene is driven globally by the demand for acetic anhydride and diketene. Acetic anhydride and Diketene are used in the production of various petrochemical products ranging from plastics to dyes. Statistics from 2013 indicate that the demand for Ketene was highest in the Asia pacific region due to the high demand for diketene and acetic anhydride, with China being the country with the highest demand (TMR 2020). This was followed by North America. In the United States, the market for Ketene is large owing to the high demand for cellulose acetate flakes. Europe trailed the United States with the third highest demand on Ketene in 2013. Projections for the global industrial utilization of Ketene looks promising and it is thus imperative that the process conditions for Ketene production are optimized to produce the highest percentage conversion of Acetone during the pyrolysis process.

Background

The earliest experiment on the conditions governing the pyrolysis of Acetone to produce Ketene was first reported in Hurd and Tallyn (1925). They focused their study on the variables which they considered most influential to the yield, and they were the temperature of the furnace, the rate of flow of Acetone and the rate of decomposition of the Acetone. They were able to show that the best condition for Ketene production occurred at a temperature of 695-705°C, a flow rate of 5 cm^3 per minute at a 25-40% decomposition of acetone. This condition produced Ketene yields between 35-45%. Morey (1939) worked on modifying the

INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

experiment of Hurd and Tallyn and reported that the use of sulphuric acid served as an excellent catalyst for the production of Ketene from Acetone. Wang and Schueler (1949) reported a cheap way to generate Ketene by the thermal decomposition of acetone in the laboratory. Ketene can be prepared from the pyrolysis of acetic acid in the presence of a catalyst or by the pyrolysis of acetone. The former is not suitable for laboratory synthesis and the latter occurs without the need for a catalyst. The general equation for the production of Acetone is given by:

$$\text{[1] } CH_3\text{-}CO\text{-}CH_3 \xrightarrow[700\text{-}800^oC]{} CH_2{=}C{=}O + CH_4$$

Optimizing the process conditions for the pyrolysis of Acetone towards the production of Ketene is imperative as this ensures that the feed is totally converted to give the product. The aim of this study is to investigate the effects of parameters that influence the production of Ketene from Acetone. The parameters investigated in this study are temperature, pressure, flow rate and the volume of the reactor. For this study, the production of Ketene is expressed as the percentage conversion of Acetone during the pyrolysis process.

Materials and methods

Computer simulation

A computer simulation was executed with the Aspen HYSYS simulator. The Aspen HYSYS simulator is a chemical engineering software capable of modelling process conditions of unit operations, chemical plants and refineries. It is a powerful tool for optimizing design and operation processes. The process conditions as well as factors chosen for the study are given in Table 1.

Table 1: Factor levels

Factor	**Unit**	**level**		
		-1	0	1
Temperature	degC	400	700	1000
Pressure	barg	0	50	100
Acetone flowrate	kg/h	5	22.5	40
Reactor volume	m^3	1	5.5	10

INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

Response Surface Modelling and Optimization

Response Surface Methodology (RSM) is a compendium of mathematical and statistical techniques that are utilized for modelling and analyzing problems where the response under analysis, is influenced by several variables and the objective is to optimize this response (Myers, Montgomery, & Anderson-Cook, 2008). RSM is a sequence-oriented process. Its objective is to lead the experimenter, in a rapid and efficient manner, from a point remote from the optimum, along the path of improvement towards the general vicinity of the optimum. This study focuses on utilizing RSM to identify the influence of operating parameters on the response in the pyrolysis of Acetone. The percentage (%) Acetone conversion was considered as the response for the pyrolysis process. The chosen RSM design for this study is the Box-Behnken Design (BBD). The BBD has the treatment combinations at the midpoints of edges of the process space and at the centre. They require three levels for each factor, are rotatable or near rotatable and can be used for fitting second order responses (Myers, Montgomery, & Anderson-Cook, 2009).

Table 2: Experimental design

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	Run	A:Temperature	B:Pressure	C:Acetone flowrate	D:Reactor volume	% Acetone conversion
		degC	barg	kg/h	m3	
1	19	400	0	22.5	5.5	0.00516
2	8	1000	0	22.5	5.5	87.9021
3	3	400	100	22.5	5.5	0.73271
4	21	1000	100	22.5	5.5	98.9897
5	10	700	50	5	1	45.3724
6	1	700	50	40	1	39.7353
7	2	700	50	5	10	50.9388
8	24	700	50	40	10	45.9416
9	5	400	50	22.5	1	0.0701
10	20	1000	50	22.5	1	94.672
11	11	400	50	22.5	10	0.610315
12	15	1000	50	22.5	10	98.867
13	17	700	0	5	5.5	38.2961
14	13	700	100	5	5.5	51.3593
15	4	700	0	40	5.5	31.8818
16	6	700	100	40	5.5	46.3198
17	12	400	50	5	5.5	1.26997
18	7	1000	50	5	5.5	99.698
19	18	400	50	40	5.5	0.209531
20	22	1000	50	40	5.5	97.0299
21	23	700	0	22.5	1	28.076
22	14	700	100	22.5	1	43.3535
23	9	700	0	22.5	10	35.5904

24	25	700	100	22.5	10	49.2258
25	16	700	50	22.5	5.5	45.8845

Myers *et al.* (2008) suggests that when K=4 and K=7, the BBD is exactly rotatable. The number of experiments required for a BBD is defined by $N = 2K(K-1) + C_0$, where K is the number of factors and C_0 is the number of centre points. Thus, the design comprised of 24 experiments and one centre point. Centre points aid the determination of curvature. One centre point was chosen because in computer experiments, there is no random error and hence replicating the centre point will give the same value. The experimental design as shown in Table 2, was run in random order and analyzed using multiple regression. The behaviour of the pyrolysis process is explained by the following quadratic polynomial:

[2] $y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1} \quad \sum_{i<j} \beta_{ij} x_i x_j + e$

In Equation 2, y is the predicted response, β_0 is the intercept, β_i, β_{ii} and β_{ij} are the interaction co-efficient of linear, quadratic and second-order terms respectively; x_i and x_j are variables; k is the number of independent parameters and e is the error. The analysis and optimization were executed with Design Expert 12 software (Stat-Ease Inc., Minneapolis, MN, USA).

Results and discussion

Model and Statistical Analysis

A square root transformation was suggested to fit the data. The second order polynomial given in Equation 2 was used to fit the data obtained from the BBD. The model in terms of coded factors is given below:

[3] Sqrt (% Acetone Conversion + 0.5) = $+6.86 + 4.43A + 0.4514B - 0.1922C + 0.2061D - 1.28A^2 - 0.3558B^2$

The model accounts for linear effects and quadratic effects of the parameters under study. The ANOVA table shows the data obtained from the BBD experiments. The ANOVA results presented in Table 3 shows the model's F-statistic of 411.8 with

INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

probability value (p-value) less than 0.0001, indicating that the model is significant. Based on the F-statistic and the calculated p-values, we observe that the terms A (Temperature), B (Pressure), C (Acetone flowrate), D (Reactor volume) and the quadratic terms A^2 and B^2 contribute significantly to the model. The other parameters, main and interaction effects, had an insignificant effect on the predicted % Acetone conversion for the pyrolysis process

Table 3: ANOVA

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	247.79	14	17.70	411.80	< 0.0001	significant
A-Temperature	235.71	1	235.71	5484.05	< 0.0001[a]	
B-Pressure	2.45	1	2.45	56.90	< 0.0001[a]	
C-Acetone flowrate	0.4432	1	0.4432	10.31	0.0093[a]	
D-Reactor volume	0.5099	1	0.5099	11.86	0.0063[a]	
AB	0.0075	1	0.0075	0.1735	0.6859	
AC	0.0313	1	0.0313	0.7285	0.4134	
AD	0.0018	1	0.0018	0.0430	0.8399	
BC	0.0080	1	0.0080	0.1870	0.6746	
BD	0.0135	1	0.0135	0.3142	0.5875	
CD	0.0013	1	0.0013	0.0306	0.8647	
A^2	4.48	1	4.48	104.31	< 0.0001[a]	
B^2	0.3173	1	0.3173	7.38	0.0217[a]	
C^2	0.0029	1	0.0029	0.0665	0.8017	
D^2	0.0643	1	0.0643	1.50	0.2494	
Residual	0.4298	10	0.0430			
Cor Total	248.22	24				

[a] Term is significant

In addition to the ANOVA, diagnostic plots showing predicted versus actual values was also used to evaluate the deviation between the experimental and predicted values. It is observved from Figure 1 below that the experimental values are well distributed along the diagonal line signifying a good fit of the model.

INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

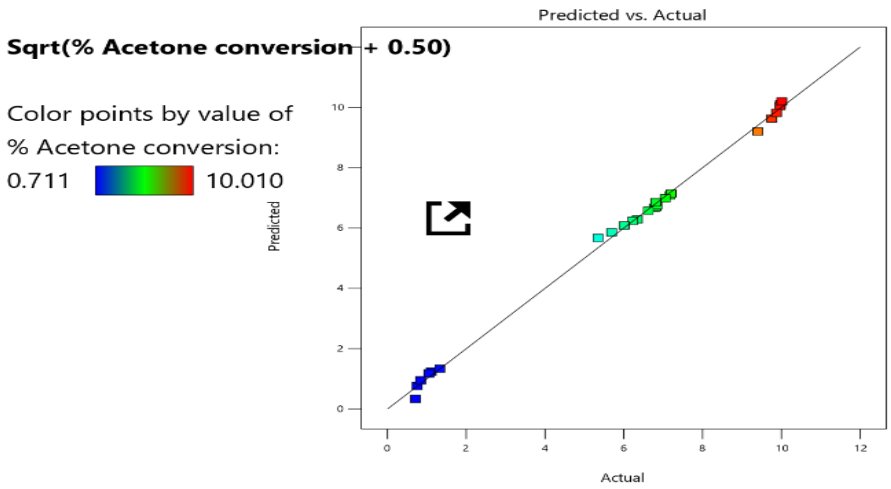
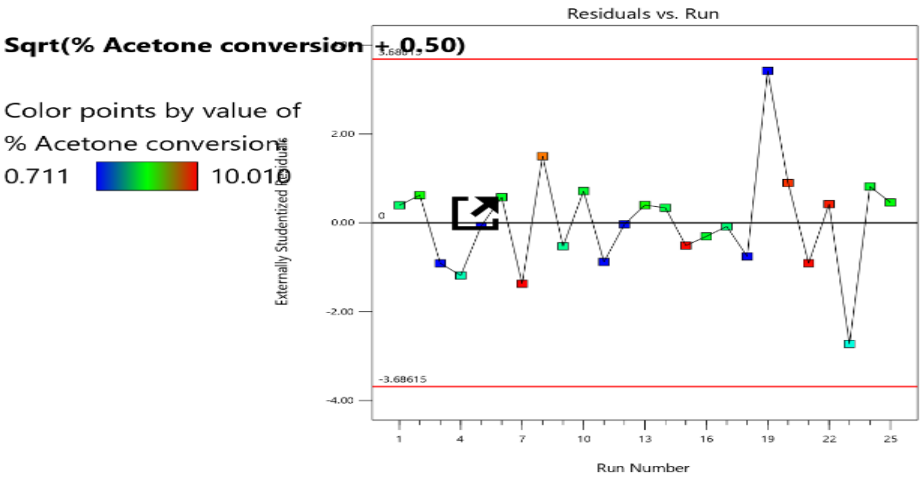


Figure 1: Plot of Predicted vs Actual

The normal half probability plots and residual plots were also used as diagnostic tools to check the adequacy of the model. The residuals versus run is a diagnosis that helps examine the influence of variables on the response during the experiment. The residual versus predicted plot gives the difference between the observed and predicted values (Navidi 2010). Regardless of the size of fitted values, both plots should show randomly distributed points about zero and without any observable patterns. It can be observed from the plot that the spread of the residuals is bound between +4 and -4 and distributed evenly with no outlier. Hence the derived quadratic polynomial model is reliable and significant.



INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

Figure 2: Plot of Residuals vs Run

The coefficient of determination (R^2) is used to explain the adequacy of a fitted model. It illustrates the proportion of the total variation explained by the fitted model. Table 4 show the fit statistics for the model. The R^2 value of 0.9980 indicates that the model can explain 99.8% of the variability in the response. The Adjusted R^2 is a variation of R^2 that provides an adjustment for the degrees of freedom (Walpole *et al*. 2011). The high value of 0.9972 indicates that the regression model explaining the relationship between the response and the parameters is well correlated.

Table 4: Fit Statistics

Standard Deviation	0.1708		**R^2**	0.9980
Mean	5.99		**Adjusted R^2**	0.9972
C.V. %	2.85		**Predicted R^2**	0.9956
			Adeq Precision	102.0647

Influence of Process Variables on %Acetone conversion

The impacts of the parameters on the %Acetone conversion in the pyrolysis process was also analyzed by the BBD. Figure 3 below shows the interaction of the main effects of the parameters on %Acetone conversion. It is observed from the illustration that %Acetone conversion increases with an increase in Temperature, Pressure and Reactor volume with a corresponding reduction in Acetone flowrate. From the ANOVA results in Table 3, Temperature has the highest effect as a parameter on the predicted %Acetone conversion ($F = 5484.05$, $p < 0.0001$) then, Pressure ($F = 56.9$, $p < 0.0001$), Reactor volume ($F = 11.86$, $p < 0.0063$) and Acetone flowrate ($F = 10.31$, $p < 0.0093$).

Response surface plots are effective tools for visualizing the nature of the response surface. Figure 4a-f shows the interaction of two parameters on the predicted %Acetone conversion while keeping the other parameters at their midpoint. The plots were made using the polynomial model given in Equation 3. Figure 4a indicates that the %Acetone conversion has a direct relationship with Temperature and Pressure. The predicted %Acetone conversion was 98.99% with the Temperature set at the highest level of 1000^{o}C and at the highest pressure of 100 bar.

INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

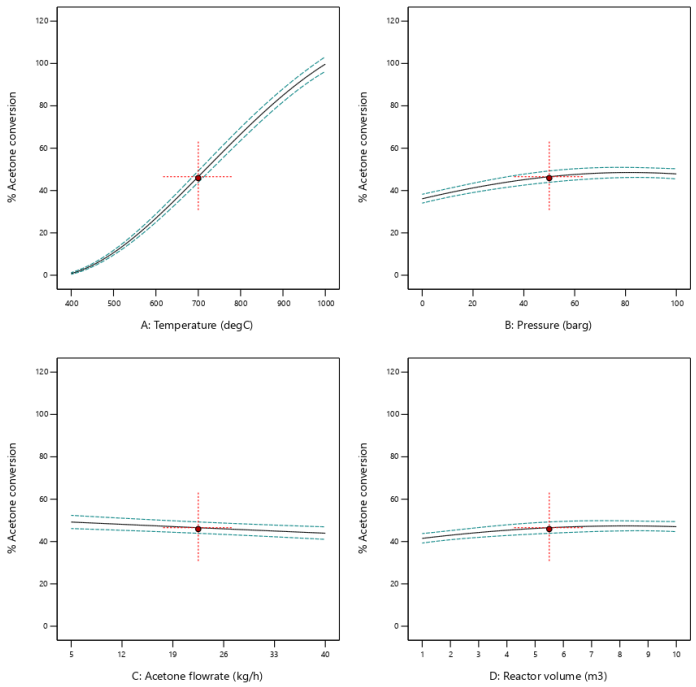
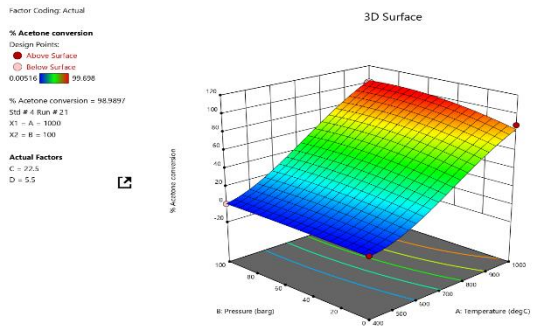


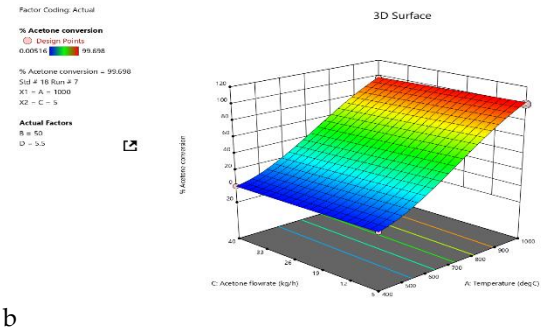
Figure 3: Effect of parameters on the %Acetone conversion

Figure 4b presents the interaction effect between Temperature and flowrate on the predicted %Acetone conversion. The result shows that the %Acetone conversion has a direct relationship with temperature and an inverse relationship with flowrate. The highest value of %Acetone conversion was 99.7%, obtained at the highest value of temperature (1000^{o}C) and the lowest value of flowrate (5kg/h).

Figure 4c shows the mutual interaction effect between the Temperature and Reactor volume on the %Acetone conversion. It can be observed that Temperature and reactor volume have a direct relationship



a



b

INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

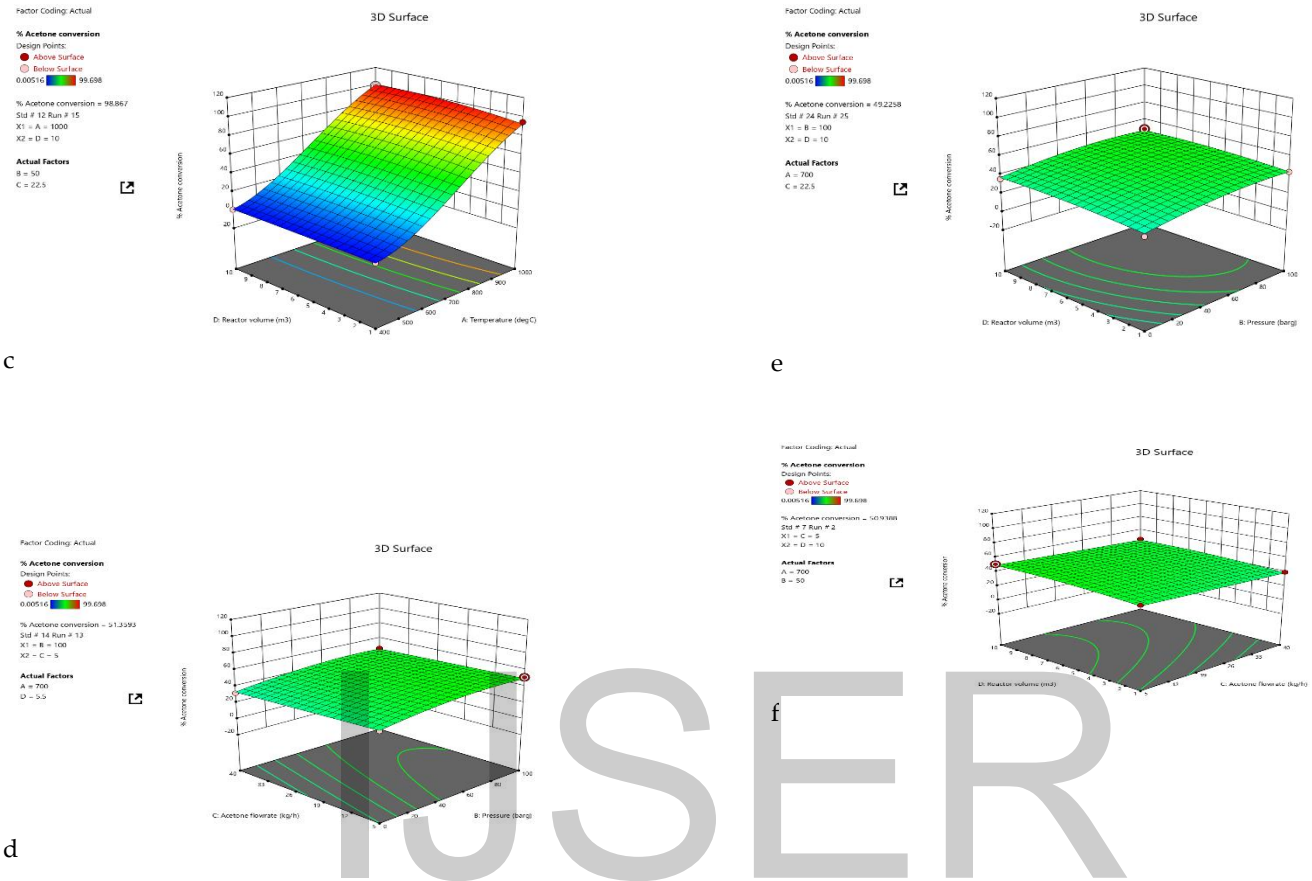


Figure 4: Response surface plots for %Acetone conversion

with %Acetone conversion with the highest value of %Acetone conversion being 98.87% at the highest temperature (1000^{o}C) and highest reactor volume (10m^{3}) respectively.

Figure 4d examines the mutual interaction between pressure and flowrate on the %Acetone conversion. The results indicate a direct relationship between %Acetone conversion and pressure, and an inverse relationship with flowrate. The desired predicted value of 51.35% was obtained for the %Acetone conversion at the lowest value of flowrate at 5kg/h and the highest pressure at 100 bar.

Figure 4e gives the mutual interaction between the pressure and reactor volume on the %Acetone conversion. It can be observed that the desired predicted value of %Acetone conversion is directly proportional to pressure and reactor volume. The % acetone conversion is 49.23% at the highest values of pressure (100 bar) and reactor volume (10m^{3}) respectively.

Figure 4f presents the relationship between %Acetone conversion and its interaction between flowrate and reactor volume. It can be observed that the graph denotes a direct relationship between %Acetone conversion and reactor volume, and an inverse

INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

relationship with flowrate. The desired predicted value of %Acetone conversion is 50.94% at the highest value of reactor volume ($10m^3$) and the lowest value of the flowrate (5kg/h).

The trend from the response surface diagrams show that the interaction of temperature and pressure have a direct influence on the predicted %Acetone conversion. During the pyrolysis process, the temperature and pressure play a critical role in the conversion of Acetone to Ketene as good heat transfer at high pressures aid the process. Further analysis shows that the size of the reactor also plays a critical role during the pyrolysis of Acetone as a larger reactor size favours the %Acetone conversion. The flowrate, however, varies inversely with %Acetone conversion, hence maintaining the flowrate at moderate levels ensures the efficient pyrolysis of Acetone.

The optimum condition of the pyrolysis process was also determined by multi-objective optimization. According to the BBD, the optimum conditions for the pyrolysis of Acetone occurs at a temperature of 992.2^oC, a pressure of 46.2 bar, a flowrate of 21kg/h and a reactor volume of $9.98m^3$ with a desirability value of 1.

Conclusion

The pyrolysis of Acetone to produce Ketene was investigated using the BBD. The influence of temperature, pressure, reaction volume and Acetone flowrate was analyzed. A model was developed and was used to evaluate the linear and quadratic effects of the analyzed factors. The interactions and effects were analyzed with ANOVA, and the significant terms were determined. Response surface inference showed that the %Acetone conversion has a direct relationship with Temperature, pressure and reactor volume while and inverse relationship was observed with the flowrate. Multi-objective optimization showed that optimum conditions for Acetone conversion was a temperature of 992.2^oC, a pressure of 46.2 bar, a flowrate of 21kg/h and a reactor volume of $9.98m^3$ with a desirability value of 1.

INTERNATIONAL JOURNAL OF SCIENTIFIC & ENGINEERING RESEARCH, VOLUME 11, ISSUE 8, AUGUST-2020
ISSN 2229-5518

References

Aspentech. (2019). HYSYS.

Jaber, A., Awang, M., & Lenn, C. (2017). Box-Behnken Design for Assessment Proxy Model of Miscible CO2-WAG in Heterogeneous Clastic Reservoir. *Journal of Natural Gas Science and Engineering*, 236-248.

Morey, G. (1939). Ketene Production and Utilization: Experimenal Study. *Industrial Engineering and Chemistry, 31*(9).

Myers, R., Montgomery, D., & Anderson-Cook, C. (2008). *Response Surface Methodology: Process and Product Optimization using Designed Experiments.*

Myers, R., Montgomery, D., & Anderson-Cook, C. (2019). *Response Surface Methodology: Process and Product Optimization Using Designed Experiments.* New Jersey: Wiley.

Navidi, W. (2010). *Principles of Statistics for Engineers and Scientists.* New York: McGraw-Hill.

Quadbeck, G. (1963). Ketene in Preparative Organic Chemistry. In W. Foerst (Ed.), *Newer Methods of Preparative Organic Chemistry* (F. Kirchner, Trans., Vol. 2, pp. 133-156). London, United Kingdom.

Stat-Ease. (2020). Design Expert 12. Minneapolis, USA.

TMR. (2020, April 14). *Transparency Market Research*. Retrieved from Transparency Market Research: https://www.transparencymarketresearch.com/ketene-market.html

Walpole, R., Myers, R., Myers, S., & Ye, K. (2011). *Probability and Statistics for Engineers and Scientists.* Boston: Prentice Hall.

Wang, S., & Schueler, F. (1949). A Simple Ketene Generator. *Journal of Chemical Education, 26*(6), 323.

Weissermel, K., & Arpe, H.-J. (2003). *Indusreial Organic Chemistry.* Darmstadt: Wiley.