MODELLING THE MANUFACTURE OF PROPYLENE GLYCOL VIA HYDROLYSIS OF PROPYLENE OXIDE

CHEG 304 - Random Variability in Chemical Processes

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ABSTRACT

A chemical reactor is required to chemically manufacture propylene glycol via hydrolysis of propylene oxide. A statistical model was determined to calculate the effect of reactor capacity, feed concentration, feed rate, feed temperature, and operating pressure on the conversion of the reaction. Screening the fractional factorial design at a 90 % confidence interval gave the significant factors; reactor capacity, feed concentration, and pressure which were used as variables for the response surface design. A response surface design generated a final statistical model to predict the conversion of the reactor, making the feed rate and temperature fixed at $1700\,\frac{ft^3}{h}$ and 80 ℉ respectively, taking the 49 % targeted conversion of propylene oxide to validate the statistical model. With 0.8, 0.05 $\frac{lbmol}{ft^3}$, and 1.7 atm of capacity, feed concentration, and pressure generated from the response optimizer in Minitab respectively, a sample of five conversions gave a sample mean of 0.5034 with a standard deviation of 0.0305. The targeted conversion fell within the 95% confidence interval of the sample mean, indicating a successfully developed statistical model.

FRACTIONAL FACTORIAL EXPERIMENT

Purpose

The conversion of propylene oxide to produce propylene glycol was determined by 5 factors; the reactor capacity, feed concentration, feed rate, feed temperature, and operating pressure. A fractional factorial design was conducted to determine three significant factors that have effects on the conversion response.

Experimental Design

The fractional design was done using a resolution V, with a $\frac{1}{2}$ fractional factorial and 2 replicates, giving 32 runs overall, the raw data is tabulated in Table A in the Appendix. Table 1 lists the 5 main factors with their minimum and maximum values.

Table 1: Range of the 5 Factors Chosen for the Fractional Factorial Design

Factors	Minimum	Maximum
Reactor Capacity (%)	60	80
Feed Concentration ($\frac{lbmol}{ft^3}$)	0.05	0.10
Feed Rate ($\frac{ft^3}{hr}$)	1300	2200
Feed Temperature (℉)	70	100
Operating Pressure (atm)	1.5	4.0

The feed temperature and operating pressure were chosen to be closer to ambient temperature and pressure of 77 ℉ and 1 atm respectively [1]. To have a large conversion of propylene oxide, the capacity, feed concentration and feed rate were set to maximize the residence time of the reactor, as a higher residence time maximizes the conversion, too high would result in a steady state condition [2].

Results and Analysis

Referring to Figure 1, the standardized residual versus fitted value plot showed no obvious pattern and the data points were scattered around y = 0, indicating a randomization in the data sets.

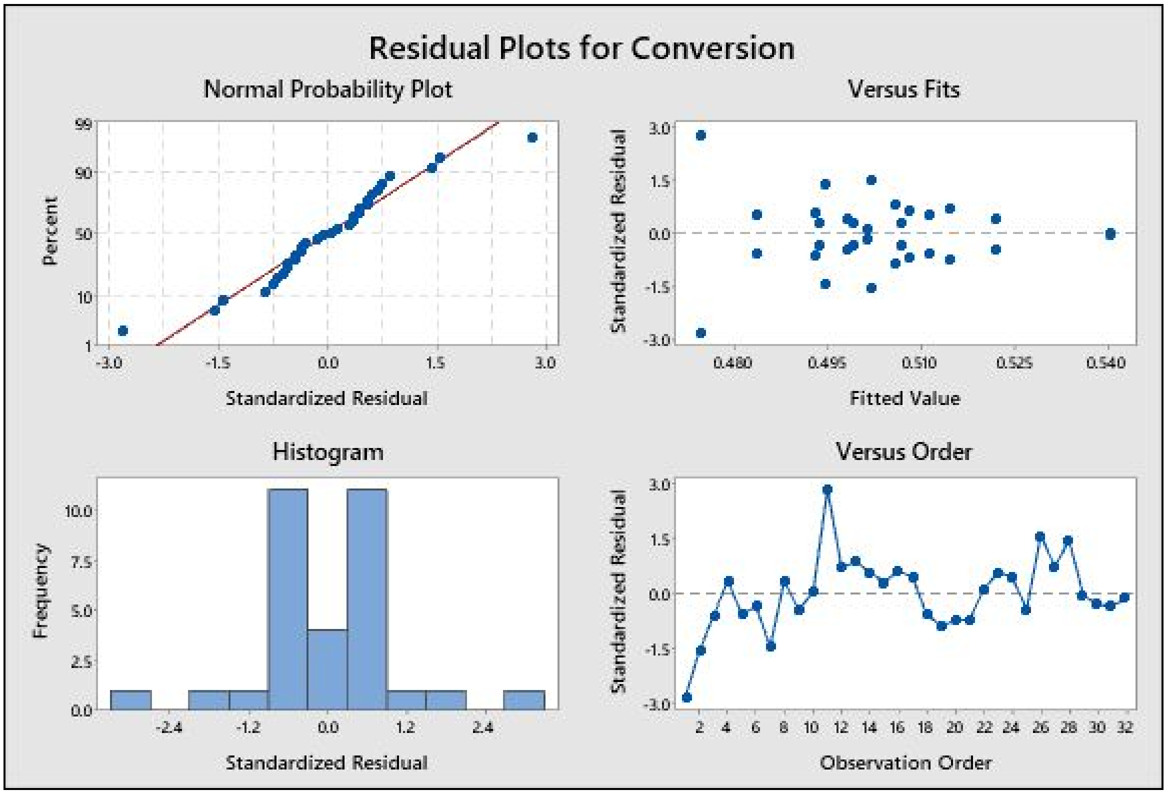

Figure 1: Residual plots for Factorial Design

At significance level, α, of 0.10, based on Table 2, it was observed that only pressure and (feed concentration $\times$ pressure) are significant with their p-values lower than α. From these results, the feed concentration itself was significant because of its significant 2-way interaction with pressure. Due to an inadequate amount of significant factors, the capacity was chosen to be the third factor since it has the second lowest p-value among the remaining factors.

Table 2: ANOVA table for Fractional Factorial Design

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	15	0.007042	0.000469	1.77	0.134
Linear	5	0.004376	0.000875	3.30	0.031
Capacity	1	0.000420	0.000420	1.59	0.226
Feed Conc	1	0.000112	0.000112	0.42	0.524
Feed rate	1	0.000036	0.000036	0.14	0.717
Feed Temp	1	0.000066	0.000066	0.25	0.624
Pressure	1	0.003741	0.003741	14.12	0.002
2-Way Interactions	10	0.002666	0.000267	1.01	0.478
Capacity*Feed Conc	1	0.000378	0.000378	1.43	0.250
Capacity*Feed rate	1	0.000288	0.000288	1.09	0.313
Capacity*Feed Temp	1	0.000220	0.000220	0.83	0.375
Capacity*Pressure	1	0.000061	0.000061	0.23	0.639
Feed Conc*Feed rate	1	0.000162	0.000162	0.61	0.446
Feed Conc*Feed Temp	1	0.000072	0.000072	0.27	0.609
Feed Conc*Pressure	1	0.000968	0.000968	3.65	0.074
Feed rate*Feed Temp	1	0.000078	0.000078	0.29	0.595
Feed rate*Pressure	1	0.000435	0.000435	1.64	0.218
Feed Temp*Pressure	1	0.000003	0.000003	0.01	0.915
Error	16	0.004238	0.000265		
Total	31	0.011280			

Discussion and Conclusion

From a resolution V with 2 replicates of $\frac{1}{2}$ fractional factorial design and ANOVA analysis performed on these 5 main factors, it was determined that the operating pressure, feed concentration and capacity of the reactor are the three main factors that significantly affect the conversion of propylene oxide. These factors are used for the response surface experiment, the second part of the design.

RESPONSE SURFACE EXPERIMENT

Purpose

A response surface design was conducted in order to further probe the three determined significant factors. Conducting a response surface design is the way to determine the curvature and interaction between the factors and the response.

Experimental Design

For the 90% confidence interval the significant factors of pressure, feed concentration, and capacity have their selected maximum, minimum, and middle values displayed in Table 3. The temperature and feed rate were set to be constant at 80 ℉ and 1700 $\frac{ft^3}{h}$ respectively, from the midpoints of their high and low values tabulated in Table 1. A face-centered cube design with 5 center points was used, generating 19 runs in total, as tabulated in Table B in Appendix.

Table 3: Range of 3 Significant Factors for Response Surface Design

Factors	Minimum	Middle	Maximum
Reactor Capacity (%)	60	70	80
Feed Concentration ($\frac{lbmol}{ft^3}$)	0.050	0.075	0.100
Operating Pressure (atm)	1.50	2.75	4.00

After analyzing the mathematical model identified, each parameter's significance was determined from their p-values. First analyzing the squared parameters, then 2-way interactions and then linear factors. If the insignificant parameter removed decreased the R^2-adj or increased the S value, it remained in the model. Each analysis was iterized with the new parameters.

Results and Analysis

The final optimized model is as described by Eq. 1. The interactions of capacity $\times$ feed concentration, feed concentration $\times$ pressure, capacity^2, and pressure^2 were removed as their p-values were greater than $\alpha = 0.1$, decreased the standard deviation (S) and increased the R^2-adj values. Exceptions retained in the final model are capacity $\times$ pressure and pressure because they reduced the R^2-adj and increased the S values. Table 4 displays all the p-values. The final S value is 0.0101147 and R^2-adj is 34.25 %. Despite R^2-adj is far from 100 %, it is the maximum value that could be obtained from this set of factors.

$$Conversion = 0.3673 + 0.042 \times Capacity + 2.84 \times (Feed\ Concentration) + 0.0198 \times Pressure - 17.07 \times (Feed\ Concentration)^2 - 0.032 \times (Capacity \times Pressure) \quad \textbf{(Eq. 1)}$$

Table 4: ANOVA table of Response Surface Design

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	0.001471	0.000294	2.88	0.058
Linear	3	0.000804	0.000268	2.62	0.095
Capacity	1	0.000212	0.000212	2.07	0.174
Feed Conc	1	0.000490	0.000490	4.79	0.047
Pressure	1	0.000102	0.000102	1.00	0.335
Square	1	0.000539	0.000539	5.27	0.039
Feed Conc*Feed Conc	1	0.000539	0.000539	5.27	0.039
2-Way Interaction	1	0.000128	0.000128	1.25	0.284
Capacity*Pressure	1	0.000128	0.000128	1.25	0.284
Error	13	0.001330	0.000102		
Lack-of-Fit	9	0.000589	0.000065	0.35	0.910
Pure Error	4	0.000741	0.000185		
Total	18	0.002801			

Figure 2 displays the relationship between the mean conversion and the main factors. Increasing the value of capacity would decrease the mean conversion throughout. Meanwhile, increasing the values of feed concentration and pressure would both increase and decrease the mean conversion. The midpoint level allows some potential curvature for each factor in the model. This figure indicates feed concentration has the largest effect on conversion, followed by pressure then capacity.

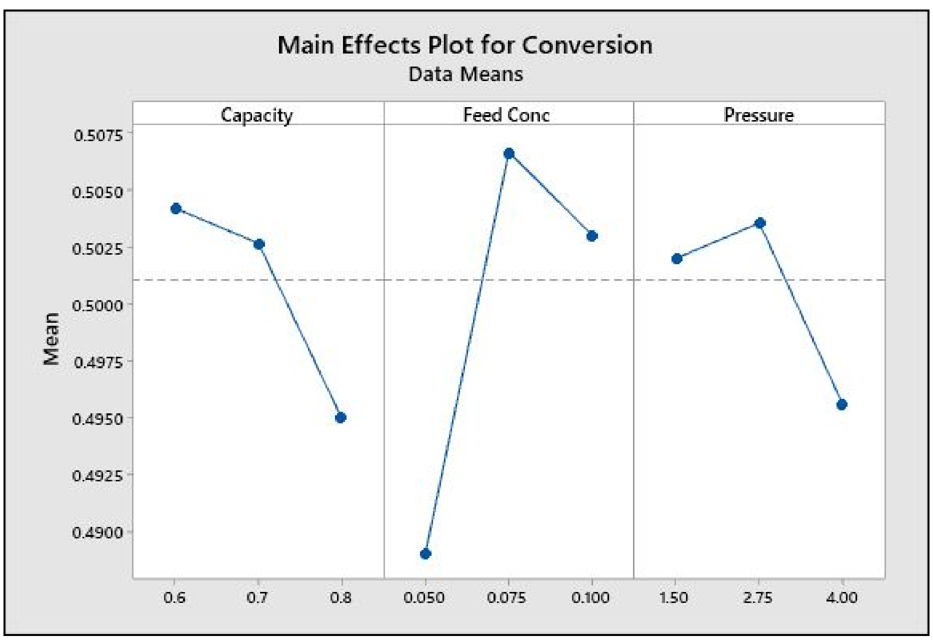

Figure 2: Main Effects Plot for Surface Response Design

Figure 3 shows the visualization of the raw data in four different residual plots. The residuals are normally distributed with potential outliers. No obvious pattern was observed on the standardized residual vs. fitted value plot.

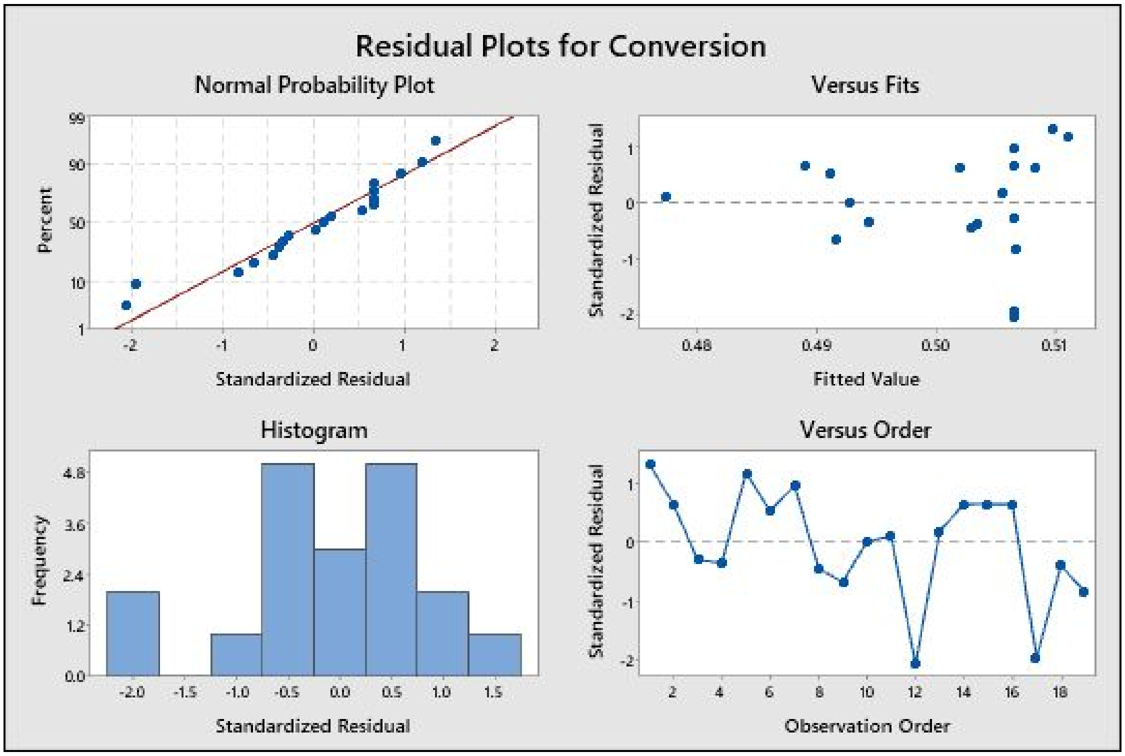

Figure 3: Residual plots for Response Surface Design

Discussion and Conclusion

The response surface design helps to develop a statistical model to predict the behavior of a reactor. With the minimum standard deviation and maximum R^2-adj values that could possibly be obtained from the design, the final mathematical model that best fits the data set with the chosen significant parameters is as shown in Eq. 1. The ANOVA table shows a high p-value for the 'lack-of-fit' error ($p = 0.910$), suggesting the model has a decent fit on the data. The removal of the interaction of capacity × feed concentration, feed concentration × pressure, capacity^2, and pressure^2 due to its insignificance provides the final mathematical model with S and R^2-adj values of 0.0101147 and 34.25 % respectively.

VALIDATION AND CONCLUSION

Eq. 1 was used to find the optimum values on the three significant factors, to have a targeted conversion of propylene oxide to be 49%. By using the response optimizer in Minitab [3], the desired conversion could be obtained by setting up the capacity, feed concentration, and pressure to be 0.8, 0.05 $\frac{lbmol}{ft^3}$, and 1.7 atm respectively, making the temperature 80℉ and feed rate 1700 $\frac{ft^3}{h}$, the same as in the response surface design. Under these conditions, 5 replicates of the conversions were generated from Matlab as follows: 0.498, 0.53, 0.515, 0.521, and 0.453. The sample mean and standard deviation were calculated to be 0.5034 and 0.0305 respectively.

Since the population standard deviation of the conversion was unknown and the sample size was small and the population conversion data is normally distributed, as shown in Figure 4. A one-sample, one-tailed t-distribution was used in determining the population mean of the conversion, μ_C within 95 % confidence interval. It was obtained that μ_C ranged from 0.4655 to 0.5413 of conversion. It is plausible to say that the conversion based on the previously specified factors could result in the targeted conversion of 0.49 as the value lies within the computed interval of population mean conversion.

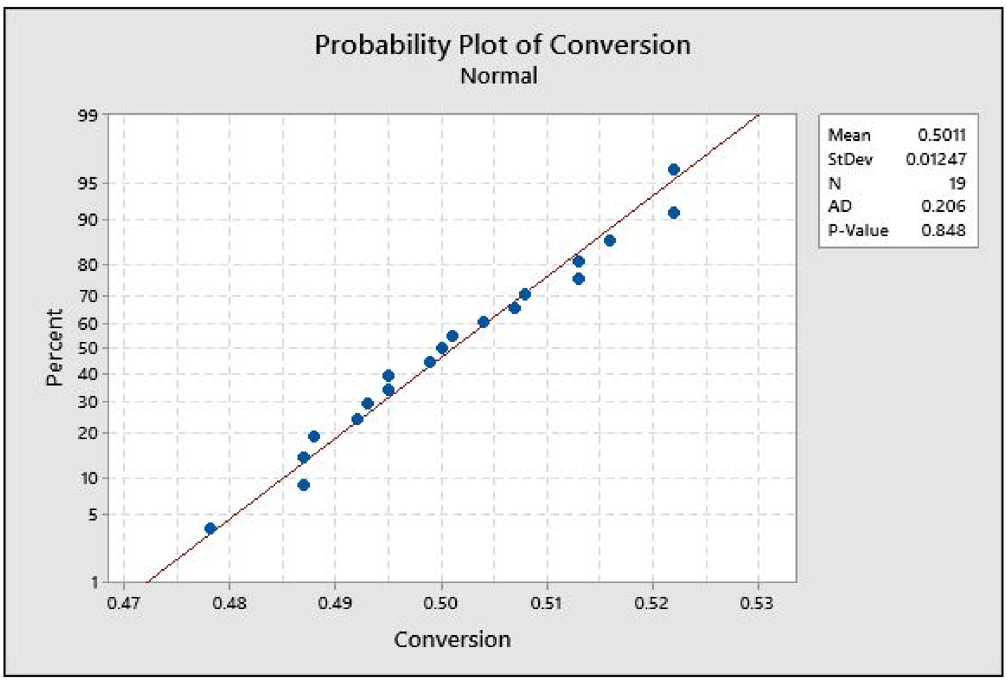

Figure 4: Normal Probability Plot of Conversion Data from Response Surface Design

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[1] A., W. A.; O., W. C. CSTR Design for Propylene Glycol Chemical Production. **2019**.

[2] Curie, M. *Distributions of Residence Times for Chemical Reactors*; 2008.

[3] Achieve Your Vision of Success. http://www.minitab.com/en-US/default.aspx (accessed May 17, 2020).

APPENDIX

Table A: Fractional Factorial Design Raw Data

Capacity	Feed Concentration ($\frac{lbmol}{ft^3}$)	Feed rate ($\frac{ft^3}{hr}$)	Feed Temperature (℉)	Pressure (atm)	Conversion
0.6	0.05	1300	70	4.0	0.442
0.8	0.05	2200	70	4.0	0.484
0.6	0.10	1300	100	4.0	0.486
0.6	0.10	2200	100	1.5	0.511
0.8	0.10	1300	100	1.5	0.505
0.6	0.10	2200	100	1.5	0.503
0.6	0.05	2200	100	4.0	0.478
0.8	0.10	1300	70	4.0	0.503
0.6	0.10	2200	70	4.0	0.493
0.8	0.05	1300	70	1.5	0.541
0.6	0.05	1300	70	4.0	0.507
0.6	0.05	1300	100	1.5	0.516
0.6	0.10	1300	70	1.5	0.516
0.8	0.05	1300	100	4.0	0.490
0.8	0.10	2200	100	4.0	0.497
0.6	0.10	1300	100	4.0	0.500
0.8	0.05	2200	100	1.5	0.527
0.8	0.05	1300	100	4.0	0.477
0.6	0.10	1300	70	1.5	0.496
0.6	0.05	2200	70	1.5	0.506
0.6	0.05	1300	100	1.5	0.500
0.8	0.10	2200	70	1.5	0.503
0.8	0.10	1300	100	1.5	0.518
0.6	0.10	2200	70	4.0	0.503
0.8	0.05	2200	100	1.5	0.517
0.8	0.05	2200	70	4.0	0.520
0.6	0.05	2200	70	1.5	0.523
0.6	0.05	2200	100	4.0	0.511
0.8	0.05	1300	70	1.5	0.540
0.8	0.10	2200	100	4.0	0.490
0.8	0.10	1300	70	4.0	0.495
0.8	0.10	2200	70	1.5	0.500

Table B: Response Surface Design Raw Data

Capacity	Feed Concentration ($\frac{lbmol}{ft^3}$)	Pressure (atm)	Conversion
0.7	0.075	1.50	0.522
0.8	0.075	2.75	0.508
0.7	0.075	2.75	0.504
0.6	0.050	4.00	0.492
0.6	0.075	2.75	0.522
0.8	0.100	4.00	0.495
0.7	0.075	2.75	0.516
0.7	0.100	2.75	0.499
0.8	0.050	1.50	0.487
0.6	0.050	1.50	0.493
0.8	0.050	4.00	0.478
0.7	0.075	2.75	0.487
0.8	0.100	1.50	0.507
0.7	0.050	2.75	0.495
0.7	0.075	2.75	0.513
0.6	0.100	4.00	0.513
0.7	0.075	2.75	0.488
0.7	0.075	4.00	0.500
0.6	0.100	1.50	0.501