



Purification Propionic Acid using n-Butanol in Semi Batch Reactive Distillation

Ahmed Hashim Raza ¹, Sunitha P ¹ and Basava Rao V V ¹

¹ Department of Chemical Engineering, University College of Technology, Osmania University, Hyderabad-500007, Telangana, India

Email: profbasavarao_1964@yahoo.com (Basava Rao V V)

Abstract

Reactive distillation is a cost-effective chemical engineering process intensification method which involves the reaction and separation simultaneously in a single unit. Previously, Propionic Acid has been purified using n-Butanol as an entrainer in a batch setup using reactive distillation in the presence of a cation exchange resin catalyst called Amberlite. The final product is n-Butyl Propionate and it can be subjected to reversible reaction to get pure propionic acid. The extension of reactive distillation in a semi-batch setup to purify Propionic Acid is yet to be studied. In the present work, the Propionic Acid is purified using n-Butanol (nB) as an entrainer through the esterification process to occur in a semi batch reactive distillation unit. The flow rate effect along with the concentration of acid at different weight percentages of catalyst are carried out. As nB possesses the lightest weight in the mixture, it volatilizes to the topmost section of the distillation column during the operation. By means of distillate, it can be eliminated from the reactive system in a typical setup of conventional batch reactive distillation (CBRD) column following which the conversion of PA gets inhibited. Hence, through the approach of semi-batch reactive distillation (SBRD) the purity of acid is verified. Contrarily in the reactive mixture, as water is the second lightest

component, it vaporizes to the top of the column and can be separated from the distillate that is being collected. Also, for the products, the reasons that the broad variability in their boiling points obtained after the reaction along with the reduced water content in the reboiler, constrain the occurrence of backward reactions hence, it can be neglected as a factor.

Keywords: Reactive Distillation, Propionic Acid, n-Butanol, Amberlite, Esterification, n-Butyl Propionate

1. Introduction

Reactive distillation is observed as a commercial method industrially for various batch processes. The extension of this batch reactive distillation (BRD) method is the semi-batch reactive distillation (SBRD), where any of the reactants can be introduced to the system with a steady flow rate. The synthesis of the desired products in the reaction of the BRD has been explored but not extensively applied. In particular, for the esterification reactions, the lighter weights of alcohols generally cause it to travel to the topmost section of the distillation column thereby decreasing its concentration in the reactive mixture and reducing the extent of the reaction [1]. Here, the implication of SBRD is to be followed for the addition of acid at a controlled flow rate to the still thereby increasing the extent of the reaction.

Propionic acid is known for its importance as an ecological solvent to coat formulations of pharmaceutical drugs, and as a raw material from a biodegradable polymer. Attaining high purity of propionic acid is necessary for various chemical industries to carry out different chemical reactions but, the attainment of high purity of acid via recovery processes remains a challenge. Some of such conventional methodologies are solvent extraction, precipitation, adsorption mechanisms or electrodialysis. Reactive distillation is a relatively easier method and cheap to conduct. Reactive distillation is beneficent as it focuses on the selectivity, rate of conversion of reactants to products, and control of heat flow during the process. It also utilises the response heat from system and abstains from the aspect of azeotropes in mixture [11-14].

The operation of reactive distillation is specifically practical for reactions involving equilibrium phases like the esterification reactions that include the hydrolysis reactions of the organic compounds involved in the reaction [8]. The reaction involving PA and nB is esterification and leads to the formation of an ester of n-butyl propionate and water. Here,

considering nB is much more kind than the other lower alcohols as nB refrains PA from polymerisation. This is made to react in the presence of an acidic medium. In the presence of strong homogeneous acids, there is a risk of corrosion and a risk of separation that can occur with the parallel reactions taking place in the setup. To avoid this, cation exchange resins in acidic media are preferable for this esterification reaction [13].

This esterification reaction is carried out in a reactor, named an esterification reactor in this setup. The alcohol (nB) is the reactive entrainer in the still. At a constant flow rate, propionic acid is introduced in the reactor. The vapours that exit the still consist of traces of alcohol (nB), water and ester (nBP). These vapours are passed into a fractionating column where due to the low-volatility of nBP and water, their condensation takes place in the partial condenser and travel down into the hydrolysis reactor. Here in this reactor, nBP and water react to give nB and PA. Due to the non-volatility of PA, it remains in the reactor and nB vapours travel upwards to the total condenser where the vapours ultimately condense. The alcohol thereby condenses and the droplets of nB are recycled back to the esterification reactor. Thus, propionic acid of higher purity is yielded.

2. Materials and Methods

2.1 Materials:

The esterification involving PA and nB is carried out with Amberlite IR120 Na⁺ as a catalyst. The apparatus to conduct the SBRD includes a Borosil Glass Packed column. The chemicals – propionic acid, n-butanol (also referred to as n-butyl alcohol), and Amberlite IR120 Na⁺ are obtained from MOLYCHEM. The glass-packed column is linked to a 2000mL three-nape round-bottomed flask consisting a magnetic stirrer in it for proper and even-mixing. This flask is placed on a heating mantle. Out of the three napes, one consists of a thermowell to fix a thermometer in it. The second neck is directly connected to the column which is 30cm in length and 3cm in diameter. This column consists of a packing of glass Raschig rings of length 3mm and diameter 2mm, while the third neck has a fixed silicon rubber with a syringe placed that is used to collect the sample.

Above the column, a double-surface condenser is placed to condense the vapours for recycling purposes. A glass column is also attached to the column where the condensed vapours are made to settle. Here, due to the difference in densities, the separation of n-butyl alcohol from water occurs. In these layers, the lower one consists of water which is removed

and the leftover liquid, that is n-butyl alcohol is transported back to the flask. The whole column is provided with a thermal insulation from the top, beginning with condenser to the flask at the bottom. This insulation is given to cease heat transfer to the ambient air. A pump is served as a means to circulate water to the system.

For the vapours to efficiently condense, double surface condensers are utilised. The distillation operation is carried out at total reflux conditions. This entire setup is facilitated for the collection of water from the condensate and the separation process occurs continuously.

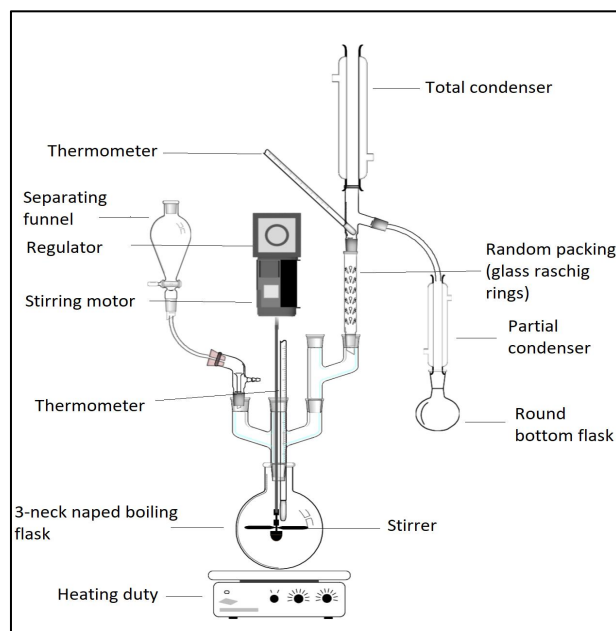


Figure 1: Schematic Representation of Semi-Batch Reactive Distillation Setup



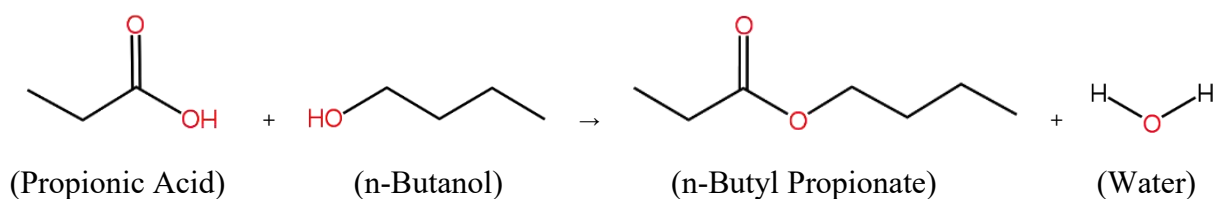
Figure 2: Photograph of Semi Batch Reactive Distillation Setup

2.2 Method of Procedure:

Initially, 99% purity of propionic acid is to be diluted to 80%, 60%, 40% of PA (propionic acid) using required amount of distilled water. After that 1:1 mole ratio of propionic acid (80%, 60%, 40%) and n-butanol (99% purity) are to be prepared (for 1:1 mole ratio 80% PA=179.696ml, n-butanol=217.37ml; for 60% PA=134.77ml, n-butanol=217.37ml; 40% PA=89.848ml: n-butanol=217.37ml) and the total solution was made up to 500ml. Similarly other mole ratios are to be prepared of mole ratios 1:1.5 and 1:2. All these are charged into the system with different weight percentages of catalysts (No catalyst, 1%) and studies can be conducted. Because of boiling point difference n-butanol is taken in the bottom (batch). The bottom temperature is adjusted by a thermostatic bath and propionic acid should be added continuously to that reactor.

Propionic acid flow rate is to be set to some value and initial reactor temperature and condensate temperature should be noted. After some time, for the vapours to produce, the contents are heated. These heated fumes are allowed to pass into the column through the Raschig packings to separate water. This separation is achieved by the condensation of water vapours from high volatile products. These condensed water droplets are made to flow through a separator situated at the bottom of the total condenser. Structurally, it is a graduated tube with a valve having a tap as an opening to drain the denser liquid (water) whereas the top liquid is fully transported back to the column. This operation is to be carried out to collect the distillate (with major proportion as water) up to the point where further water-removal is inconceivable.

After completion of the process, the residue samples are taken to analyse the mole fractions of free propionic acid (FPA) and total propionic acid (TPA). The above procedure is repeated to different flow rates of inlet propionic acid and different initial concentrations of propionic acid (80%, 60%, 40%) to investigate the effect of flow rates on conversion of free acid, total acid and poly acid formation. The following chemical structures are drawn using King Draw: Chemistry Station software and the reaction is as follows:



3. Result and Discussion

The following cases show the distillation operation occurring in the absence of catalyst. All these graphs are plotted using Origin2022 software.

3.1 Effect of Flowrate on Water Collected in Distillate

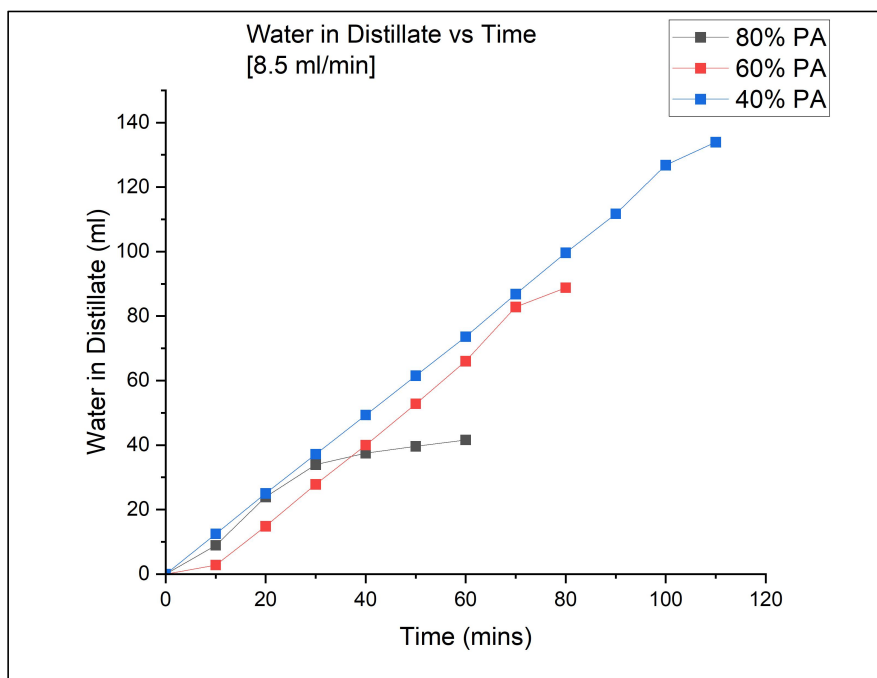


Figure 3: Water in Distillate vs Time [8.5 ml/min]

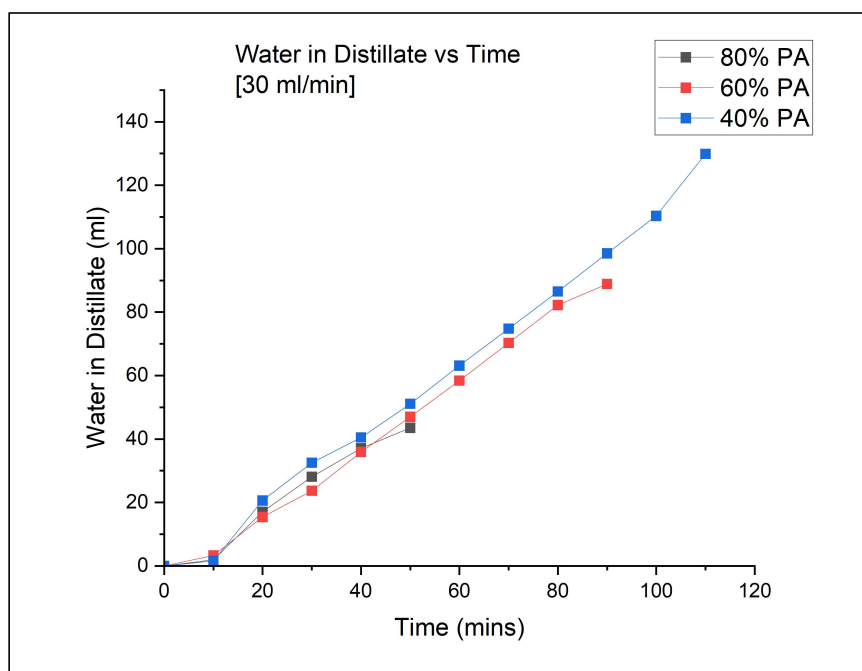


Figure 4: Water in Distillate vs Time [30 ml/min]

The water collected in distillate has an increasing trend in all the cases signifying that the water is being collected at all times. Despite an increasing trend, it can be observed that there is a smaller increase in slope followed by a greater slope then consistency at the end.

The consistent slope for the first 10 minutes show that there is reaction occurring due to which there is no separation occurring followed by a greater slope that shows mass transfer occurring. Towards the end of the process, the separation operation occurs. It is also observed that the water collected as more when a high flowrate of 30 ml/min was used than a slower flowrate of 8.5 ml/min.

3.2 Effect of Concentration of PA on Acidity

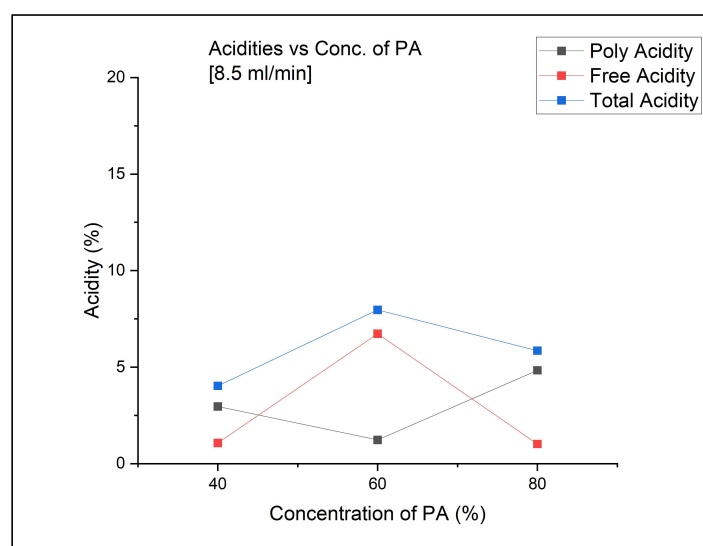


Figure 5: Acidities vs Concentration of Propionic Acid [8.5 ml/min]

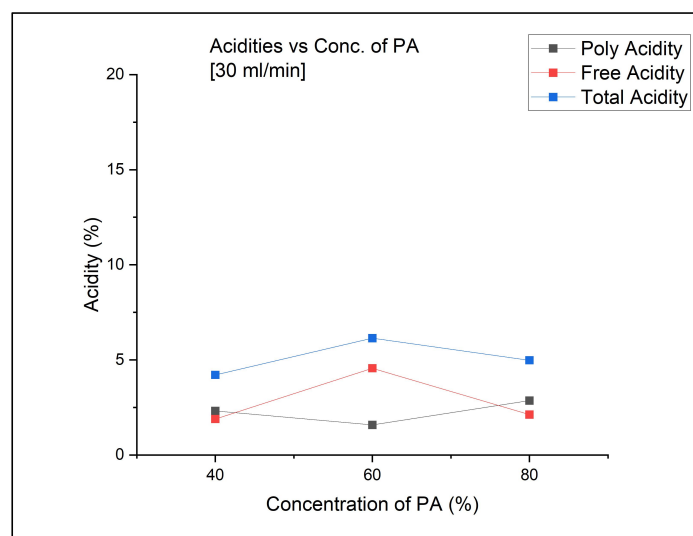


Figure 6: Acidities vs Concentration of Propionic Acid [30 ml/min]

The poly acidity is only decreasing for 60% PA while it is increasing for the rest of the concentrations. The free acidity is only increasing for 60% PA while it is decreasing for the rest of the concentrations. The total acidity is decreasing for all concentrations of PA at all flowrates. The total and free acidities are the highest for both flowrates and poly acidity is the lowest for 60% PA.

The reason behind is that its content of water in the acid that is being used for the reaction. For 80% the content of water is low and more acid content is present in the reactor causing more polymerisation while in 40%, more water content leads to inhibition of reactions causing polymerisation again. Thus, it means at 60% PA, the amount of water present in the reactor is ideally sufficient to carry out the distillation followed by separation.

Comparing the graphs, it can also be concluded that the total acidity is higher at smaller flowrates due to inhibition in polymerisation of acid molecules which is relatively lower than the higher flowrate.

3.3 Effect of Catalyst on Water Collected in Distillate

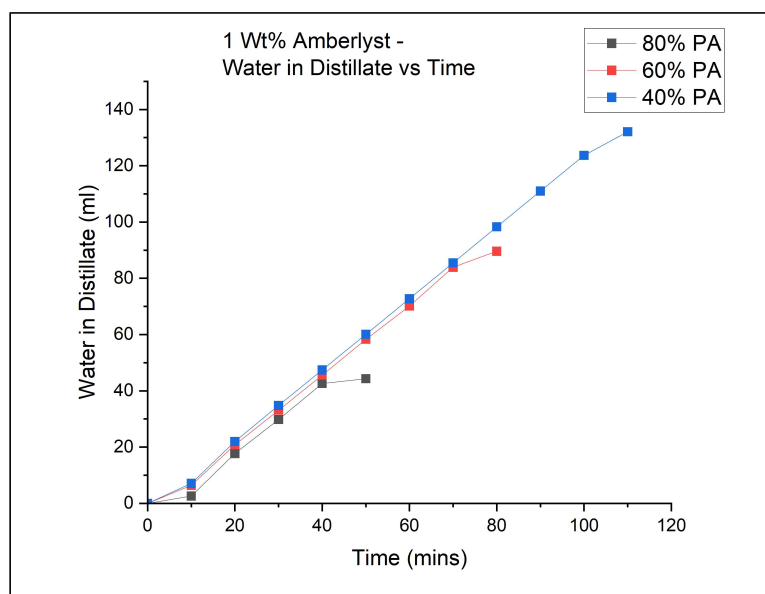


Figure 7: Water in Distillate vs Time at 1 wt% Amberlite Catalyst

The water collected in distillate in the presence of Amberlite catalyst was found to be more at all concentrations in comparison with the reactions carried out with no catalyst. The S-curve trend in the plot was found to be forming in the 80% and 60% PA. This shows that the catalysis has set favourable conditions for the reaction followed by mass transfer to occur throughout the distillation operation.

3.4 Effect of Catalyst on Acidities

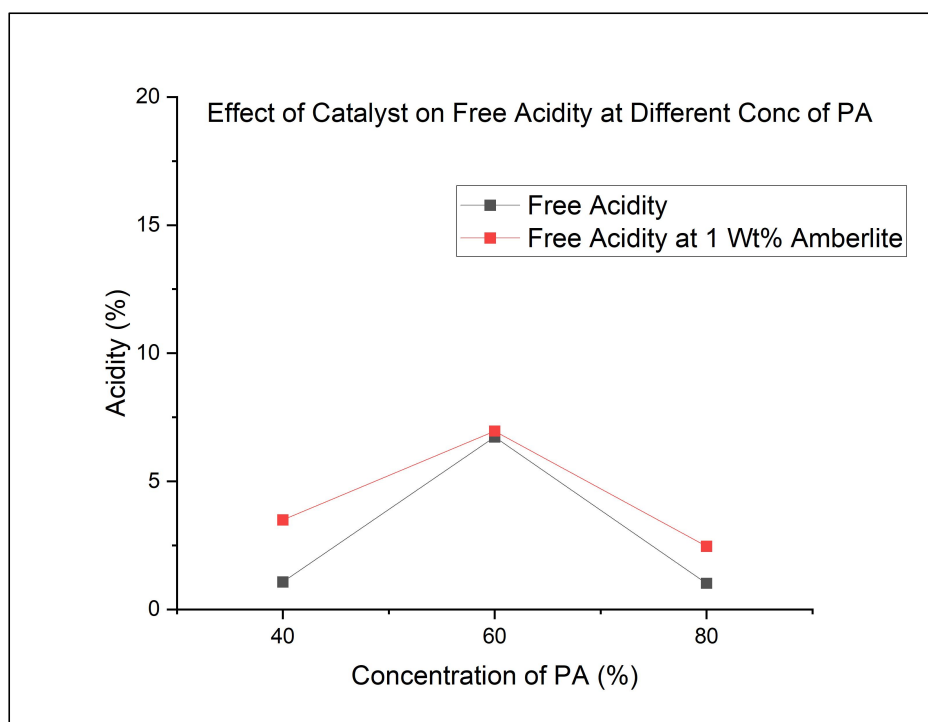


Figure 8: Effect of Catalyst on Free Acidity at Different Concentrations of PA

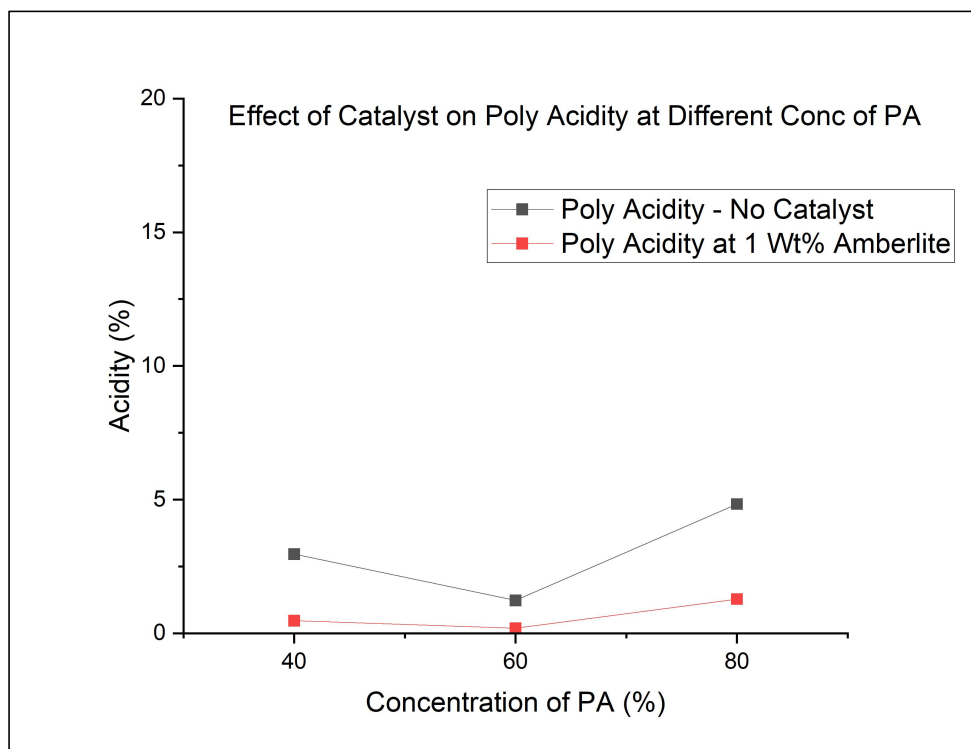


Figure 9: Effect of Catalyst on Poly Acidity at Different Concentrations of PA

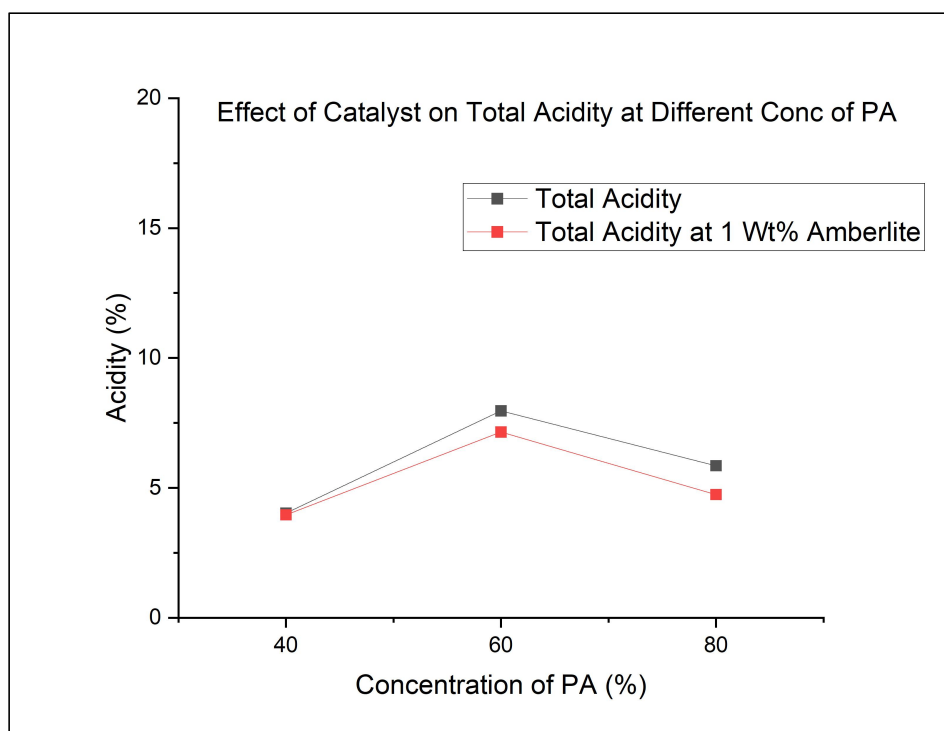


Figure 10: Effect of Catalyst on Total Acidity at Different Concentrations of PA

With the use of the Amberlite catalyst, the poly acidity was found to decrease only in 60% PA and had increased in the other two concentrations. The free acidity and the total acidity decreased in both usage of catalyst for 80%, 60% and 40%. This shows that 1 wt% of Amberlite catalyst has altered the rate of reaction and has made to reduce the polymerisation occurring in the reaction in 60% while it was not affecting the 80% and 40% of Propionic Acid esterification with n-butanol. The reason behind this is that 60% is ideal in amount of water that is present.

4. Design of Experiments (DOE)

To analyse the effects of different influential factors – flowrate and concentration of PA along with the catalyst weight percentage involved in the operation on various acidities, several studies from the design of experiments are conducted. Those are as follows:

4.1 Research Surface Methodology (RSM):

- Three dimensional plots between acidities vs concentration and flowrate in the presence and absence of catalyst are plotted using Origin2022. These plots signify the continuity for concentration and flowrates that lie in the range of values assigned in the data.

- A growth in free and total acidities is observed at 60% of PA with highest peak situated at the lower flowrate in Fig. 11 and 13 while an opposite trend is noted in Fig. 12 in the absence of Amberlite.
- In the presence of Amberlite, for a fixed flowrate the free and total acidity at 60% PA are again found to be the highest in Fig. 14 and 16 while the catalyst is influencing in lowering the poly acidity even more at the same acid concentration in Fig. 15.

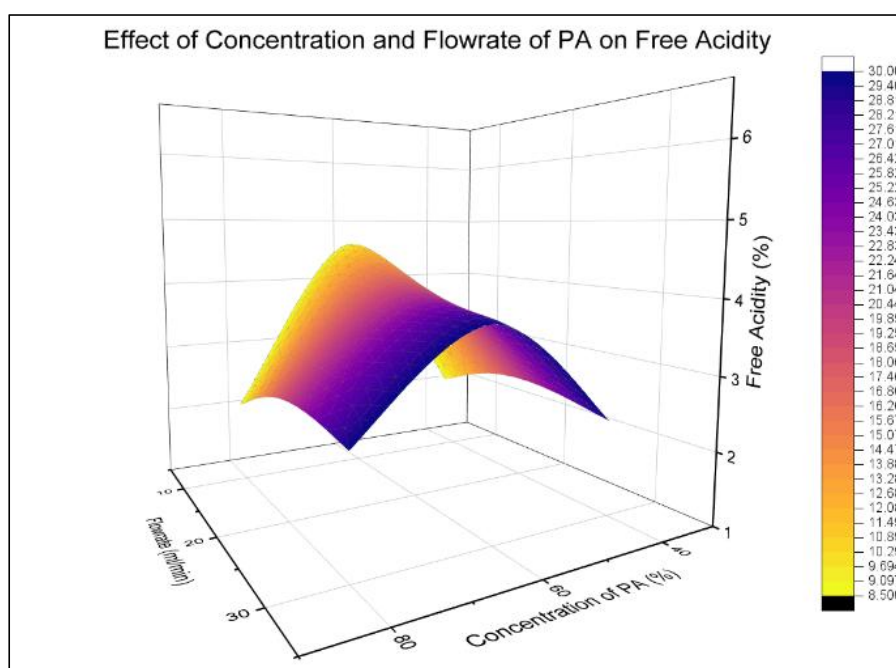


Figure 11: Effect of Concentration and Flowrate of PA on Free Acidity

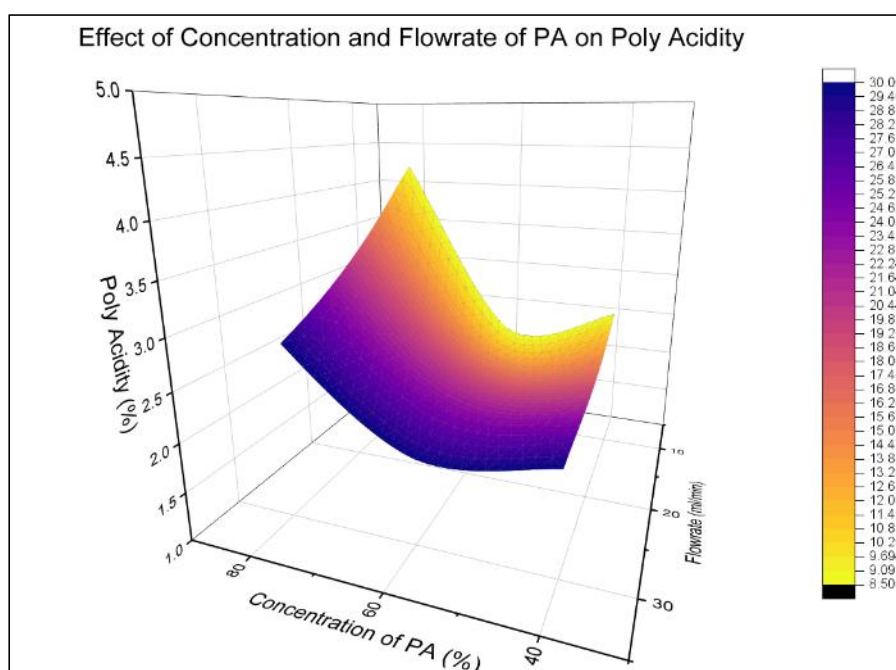


Figure 12: Effect of Concentration and Flowrate of PA on Poly Acidity

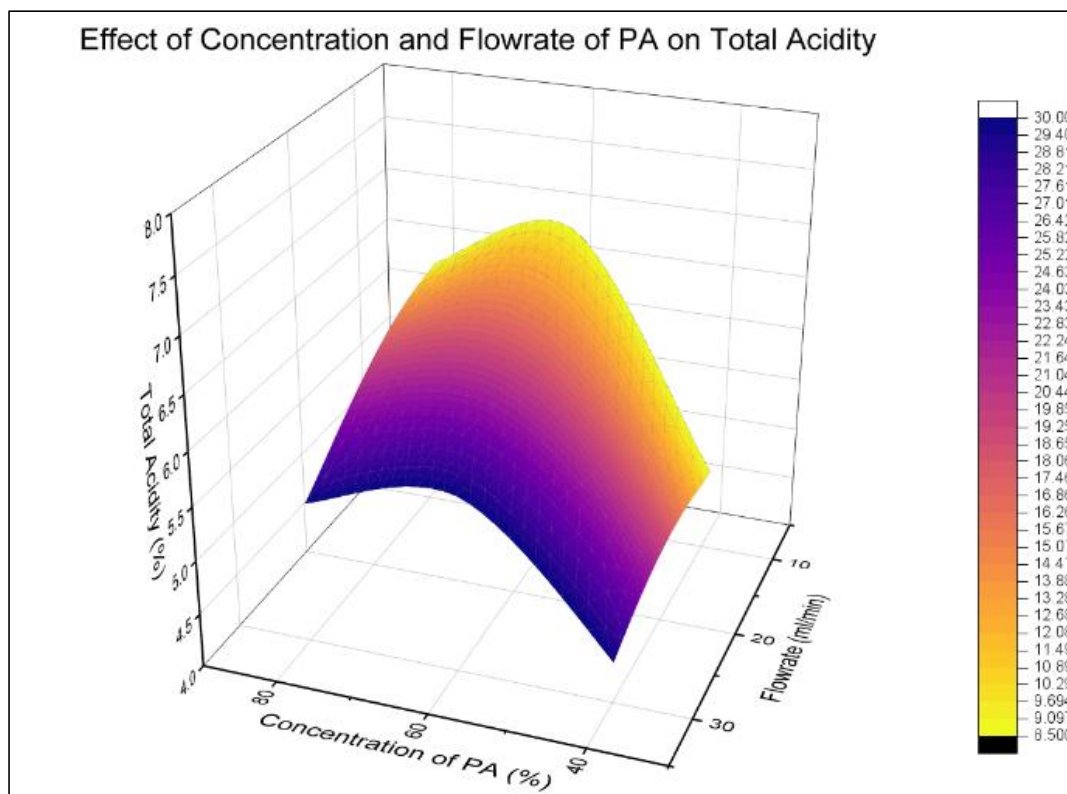


Figure 13: Effect of Concentration and Flowrate of PA on Total Acidity

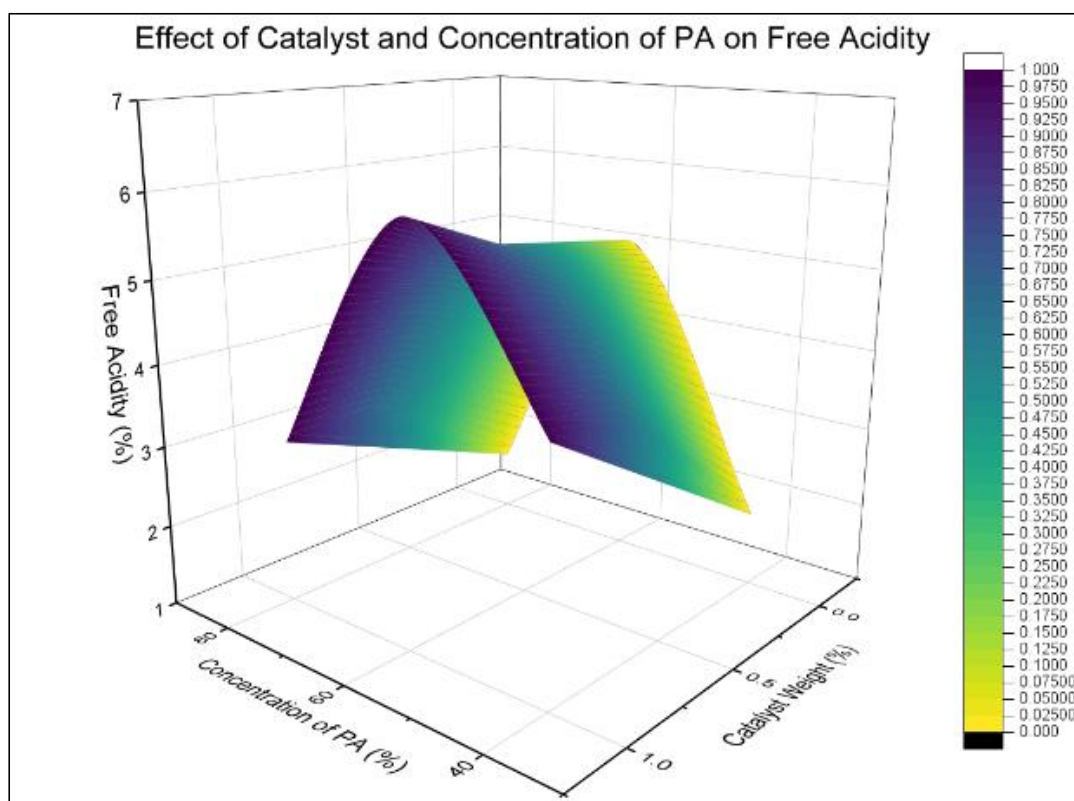


Figure 14: Effect of Catalyst and Concentration of PA on Free Acidity

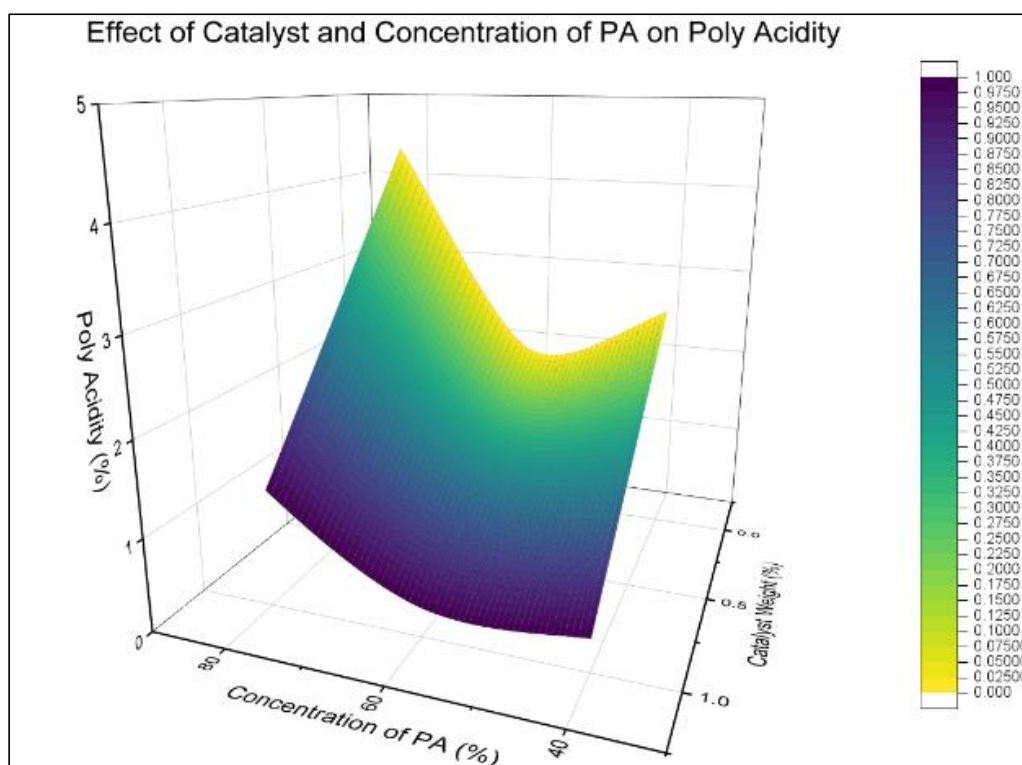


Figure 15: Effect of Catalyst and Concentration of PA on Poly Acidity

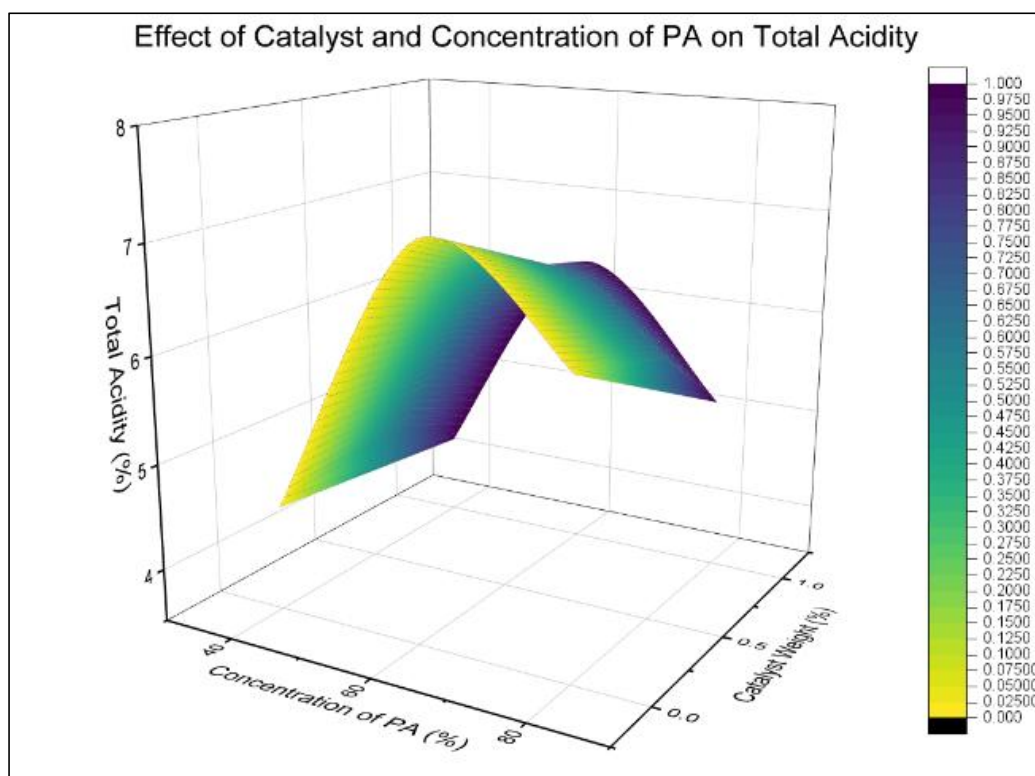


Figure 16: Effect of Catalyst and Concentration of PA on Total Acidity

4.2 Analysis of Variance (ANOVA):

Design Expert 13 software was used to test ANOVA for the given parameters, and to estimate the regression equations for the same. The results are tabulated in Table 1

Table 1: Analysis of Variance [ANOVA]

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	16.43	6	2.74	21.54	0.0450	significant
A-Catalyst	0.4958	1	0.4958	3.90	0.1869	
B-Flowrate	0.2281	1	0.2281	1.80	0.3123	
C-Concentration	7.40	1	7.40	58.27	0.0167	
AB	0.3885	1	0.3885	3.06	0.2225	
AC	1.61	1	1.61	12.66	0.0707	
BC	1.19	1	1.19	9.35	0.0924	
Residual	0.2542	2	0.1271			
Cor Total	16.68	8				

The implication from Table 1 in the Model F-value of 21.54 shows that it is significant. The occurrence of an F-value to be this large is 4.50% and the reason would be unwanted variations. Here, the indication of model terms with p-values less than 0.05 are for significant results and the values greater than 0.1 are not significant. In this case, C is a significant model term.

4.3 Coefficients in Terms of Coded Factors:

Table 2: Coefficients in Terms of Coded Factors

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	2.37	1	0.1691	1.64	3.09	
A-Catalyst	0.3910	1	0.1979	-0.4607	1.24	1.71
B-Flowrate	0.2180	1	0.1627	-0.4821	0.9181	1.25
C-Concentration	-1.51	1	0.1979	-2.36	-0.6593	1.71
AB	-0.4220	1	0.2413	-1.46	0.6164	1.32
AC	-0.9190	1	0.2583	-2.03	0.1924	1.52
BC	-0.7380	1	0.2413	-1.78	0.3004	1.32

The coefficient estimate in Table 2 depicts the changes in response which are expected per unit change in factor value when all the remaining factors are held constant. The intercept is the total mean response of all the runs in an orthogonal design while the adjustments around

that mean based on the factor settings are coefficients. In this case, for the factors that are orthogonal the variance inflation factors (VIFs) are greater than one which indicate multicollinearity leading to more severe correlation of factors.

4.4 Coded Equation:

For the given levels of each factor, an equation in terms of coded factors can be utilised for making predictions about the response. This coded equation is advantageous to identify the relative impact of the factors by comparing the factor coefficients.

$$0.3910A + 0.2180B - 1.51C - 0.4220AB - 0.7380BC - 0.9190CA + 2.37$$

[Here A – Catalyst, B – Flowrate, C – Concentration]

4.5 Actual Equation:

For the given levels of each factor, an equation in terms of actual factors can be utilised for making predictions about the response. This equation cannot be used for determining the relative impact of each factor as the coefficients are scaled to accommodate the units of each factor and also for the reason that the intercept is not at the centre of the design space.

$$7.80735A + 0.265488B + 0.036477C - 0.078512AB - 0.003433 BC - 0.0919CA - 1.36065$$

[Here A – Catalyst, B – Flowrate, C – Concentration]

4.6 Regression Plots:

Several graphs were plotted in Design Expert 13 in terms of residuals.

- The first plot in Fig. 17 relates the probability of occurrence of mean data points lying close to the reference line for the provided range of poly acidities in between 0.19 and 4.832 thereby showing that the residuals are minimal. Hence, this plot is of a normal distribution.

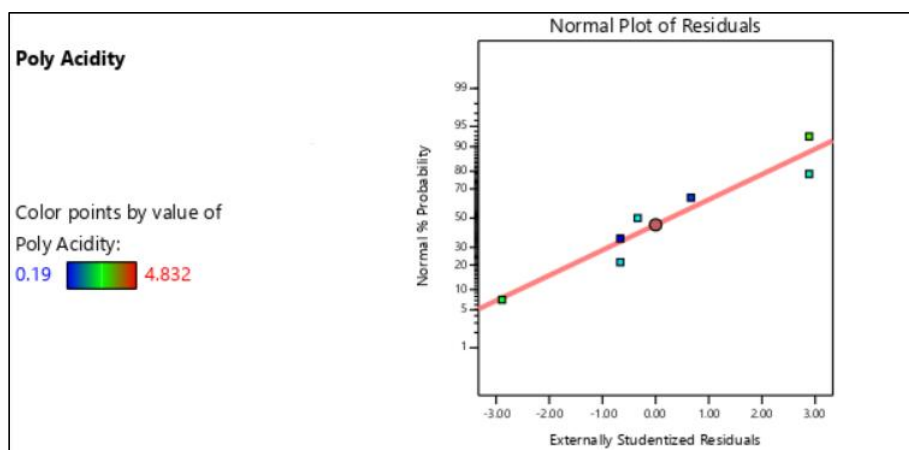


Figure 17: Normal Plot of Residuals

- The plots in Fig. 18 and 19 are in the form of control charts. The distribution in both the cases depicted that the predicted values and the run values respectively - when drawn against the residuals are approximately equivalent to the average outputs for poly acidities provided in the data. Hence, these plots prove that the overall distillation operation is under control.

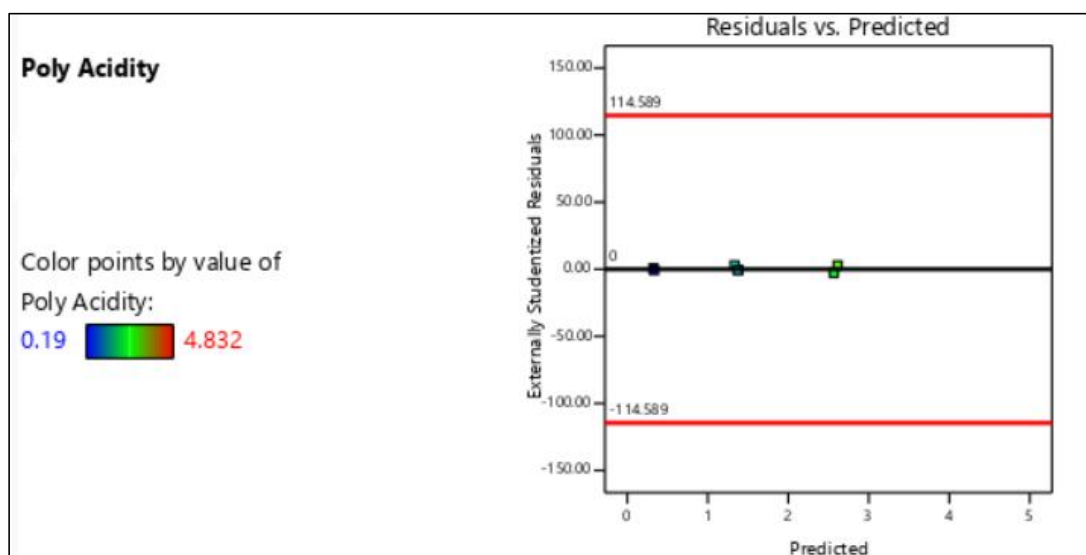


Figure 18: Residuals vs Predicted

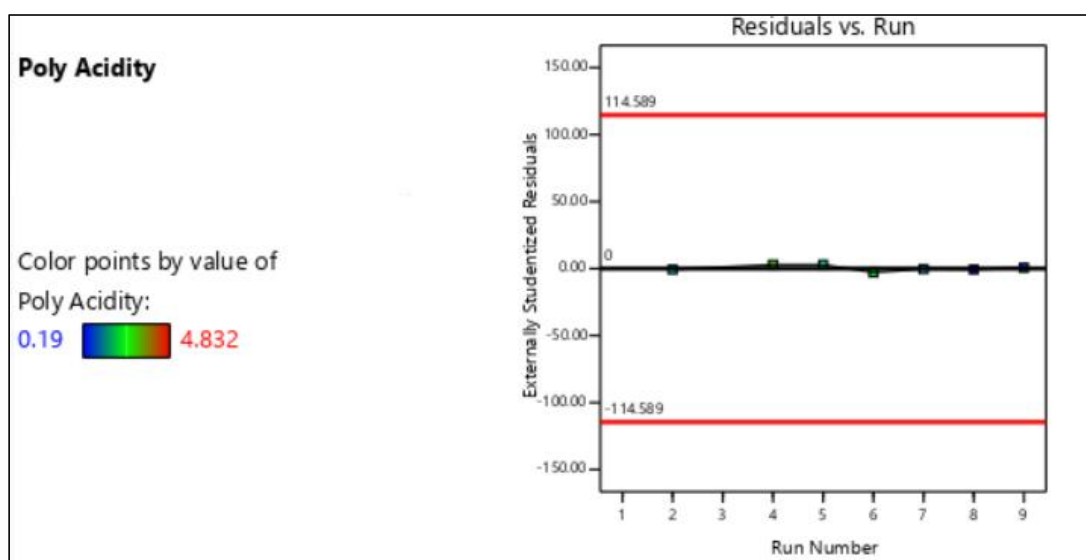


Figure 19: Residuals vs Run

- The predicted vs actual plot in Fig. 20 shows that there has been a very low variation in the output values of poly acidities for the assigned parameters consisting of catalyst wt%

along with the flowrates and concentrations. Thus, the distribution can be concluded to be of normal type.

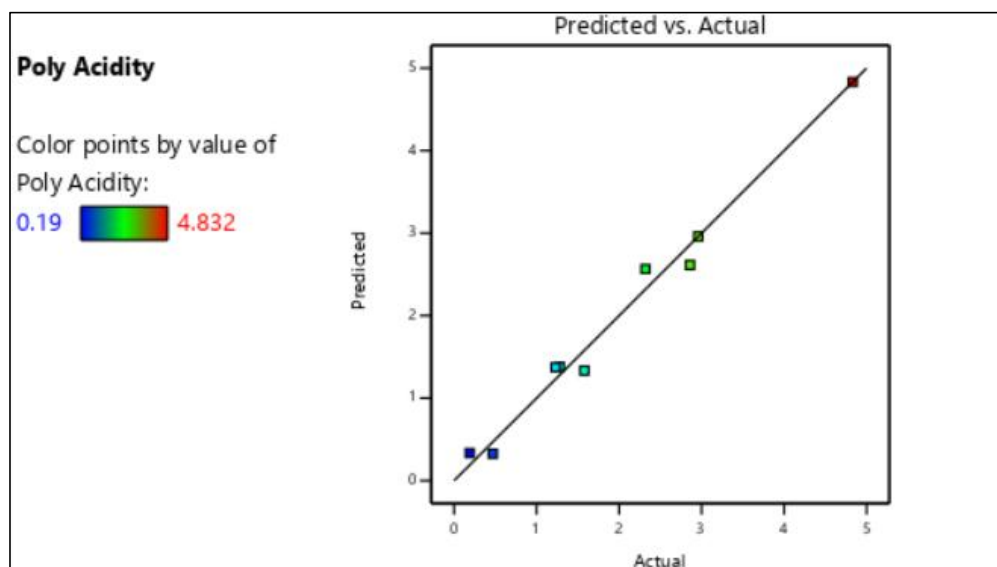


Figure 20: Predicted vs Actual

5 Conclusions

The low poly acidity at 60% is favourable and the reason behind it is its content of water in the acid that is being used for the reaction. For 80% the content of water is low and more acid content is present in the reactor causing more polymerisation while in 40%, more water content leads to inhibition of reactions causing polymerisation again. Hence the 60% propionic acid is the most ideal acid amount for reactive distillation at any type of flowrates. The design of experiments conclude that the operation is under control and that the results are following a normal distribution trend in the series of outputs that are obtained.

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