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Screening of Catalyst and Important Variable for The Esterification of Acrylic Acid with 2 Ethylhexanol

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Abstract. The global demand of 2-ethylhexyl acrylate (2EHA) market has witnessed a significant growth in the past few years and this growth is anticipated to increase in the coming years. 2EHA is one of the basic organic building blocks that mainly used in the production of coatings, adhesives, superabsorbents, thickeners and plastic additives. Homogenous acid-catalysed esterification of acrylic acid (AA) with 2-ethylhexanol (2EH) is commonly used for the production of 2EHA. The homogeneous catalysts such as sulfuric and para-toluene sulfonic acid have resulted the costly and complicated downstream process that generates acidic, corrosive and non-environmental friendly waste. Therefore, it is importance to develop a cheaper process that employing heterogeneous catalysts and alternative raw material from wastewater containing acrylic acid. In this research, the study for the esterification of AA with 2EH catalysed by ion-exchange resin was conducted. The best sulfonic acid functional cation-exchange resin among SK104, SK1B, PK208, PK216, PK228, RCP145, and RCP160 was screened. PK208 outperformed the other resins and it was used subsequently in the parametric studies. The effect of important parameters (initial concentration of acrylic acid (AA), temperature, molar ratio of reactant (AA and 2EH), catalyst loading, and polymerisation inhibitor loading) was studied using 2 factorial design to determine the significant parameters to the esterification. It was found that the initial concentration of AA and temperature were most significantly affecting the esterification of AA with 2EH.

1. Introduction

2-Ethylhexyl Acrylate (2EHA) is an acrylate ester produced in a large scale owing to the wide application of its polymer in the manufacturing of coating materials, adhesives, and impregnating agents. 2EHA appears in clear and volatile liquid naturally. It is slightly soluble in water and completely soluble in alcohols, ethers, and solvents.

2EHA is manufactured through the direct esterification of acrylic acid (AA) with 2-ethyl hexanol (2EH). Traditionally, sulphuric or p-toluenesulfonic acid have been used as the catalysts to accelerate the reaction rate in production of 2EHA [1]. However, the use of these strong acidic compounds as catalysts has resulted the elevated downstream processing and operation costs. Furthermore, the unrecycled homogeneous acidic catalysts also cause environmental problem. In recent years, the



research interest has been shifted to the heterogeneously catalysed AA esterification reaction study to overcome these problems.

One of the important characteristics of the heterogeneous catalysts is water resistance since the by-product during the esterification of AA with alcohol is water. A few of heterogeneous catalysts have been found to be water resisted which including organic functional polymers, zeolites, salts of heteropolyacids, some of the sulfated oxides, and other solid oxides [2][3]. Some of it such as salts of heteropolyacids were not used in the commercial process due to the leaching problems [4].

Ion exchange resins (IER) have attracted considerable attention in the researches about the esterification of organic acid with alcohol. Amberlyst, Dowex, Nafion, and Purolite are among the commonly used IER catalysts in the esterification of organic acid with alcohol. Altiokka and Odes [5], Essayem et al. [6] and Okuhara et al. [3] employed several type of heterogeneous catalysts in the esterification of AA with propylene glycol, butane and butanol respectively. They found that IER type of catalyst outperformed the other type of catalyst for the esterification reaction.

The research on heterogeneously catalysed 2EHA synthesis is still rare. Komon et al. [4] performed the best catalyst screening among the Amberlyst group (Amberlyst 39, Amberlyst 46, Amberlyst 70, and Amberlyst 13) before carrying out the kinetics study of the esterification of AA with 2EHA catalysed by Amberlyst 70. Meanwhile, Chin et al. [7] has done the kinetic and one factorial at time (OFAT) parametric study for the identical reaction catalysed by Amberlyst 15.

The objective of this study was to screen the best IER catalyst among SK104, SK1B, PK208, PK216, PK228, RCP145 and RCP160. Afterward, the effect of important parameters such as AA initial concentration, temperature, molar ratio, catalyst loading, and polymerisation inhibitor loading on the production of 2EHA with AA were evaluated. The 2 factorial design were used to determine the interaction factors accurately in a timely and cost saving mode.

2. Methodology

2.1. Materials

Both reactants, 2-ethyl hexanol (99.99%) and acrylic acid (99.99%) as well as polymerisation inhibitor, phenothiazine were supplied by Sigma Aldrich. Another polymerisation inhibitor, 4-Methoxyphenol (MEHQ) was supplied by ReagentPlus. Diaion SK104, SK1B, PK208, PK216, PK228, RCP145, and RCP160 were sponsored by Mitsubishi Chemical Corporation. All these chemicals and catalyst were used without further purification. Ultra-pure water was obtained from ultra-pure water system MILLIPORE model SAS 67120.

2.2. Apparatus

All the experiments were conducted in a 500 mL 3-necked round bottom flask fitted with reflux condenser and thermocouple. Rotamantle was the source of heating and stirring. The temperature was maintained within desired temperature (± 1 K) by PID temperature controller. In a typical procedure, a pre-determined amount of alcohol and acrylic acid with the corresponding amount of polymerisation inhibitor were preheated separately until achieving the desired temperature before it was mixed. Subsequently, catalyst with a pre-fixed loading was transferred to the reactor and the reaction was started. A product sample of circa 0.5 mL was withdrawn every 1 hour interval. To avoid any further reaction, the collected samples were rapidly cooled down in 277 K chiller prior to the GC analysis in spite of the very slow reaction rate for the un-catalysed reaction.

2.3. Catalyst characterisation

2.3.1. Ion Exchange Capacity (IEC).

0.1 g of catalyst was immersed in 100 ml of 0.1 M NaCl solution for 24 hours. The NaCl solution was then titrated using 0.01 M KOH with phenolphthalein as the indicator. The ion exchange capacity in milliequivalents/gram (meq/g) is calculated using Equation (1):

$$\text{IEC v TLC} = \frac{V_{\text{KOH}} \times M_{\text{KOH}}}{\text{mass}_{\text{catalyst}}} \quad (1)$$

where V is volume and M is molarity.

2.3.2. Leaching test.

0.5 g of catalyst was immersed in 50 ml of water and 2 ethyl hexanol (2EH) at 95 °C for 4 hours (imitate the reaction duration) respectively for sulphonic acid leaching analysis. The solution was then titrated using 0.01 M KOH with phenolphthalein as indicator. The total leaching capacity (TLC) in meq/g is calculated based on Eq. (2.1) while the percentage of leaching (L%) is calculated using Equation (2) respectively:

$$L = \frac{\text{TLC}}{\text{IEC}} \times 100 \quad (2)$$

2.3.3. Performance test.

For the performance test, 7 types of DIAION resins (SK104, SK1B, PK208, PK216, PK228, RCP145, and RCP160) were tested for their activity at the temperature of 368 K, catalyst loading of 10% w/w (catalyst/acrylic acid) and molar ratio of AA:2EH is 1:3. The samples were withdrawn at every 1 h for 4 h. To avoid any further reaction, the collected samples were cooled rapidly at 277 K prior for gas chromatography (GC) analysis. The best catalyst was selected in subsequent experimental work.

2.3.4. Screening of Important operating parameters.

Design Expert DX7 that is statistical software is used to generate the design of experimental (DOE) for screening and optimization studies to identify the vital factors that affect the esterification process. It is advisable to proceed with two level factorial design first as the factors is more than 3. Two level factorial fractional designs (half factorials) which is available to explore many factors is selected. This design setting each factor to only two levels for the screening studies. It is sufficient and efficient designs used to screen many factors to find the few that are critically significant and to estimate the effects of all interactions. After the screening studies has identified the critical variable that affect the esterification performance, response surface method (RSM) central composite design (CCD) is proceeded. In this design, the consideration of three groups of design points that is two-level factorial or fractional factorial design points, axial points and center points is proceed to quantify the relationships between that chosen critical factors for optimization purpose. Table 1 and 2 shows the high and low level of each variable and the list of design experiment from the software tools respectively.

Table 1. Value for high and low level

Parameters	High level	Low level
Initial AA concentration	100% w/w	10% w/w
Temperature	100°C	80°C
Molar ratio	1:1	1:5
Catalyst loading	3% w/w	10% w/w
Inhibitor loading	0% w/v	0.5% w/v

Table 2. Experimental design for 2 factorial analysis (half factorial)

Experiment	AA Conc. (% w/w)	Temperature (°C)	Molar Ratio (AA:2EH)	Cat. Loading (% w/w)	Inhibitor Loading (% w/v)
1	10	80	1:1	3	0.5
2	100	80	1:1	3	0
3	10	100	1:1	3	0
4	100	100	1:1	3	0.5
5	10	80	1:5	3	0
6	100	80	1:5	3	0.5
7	10	100	1:5	3	0.5
8	100	100	1:5	3	0
9	10	80	1:1	10	0
10	100	80	1:1	10	0.5
11	10	100	1:1	10	0.5
12	100	100	1:1	10	0
13	10	80	1:5	10	0.5
14	100	80	1:5	10	0
15	10	100	1:5	10	0
16	100	100	1:5	10	0.5
17	55	90	1:3	6.5	0.25
18	55	90	1:3	6.5	0.25
19	55	90	1:3	6.5	0.25

3. Results and Discussion

Figure 1 displays the divinylbenzene crosslinkage (DVBCL) percent, ion exchange capacity (IEC), and sulfonic acid (SO₃⁻) leaching properties of each IER used in this studies. Three types of ion exchange resins were tested. It included highly macroporous resins (RCP145 and RCP160), macroporous resins (PK208, PK216, and PK228) and gelular resins (SK104 and SK1B).

All IER (SK104, SK1B, PK208, PK216, PK228, RCP145, and RCP160) has been tested for their catalytic performance in the synthesis of 2EHA via esterification of AA with 2EH. The yield of 2EHA obtained through the esterification reaction catalysed by different types of resin is shown in Figure 2. PK208 has outperformed all the other catalysts over 4 hours of reaction by showing the highest yield of 2EHA (41.2% yield). The yield of 2EHA obtained for the other catalysts is arranged in the descending order as follow: SK1B (35.5%), RCP145 (33.6%), SK104 (31.3%), PK216 (26.1%), RCP160 (15.8%) and PK228 (15.1%).

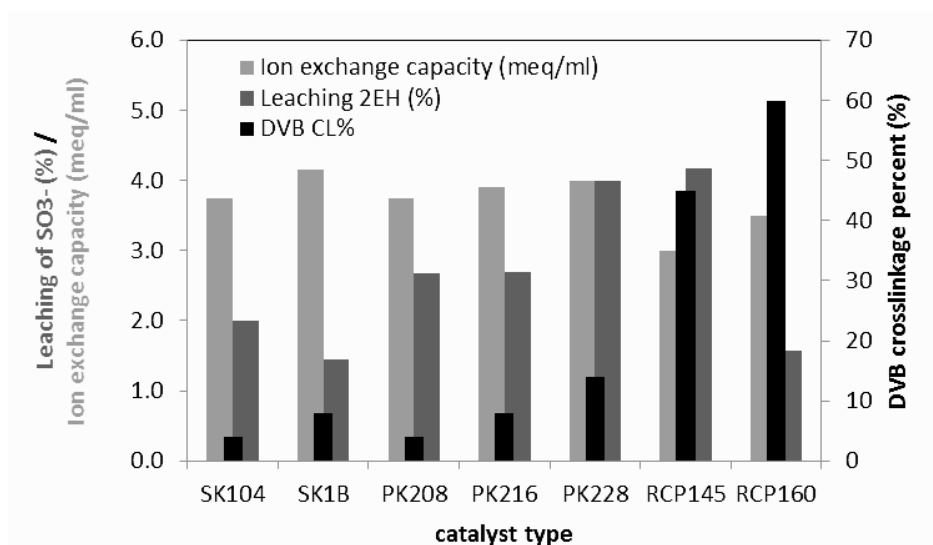


Figure 1. Percentage of DVB crosslinkage for the IER catalysts. Percentage of IEC for the IER catalyst. Leaching of sulfonic acid for the IER catalysts

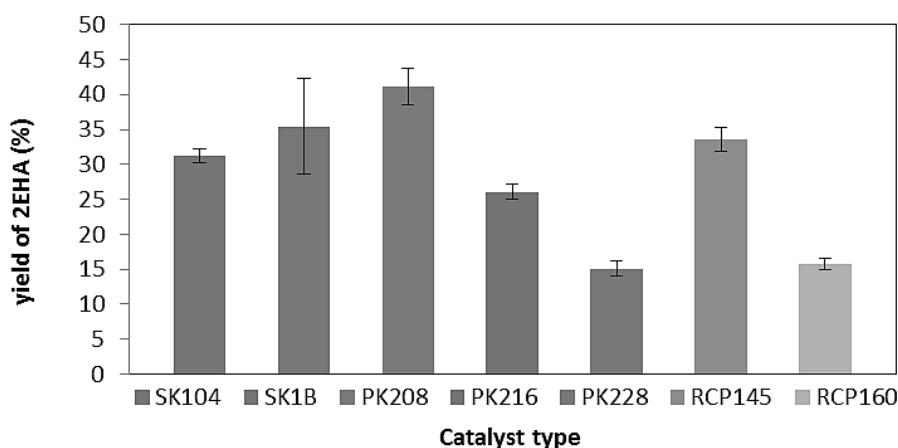


Figure 2. Yield of 2EHA for the reaction catalysed by different types resin catalysts for 4 h. Operating condition: Initial conc. AA: 100%; Temperature: 95°C; Catalyst loading of 10% w/w (catalyst/AA); molar ratio of AA:2EH is 1:3

Figure 1 shows that RCP145 and PK228 possessed the poorest sulfonic acid leaching properties as compared to the others. Despite the poor sulfonic acid leaching property, RCP145 has shown the substantial yield as shown in Figure 2 due to the reaction catalysed by leached sulfonic acid in homogeneous phase. So, these heterogeneous catalysts are not considered as the good catalysts due to its severe leaching. The leaching properties for the other catalysts were within the acceptable levels.

It is generally known that for IER catalysts, the catalytic performance was typically attributed by the IEC of the resins. Nevertheless, Figure 1 shows that the IEC of IER catalysts did not differ much (ranged from 3–4.15), implying that the catalytic performance of IER catalysts in the present study was not solely affected by IEC but the DVB crosslinkage percentage (CL%) and sulfonic acid leaching percentage (L%).

DVB crosslinkage percent (CL%) generally have impact on the structure (porosity and surface area) and swelling properties of the catalyst. The higher DVB CL%, the more porous the catalyst would be thus increasing the surface area of the catalyst. The degree of crosslinkage of resins is also closely related to its pore sizes. Resins with the lower degree of crosslinkage have a larger pore size.

Reactants can easily diffuse and travel to the active sites due to its lower mass transfer resistances. Thus, a higher rate can be obtained for the reaction catalyzed by resins with a lower degree of crosslinkage [8]. On the other hand, DVB CL% has negative effect on swelling properties, in which the catalysts swell lesser with the higher DVB CL%. It is noticeable that the increasing of DVB CL% for each category of the resins would lead to a negative response in its catalytic performance (Figure 1 and 2). The increase of surface area in this case does not enhance the catalytic activity as the active site distribution over surface area would be decreased. Moreover, the size of 2EH which is bigger than the other alcohols would have difficulty to penetrate through the porous site of resin with higher DVB CL%. PK208, the best catalyst giving the highest yield of 2EHA, was selected to be used in subsequent studies.

3.1. Screening of important operating parameter via 2 factorial design.

The effect of some of the factors to the reaction can sometimes be less significant. These insignificant factors would lead to wrong results on the importance of the most significant variables [9]. The purpose of using screening design is to be economical, by saving time and money on chemicals, and to identify the significant factors [10].

Table 3 shows that the initial AA concentration and temperature significantly affected the 2EHA yield in the esterification of AA with 2EH (p-value < 0.0001). However, other factors such as 2EH to AA molar ratio, catalyst loading and inhibitor loading were insignificant (p-value > 0.0001). The initial AA concentration was the major contributing factor (66.52%), followed by the temperature (11.9%) as shown in Table 4. The interaction of initial AA concentration with temperature was also prominent (9.13%). The yield of 2EHA increased from 1.3 to 14.7 % with the increase of initial AA concentration from 10 to 100 % w/w (Figure 3(A)). In addition, the yield of 2EHA also increased from 5.2 to 10.8 % when the reaction temperature was increased from 80 to 100 °C (Figure 3(B)).

Table 3. P-values of responses against factors.

Factor	p-value for response
Initial AA concentration	<0.0001
Temperature	<0.0001
Molar ratio	0.0344
Catalyst loading	0.0003
Polymerisation inhibitor loading	0.0381

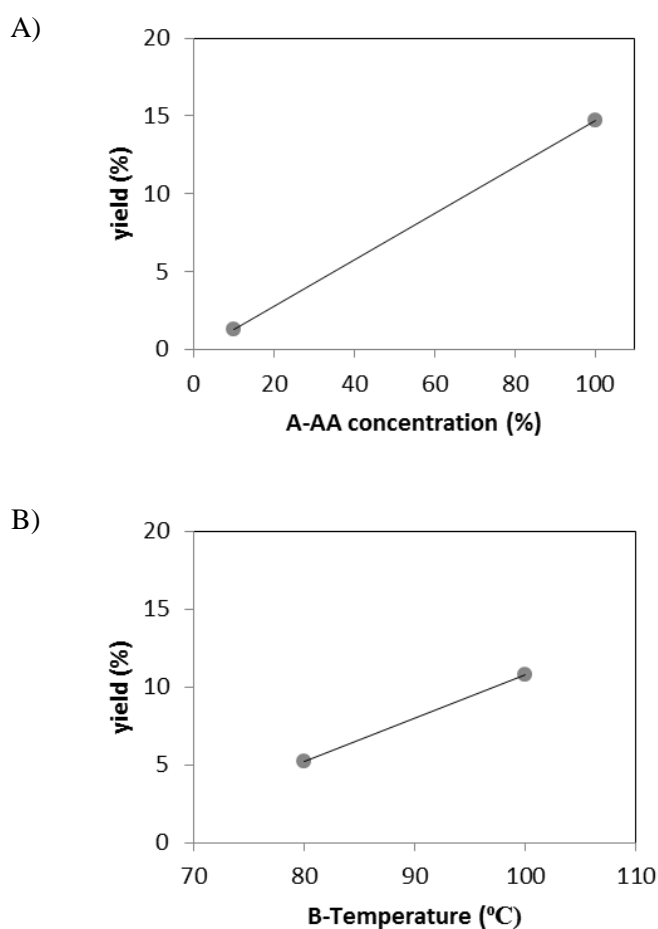
Table 4. The percentage contribution of factors on response variables.

Factor	Percentage contribution
A-AA concentration	66.52
B-Temperature	11.90
C-Molar ratio	0.50
D-Catalyst loading	2.58
E-Inhibitor loading	0.47
AB	9.13
AC	4.02×10^{-3}
AD	1.31
AE	0.21
BC	0.36
BD	1.04×10^{-3}
BE	0.016
CD	-
CE	0.02
DE	0.08

The significance of the initial AA concentration and reaction temperature was implied by the steeper slope of the line plots for these factors as shown in Figure 3. A higher initial AA concentration is preferred in esterification reaction of AA with 2EH to produce 2EHA. The dilute AA with large amount of water would swollen the resin catalyst and subsequently blocking the access of the reactant to internal pore of the catalyst. Thus would limited the access to effective active site which also lead to decrease of effective active site over surface area. Besides, the water in the reactant would also shift the reaction to reactant side since esterification is a reversible reaction. Moreover, it was believed that the poor accessibility of reactants to acid sites might be occurred in the diluted system. The presence of huge amount of water would interrupt the adsorption of the reactant to the active site of catalyst [11][12][13]. The affinity of IER to the polar solvent, water, is stronger than the affinity to the organic solvent, 2EH.

The increase of temperature also gave a better yield. This is attributed to the increasing kinetic energy of the reactant molecules and hence increasing effective collision between AA and 2EH molecules. Thus, the minimum amount of energy required to form products [7].

The other factors like molar ratio of AA:2EHA, catalyst loading and polymerisation inhibitor loading are the insignificant factors ($p > 0.0001$). The effect of molar ratio of AA:2EHA to the yield of 2EHA was negligible in the present study due to the presence of water in the reactant. The water in the reactant has traded off the positive effect of using excess amount of 2EH in driving the reaction equilibrium to 2EHA side.



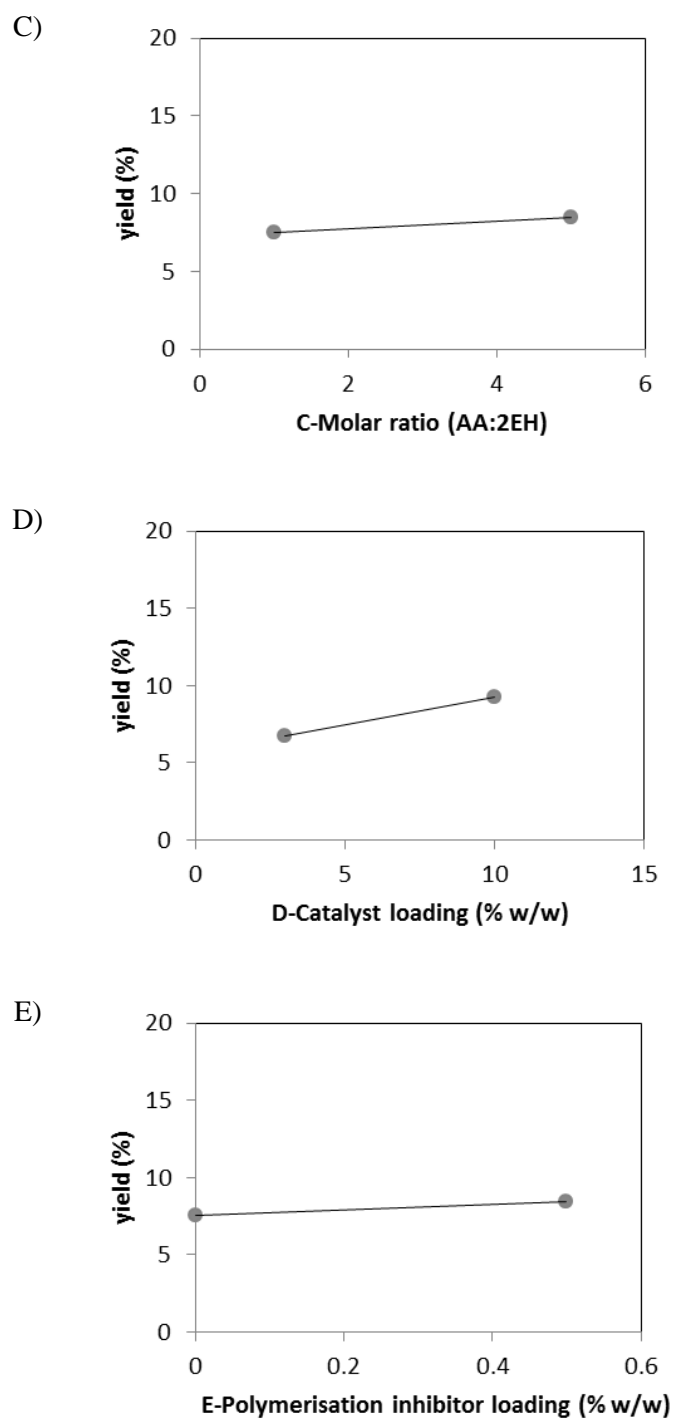


Figure 3. Effect of the initial AA concentration (A), temperature (B), molar ratio of AA:2EH (C), catalyst loading (D) and polymerisation inhibitor loading (E) on the performance in term of yield of esterification AA with 2EH.

The catalyst amount used has provided a sufficient number of active site. Similarly, the amount of the polymerisation inhibitor used was adequate to diminish the AA polymerisation reaction since this side reaction is minimal at the reaction temperature below 100° C.

Statistically, the model F-value of 133.31 in Table 5 implies the model is significant. The model equation is shown in Equation (3). There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. The "Curvature F-value" of 122.71 infers there is significant curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space. The "Lack of Fit F-value" of 5.82 indicates the Lack of Fit is not significant relative to the pure error. This model equation can be used to predict the yield of 2EHA accurately at different reaction operating conditions. There is a 15.44% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good.

$$\text{Yield} = -0.17480 - 0.39279 \cdot A - 0.020243 \cdot B + 0.29406 \cdot C + 0.049829 \cdot D + 2.29400 \cdot E + 5.60806 \cdot 10^{-3} \cdot A \cdot B + 6.07063 \cdot 10^{-3} \cdot A \cdot D \quad (3)$$

Table 5. Analysis of variance (ANOVA) table for 2 factorial studies.

Source	Sum of Squares	df	Mean Square	F-Value	
Model	740.35	7	105.764	133.310	significant
A-AA Concentration	660.13	1	660.128	832.056	
B-Temperature	118.13	1	118.129	148.895	
C-Molar Ratio	4.92	1	4.919	6.201	
D-Catalyst Loading	25.65	1	25.652	32.333	
E-Inhibitor Loading	4.68	1	4.678	5.896	
AB	90.58	1	90.577	114.167	
AD	13.00	1	13.002	16.388	
Curvature	97.36	1	97.356	122.712	significant
Residual	7.14	9	0.793		
Lack of Fit	6.81	7	0.972	5.822	not significant
Pure Error	0.33	2	0.167		
Cor Total	844.84	17			

4. Conclusions

The best catalyst was PK208 ascribing to its complementary IEC, DVB CL%, and leaching properties. Two level half factorial design screening was successfully employed to determine the significant factors. The initial AA concentration and temperature were found to significantly ($p < 0.0001$) affect the yield of 2EHA in the esterification of AA with 2EH. These significant factors underlie the process optimisation study in the future.

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