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Comparative Study Between Different Catalysts For Esterification Of Acrylic Acid

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Abstract: Esterification of acrylic acid with methanol has been carried out in a batch reactor. Comparative study of reaction by using different catalyst as well as without catalyst has been studied. The esterification reaction was catalyzed by Sulphuric acid, p-toulene Sulphonic Acid and solid acid catalyst prepared from cenosphere. The different catalysts (H_2SO_4, p-TSA, cenosphere), reaction temperatures (50–80 °C) were tested for the esterification reaction in this system. The kinetic studies were performed and the conversion as function of time were plotted using experimental data. The rate equation has a remarkable fit to the data of second order reversible reaction and can be used to describe the behavior of the system at various reaction temperature. Maximum conversion, approximately 50%- 70% was obtained at 60°C by using sulphuric acid and p-toulene Sulphonic Acid as a catalyst. It was found that, the increase in the rate constant and conversion due to increasing temperature of the reaction at a certain mole ratio. This can be accounted for the exothermic nature of the esterification reaction. Sulphuric acid was found to be more efficient catalyst for esterification as it induces the maximum conversion of acrylic acid.

Index Terms **- Esterification, Acrylic acid, Methanol, Kinetics, Reaction Rate Constant**

I. INTRODUCTION

Esterification is a chemical process in which an alcohol (R-OH) and an organic acid (R-COOH) are combined to form an ester (R-COOR) and water. This chemical reaction leads to the formation of at least one ester product through an esterification reaction between a carboxylic acid and an alcohol. When carboxylic acids are heated with an alcohol using an acid catalyst, esters are formed. The catalyst used is usually concentrated sulfuric acid. Esterification is one of the most important organic reactions synthesis. Esters are found everywhere, both natural and synthetic organic compounds [1]. Main examples of esterification are biodiesel, solvents, ethyl acetate and methyl acetate, paints and varnishes, drugs, plastics and coatings and some of them are used such as herbicides and pesticides.

The reaction is limited by the slow reaction rate and small amount conversion due to reaching thermodynamic equilibrium. Although esterification is so important commercially the process must overcome these barriers in a cost-effective manner and in an environmentally friendly way.

Acrylic esters are versatile monomers and are widely used production of surface coatings, adhesives, textiles and plastics. The traditional step of manufacturing acrylic esters involves several steps distillation columns, column reactor, dehydration columns, an azeotropic column and a column for product separation of heavy by-products [2]. In addition, there is an inhibitor to use throughout the process to minimize polymerization of acrylic acid and acrylic ester. To avoid this local an inhibitor must be added to each distillate cooling cycle. In addition, reduced pressure is used in the equipment.

Copolymers formed from MMA and other vinyl monomers used for transparent plastics, coatings, and adhesives. Methyl methacrylate is still required for the growth at high profit margin and high financial gain. For direct esterification of acrylic acid, methanol used for the synthesis of methyl methacrylate is the simplest method. Strong acids such as sulfuric acid and hydrochloric acid, which was traditionally used as catalysts esterification in a homogeneous system.

Methyl methacrylate (MMA) is an important industry chemicals to make durable resin products, example organic glass, effective immune polyvinyl chloride modifiers, and surface coatings. 1−3 Poly(methyl methacrylate) made MMA is characterized by good transparency, impact resistance and excellent electrical performance [3].

II. EXPERIMENTATION

2.1 Apparatus required

Magnetic Stirrer, Batch Reactor Set-Up, Condenser.

2.2 Chemicals required

Acrylic Acid, Methanol.

2.3 Preparation of Catalyst

Cenosophere was used as a solid acid catalyst in esterification reaction. Wet Impregnation method was used for preparing Solid acid catalyst cenosphere. 15.4 mL of an Ammonium Sulfate solution was added gradually to 15 g of FACs with constant stirring at 250 rpm. The mixture was stirred properly to fill up the pores of FACs. Then, it was kept for drying in hot air oven at 80 °C for about 2 h. The dried material was then calcined in a muffle furnace at 400 °C for 4 h. Finally, the calcined material was stored in a dry storage bottle before using it for the esterification reaction [4].

2.4 Esterification Reaction of Acrylic Acid

Esterification Reaction of Acrylic Acid is performed with different catalyst and temperature. Reaction was held in eighth batches with different catalyst and different temperatures [5][6][7][8].

2.5 Batch Reactor Set-up- Without catalyst

The setup consisted of a batch reactor with 1000 ml three neck borosil flask equipped with magnetic stirrer and a condenser attached to it is used. 36 ml Acrylic acid was 1st poured into the 3 neck borosil flask by setting constant temperature at 50°C and maintaining the rpm of magnetic stirrer at 500. When the temperature reached 50°C, 20 ml methanol was added. After adding methanol immediately 1ml sample was taken out for titrimetric analysis to know the conversion, this was taken as zeroth time reading. Similarly after every 30 mins the sample titration with 0.5N NaOH after adding phenolphthalein indicator till 6 hrs. Likewise the reaction is carried out with 60°C and 80°C. This was considered for 1:2 molar ratio. Same 2 batches are conducted for molar ratio 1:1 to get accurate result so that comparative study can be done. For that 72 ml Acrylic acid and 40 ml methanol is taken [9].

2.6 With Catalyst - Cenosphere

The Reaction set up was arranged same as held in esterification reaction without catalyst. 36 ml Acrylic acid was 1st poured into the 3 neck borosil flask by setting constant temperature at 50°C and maintaining the rpm of magnetic stirrer at 500. When the temperature reached 50°C, 20 ml methanol was added and 2 g of solid acid catalyst was added. After adding methanol and SAC immediately 1ml sample was taken out for titrimetric analysis to know the conversion, this was taken as zeroth time reading. Similarly, after every 30 mins the sample titration with 0.5N NaOH after adding phenolphthalein indicator till 6 hrs. Likewise reaction is carried out with 60°C and 80°C.
This was considered for 1:2 molar ratio. Same 2 batches are conducted for molar ratio 1:1 to get accurate result so that comparative study can be done [10].

2.7 With Catalyst - Sulphuric Acid

The Reaction set up as well all the procedure was same as held in Esterification Reaction using solid Acid catalyst, only the catalyst here used is 1.09 ml Sulphuric acid. Same 2 batches are conducted for molar ratio 1:1 to get accurate result so that comparative study can be done[11].

2.8 With Catalyst - p-toulene Sulphonic Acid

The Reaction set up as well all the procedure was same as held in Esterification Reaction using solid Acid catalyst, only the catalyst here used is 2g p-toulene sulphonic acid. Same 2 batches are conducted for molar ratio 1:1 to get accurate result so that comparative study can be done[11].

III. OBSERVATION AND RESULTS

3.1 Esterification- Without Catalyst

Esterification reaction was held in a batch reactor with constant stirring without adding catalyst and titrimetric analysis is performed to know the conversion rate. The reaction was held in batches for both 1:1 and 1:2 molar ratios. In 1:1 molar ratio equilibrium state is achieved quickly and the conversion rate becomes constant, accurate reading was not achieved. Batch I represent 50°C and Batch II represent 60°C. Following are the data for 1:2 molar ratio [12]:

Table 1: Without catalyst Batch- I data

Time (min.)	Time (hr)	Burette Reading (ml)	Conc.(Xa)	Conversion	$ln\frac{Xe-(2Xe-1)Xa}{Xe-Xa}$
0	0	8.1	0.81	0	0
30	0.5	7.9	0.79	0.02469	0.263933
60	1	7.8	0.78	0.03703	0.562527
90	1.5	7.5	0.75	0.07407	0.920364
120	2	7.5	0.75	0.07407	1.391383
150	2.5	7.3	0.73	0.09876	2.146051
180	3	7.1	0.71	0.12345	2.448539
210	3.5	6.8	0.68	0.16049	2.868594
240	4	6.6	0.66	0.18518	3.576122
270	4.5	6.5	0.65	0.19753	3.576122
300	5	6.4	0.64	0.20987	3.576122
330	5.5	6.4	0.64	0.20987	3.576122

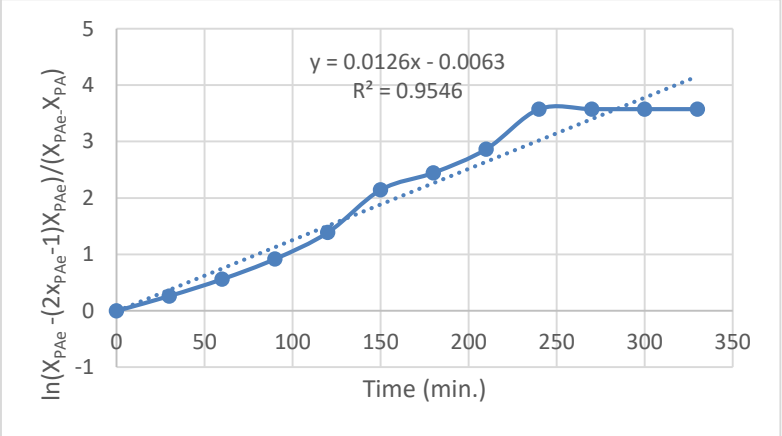

Fig. 3.1 Rate constant determination curve without catalyst Batch I

The rate equation of second order fit the given data. Rate constant calculated from given experimental data is 5.301×10^{-4} l mol^{-1}sec.

Table 2: Without catalyst Batch- II data

Time(min.)	Time (hr)	Burette Reading (ml)	Conc.(Xa)	Conversion	$ln\frac{Xe-(2Xe-1)Xa}{Xe-Xa}$
0	0	9.8	0.98	0	0
30	0.5	9.4	0.94	0.04081	0.177681
60	1	9	0.9	0.08163	0.270875
90	1.5	8.6	0.86	0.12244	0.575364
120	2	8.2	0.82	0.16326	0.575364
150	2.5	7.8	0.78	0.20408	0.808458
180	3	7.6	0.76	0.22448	1.07992
210	3.5	7.6	0.76	0.22448	1.618288
240	4	7.5	0.75	0.23469	2.172223
270	4.5	7.4	0.74	0.24489	2.598566
300	5	7.3	0.73	0.25510	3.312164
330	5.5	7.4	0.74	0.24489	3.312164
360	6	7.4	0.74	0.24489	0.287682

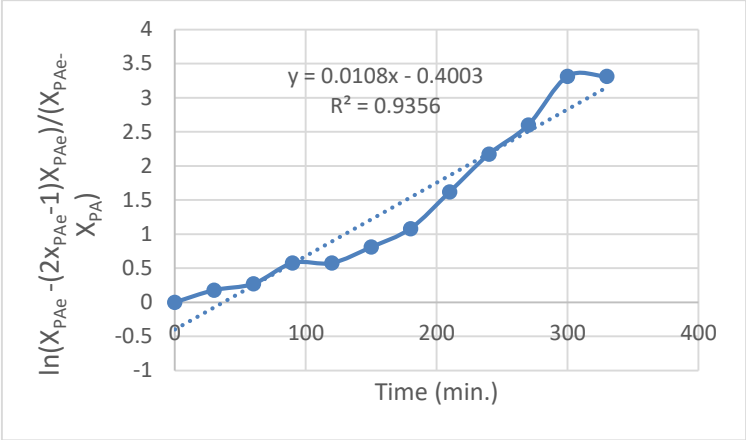

Fig. 3.2 Rate constant determination curve without catalyst Batch II

The rate equation of second order fit the given data. Rate constant calculated from given experimental data is 1.8917×10^{-5} l mol^{-1}sec.

3.2 Esterification Reaction – Using Solid Acid Catalyst

Esterification reaction was held in a batch reactor with constant stirring with addition of solid acid catalyst. Titrimetric analysis is performed to know the conversion rate. The reaction was held in batches for both 1:1 and 1:2 molar ratios. In 1:1 molar ratio equilibrium state is achieved quickly and the conversion rate becomes constant, accurate reading was not achieved.. Batch I represent 50°C and Batch II represent 60°C. Following are the data for 1:2 molar ratio:

Table 3 : Using SAC Batch I data

Time (min)	Time (hr)	Burette Reading (ml)	Conc. (Xa)	Conversion	$ln\frac{Xe-(2Xe-1}{Xe-Xa}$
0	0	9.9	0.99	0.01980	0.137237
30	0.5	9.8	0.98	0.02970	0.208382
60	1	9.6	0.96	0.04950	0.357005
90	1.5	9.5	0.95	0.05940	0.435112
120	2	8.6	0.86	0.14851	1.359961
150	2.5	8.5	0.85	0.15841	1.510812
180	3	8.3	0.83	0.17821	1.881051
210	3.5	8.3	0.83	0.17821	1.881051
240	4	8.2	0.82	0.18811	2.120659
270	4.5	8	0.8	0.20792	2.845945
300	5	7.9	0.79	0.21782	3.554782
330	5.5	7.8	0.78	0.22772	0.137237

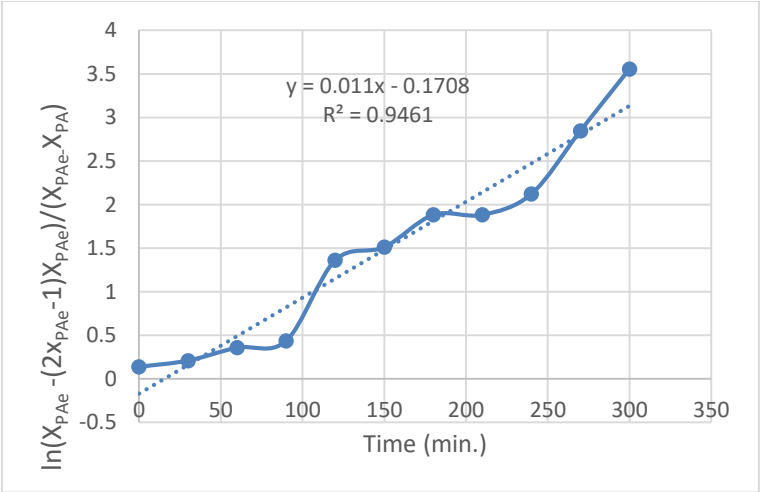

Fig. 3.3 Rate constant determination curve using SAC Batch I

The rate equation of second order fit the given data. Rate constant calculated from given experimental data is 4.5499×10^{-6} l mol^{-1}sec.

Table 4: Using SAC Batch II data

Time (min.)	Time (hr)	Burette Reading(ml)	Conc. (Xa)	Conversion	$ln\frac{Xe-(2Xe-1)Xa}{Xe-Xa}$
0	0	10.1	1.01	0	0
30	0.5	9.9	0.99	0.01980	0.129812
60	1	9.7	0.97	0.03960	0.266165
90	1.5	9.5	0.95	0.05940	0.410951
120	2	9.3	0.93	0.07920	0.566663
150	2.5	9.1	0.91	0.09900	0.736738
180	3	8.9	0.89	0.11881	0.926143
210	3.5	8.7	0.87	0.13861	1.142519
240	4	8.5	0.85	0.15841	1.398595
270	4.5	8.3	0.83	0.17821	1.718159
300	5	8.1	0.81	0.19801	2.154521
330	5.5	7.9	0.79	0.21782	2.87764

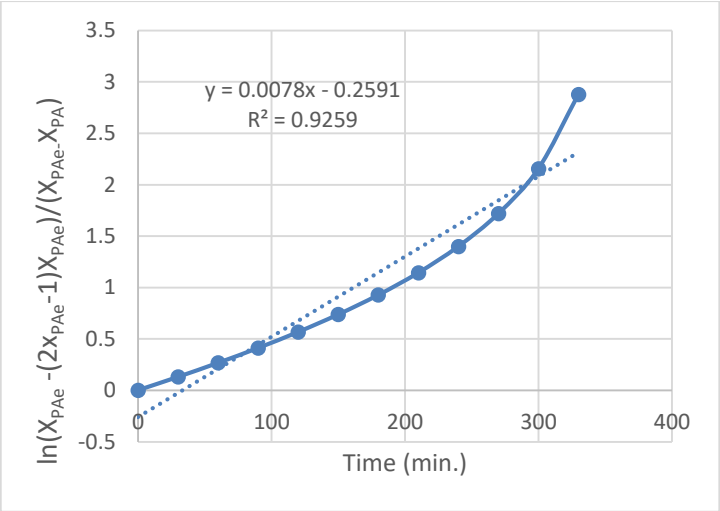

Fig. 3.4 Rate constant determination curve using SAC Batch II

The rate equation of second order fit the given data. Rate constant calculated from given experimental data is 3.3427×10^{-5} l mol^{-1}sec.

3.3 Esterification Reaction- Using Sulphuric acid catalyst

Esterification reaction was held in a batch reactor with constant stirring with addition of sulphuric Acid. Titrimetric analysis is performed to know the conversion rate. The reaction was held in batches for both 1:1 and 1:2 molar ratios. In 1:1 molar ratio equilibrium state is achieved quickly and the conversion rate becomes constant, accurate reading was not achieved. Batch I represent 50°C and Batch II represent 60°C. Following are the data for 1:2 molar:

Table 5: Using Sulphuric Acid Batch I data

Time(min.)	Time (hr)	Burette reading (ml)	Conc. (Xa)	Conversion	$ln\frac{Xe-(2Xe-1)Xa}{Xe-Xa}$
0	0	5.5	0.55	0	0
30	0.5	3.4	0.34	0.3818	0.620088
60	1	3.1	0.31	0.4363	0.792264
90	1.5	2.8	0.28	0.4909	1.017862
120	2	2.5	0.25	0.5454	1.336367
150	2.5	2.5	0.25	0.5454	1.336367
180	3	2.2	0.22	0.6	1.856298
210	3.5	2.1	0.21	0.6181	2.130394
240	4	2	0.2	0.6363	2.522086
270	4.5	2.1	0.21	0.6181	2.130394
300	5	1.9	0.19	0.6545	3.201267
330	5.5	1.9	0.19	0.6545	3.201267

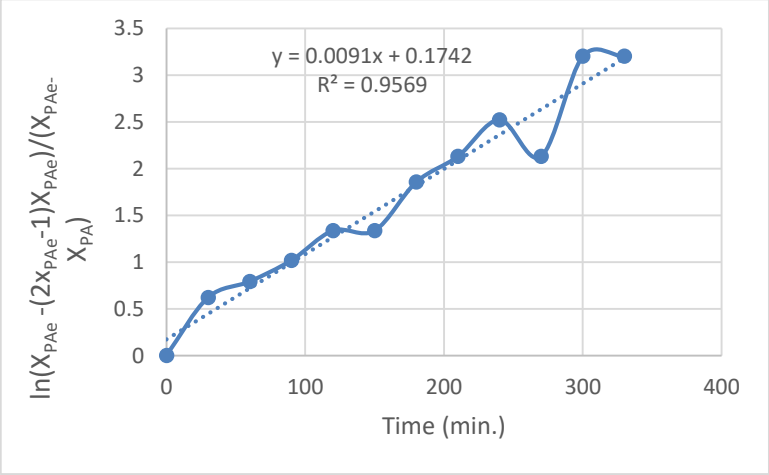

Fig. 3.5 Rate constant determination curve using sulphuric acid Batch I

The rate equation of second order fit the given data. Rate constant calculated from given experimental data is 4.723×10^{-4} l mol^{-1}sec.

Table 6: Using Sulphuric Acid Batch II data

Time(min.)	Time (hr)	Burette Reading.(ml)	Conc. (Xa)	Conversion	$ln\frac{Xe-(2Xe-1)Xa}{Xe-Xa}$
0	0	3.51	0.351	0	0
30	0.5	2.4	0.24	0.31623	0.372784
60	1	2.2	0.22	0.37321	0.48368
90	1.5	2.2	0.22	0.37321	0.48368
120	2	2.1	0.21	0.40170	0.548341
150	2.5	1.8	0.18	0.48717	0.796583
180	3	1.7	0.17	0.51566	0.90557
210	3.5	1.6	0.16	0.54415	1.034559
240	4	1.4	0.14	0.60113	1.387718
270	4.5	1.4	0.14	0.60113	1.387718
300	5	1.3	0.13	0.62966	1.648184

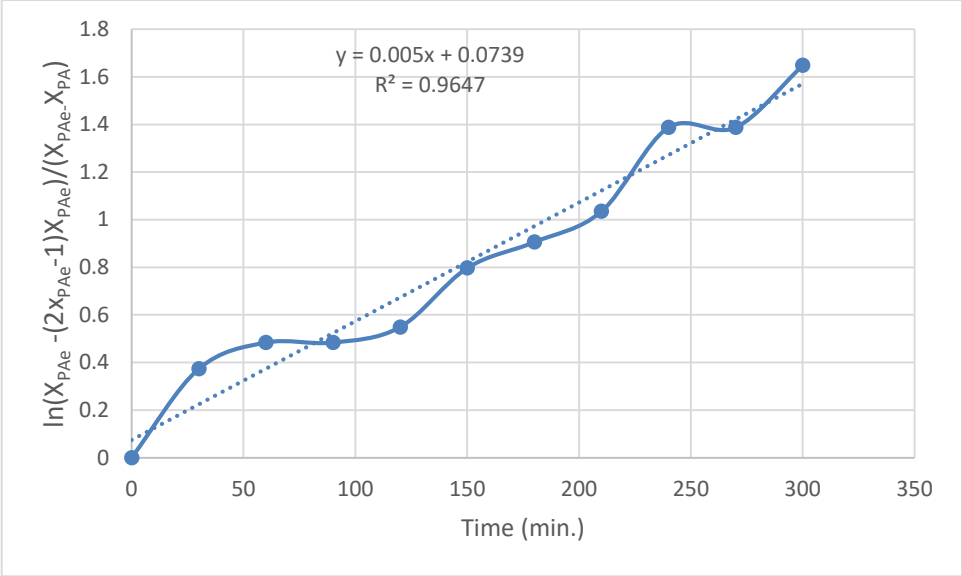

Fig. 3.6 Rate constant determination curve using sulphuric acid Batch II

The rate equation of second order fit the given data. Rate constant calculated from given experimental data is 4.801×10^{-5} l mol^{-1}sec.

3.4 Esterification Reaction- Using p-TSA catalyst

Esterification reaction was held in a batch reactor with constant stirring with addition of p-TSA. Titrimetric analysis is performed to know the conversion rate. The reaction was held in batches for both 1:1 and 1:2 molar ratios. In 1:1 molar ratio equilibrium state is achieved quickly and the conversion rate becomes constant, accurate reading was not achieved. Batch I represent 50°C and Batch II represent 60°C. Following are the data for 1:2 molar ratio:

Table 7 : Using p-TSA Acid Batch I data

Time (min.)	Time (hr)	Burette Reading (ml)	Conc. (Xa)	Conversion	$ln\frac{Xe-(2Xe-1}{Xe-Xa}$
0	0	3.3	0.33	0	0
30	0.5	2.9	0.29	0.12121	0.276941
60	1	2.5	0.25	0.24242	0.462105
90	1.5	1.9	0.19	0.42424	0.549454
120	2	1.8	0.18	0.45454	0.596743
150	2.5	1.6	0.16	0.51515	0.756483
180	3	1.7	0.17	0.48484	1.4166
210	3.5	1.7	0.17	0.48484	1.4166
240	4	1.4	0.14	0.57575	1.695851
270	4.5	1.4	0.14	0.57575	1.87393
300	5	1.4	0.14	0.57575	1.87393

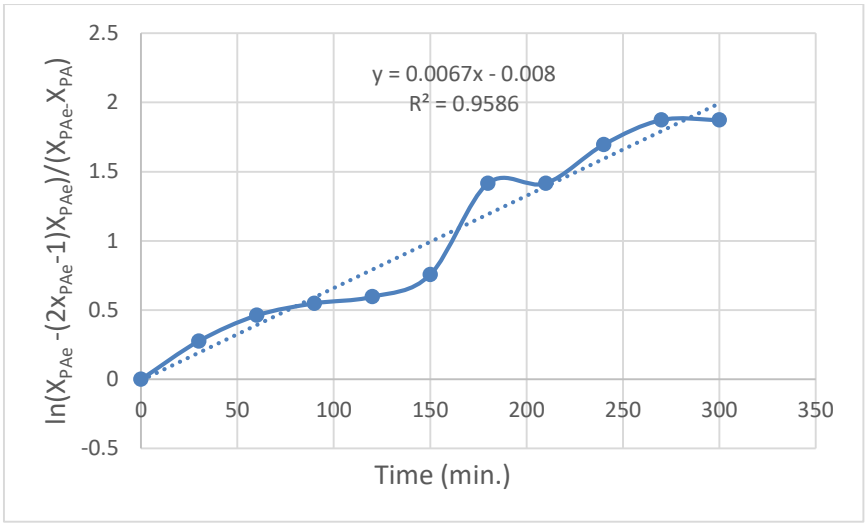

Fig. 3.7 Rate constant determination curve using p-TSA Batch I

The rate equation of second order fit the given data. Rate constant calculated from given experimental data is 5.301×10^{-4} l mol^{-1}sec.

Table 8: Using p-TSA Acid Batch II data

Time (min)	Time (hr)	Burette Reading(ml)	Conc.(Xa)	Conversion	$ln\frac{Xe-(2Xe-1)Xa}{Xe-Xa}$
0	0	6.5	0.65	0	0
30	0.5	5.5	0.55	0.15384	0.157963
60	1	5	0.5	0.38271	0.369874
90	1.5	4.8	0.48	0.40740	0.897942
120	2	4.7	0.47	0.41975	1.036092
150	2.5	4.4	0.44	0.45679	1.408767
180	3	3.6	0.36	0.55555	1.202153
210	3.5	3.6	0.36	0.55555	1.202153
240	4	3.4	0.34	0.58024	2.068013
270	4.5	3.3	0.33	0.59259	2.068013
300	5	3.3	0.33	0.59259	2.068013
330	5.5	2.8	0.28	0.65432	2.068013

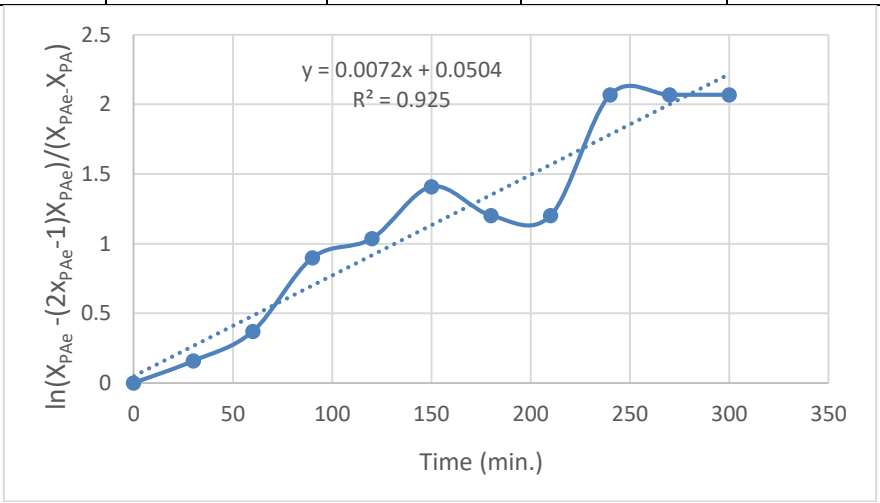

Fig. 3.8 Rate constant determination curve using p-TSA Batch II

The rate equation of second order fit the given data. 1.8917×10^{-5} l mol^{-1}sec.

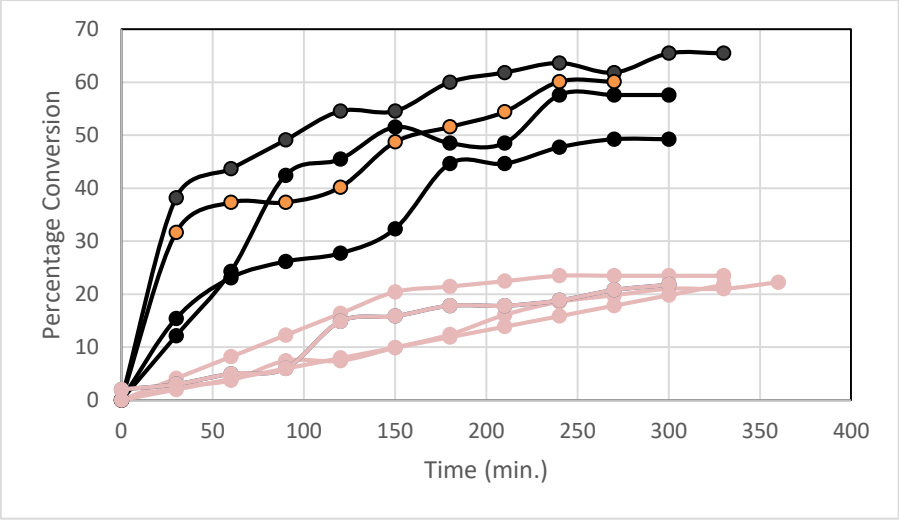

Fig. 3.9 Percentage Conversion of Acrylic Acid

It was found that conversion increase with time as well as with temperature. Black line in the figure describes the reaction taken places at different catalyst at 60^0C which shows better conversion rate whereas other color line is for reaction at 50^0C which also gives significant results.

It has also been observed that when reaction was carried at 80°C, reaction speed up fast due to increase in temperature and polymerization of acrylic acid takes place and jelly like structure is observed. It may also happen that Methyl Acrylate formed polymerizes because it has very low boiling point around 80^0C [13].

3.5 Overall Conversion Result

Esterification Reaction performed gives different conversion depending upon the types of catalyst used and temperature of reaction mixture.

Table 9: Methyl Acrylate Percentage Conversion Data

Sr. No	Catalyst	Batch I (50°C) % conversion	Batch II (60°C) %conversion
1	Without Catalyst	22.22	24.48
2	Solid Acid Catalyst	23.76	22.77
3	Sulphuric Acid	71.05	67.27
4	p-toulene Sulphonic Acid	65.43	63.63

IV. Conclusion

4.1 Effect of Molar ratio

Esterification of Acrylic Acid with methanol is an equilibrium limited reversible chemical reaction. It has been observed through the experiment that excessive use of methyl alcohol increases the conversion of acrylic acid. With 1:1 molar ratio the equilibrium state achieved too quickly and conversion rate is not increased too much level it doesn't give accurate reading. While in comparison to 1:1, 1:2 gave satisfactorily result with maximum conversion levels. The initial molar ratio of acrylic acid and ethanol has an important effect on the equilibrium conversion, which increases with methanol excess. The increment in the amount of the reactants shifts the chemical equilibrium towards the product side.

4.2 Effect of Temperature

Esterification is a temperature sensitive reaction hence while performing esterification reaction temperature should be monitoring regularly. Temperature plays a major role by affecting the yield of ester produced because methanol chemical has been used and it has very low boiling point, it may vaporizes readily if temperature goes beyond the optimum limit. According to experimental study, it has been seen that reaction taken places at 60°C gives maximum conversion in comparison to 50°C may be because 60°C lies in the intermediate of boiling point of reactants. While at 80°C the reaction mixture polymerizes because methanol boiling point is 64.7°C means if the reaction goes beyond 64°C, all methanol will vaporize and acrylic acid is a monomer, it has property to polymerize. While methyl acrylate also have low

boiling point (80.5°C), if constant temperature is not maintained the produces MMA also can polymerize. Esterification reaction is a reversible reaction so if temperature goes beyond it will favor backward reaction hence, temperature is the important parameter to be taken care while performing esterification.

4.3 Effect of Catalyst

Catalyst plays an important role in speeding up the rate of reaction by reducing activation energy of reaction. In the study, reaction has been conducted without catalyst as well as with catalyst both heterogeneous and homogeneous to compare the result and to get the best efficient catalyst [4]. From the experimental analysis, solid acid catalyst which is a heterogeneous catalyst prepared from waste of thermal power plant not seems to be an efficient catalyst. The conversion rate of ester while performing without catalyst and with SAC doesn't differ by much rate whereas sulphuric acid, a homogeneous catalyst gives maximum conversion of 71.05% at 60°C while 67.27% at 50°C.It gives maximum conversion because it can donate 2 H^+ ions for each acid molecule present and also p-toulene sulphonic acid is appeared to be efficient catalyst for giving better conversion rate of 65.43% at 60°C while 63.63% at 50°C[5][6].

REFERENCES

[1] Z. Khan, F. Javed, Z. Shamair, A. Hafeez, T. Fazal, A. Aslam, W.B. Zimmerman, F. Rehman, Current developments in esterification reaction: A review on process and parameters, J. Ind. Eng. Chem. 103 (2021) 80–101. https://doi.org/10.1016/j.jiec.2021.07.018.

[2] R. Ran, J. Li, G. Wang, Z. Li, C. Li, Esterification of Methacrylic Acid with Methanol: Process Optimization, Kinetic Modeling, and Reactive Distillation, Ind. Eng. Chem. Res. 58 (2019) 2135–2145. https://doi.org/10.1021/acs.iecr.8b03842.

[3] R.J. Parod, Methyl acrylate, Encycl. Toxicol. (2005) 69–71. https://doi.org/10.1016/B0-12-369400-0/00610-4.

[4] V.S. Chandane, A.P. Rathod, K.L. Wasewar, S.S. Sonawane, Synthesis of cenosphere supported heterogeneous catalyst and its performance in esterification reaction, Chem. Eng. Commun. 205 (2018) 238–248. https://doi.org/10.1080/00986445.2017.1384922.

[5] N.S.A. Zeki, M.H. Al-Hassani, H.A. Al-Jendeel, Kinetic Study of Esterification Reaction, Al-Khwarizmi Eng. J. 6 (2010) 33–42.

[6] G. Jyoti, A. Keshav, J. Anandkumar, Experimental and Kinetic Study of Esterification of Acrylic Acid with Ethanol Using Homogeneous Catalyst, Int. J. Chem. React. Eng. 14 (2016) 571–578. https://doi.org/10.1515/ijcre-2015-0131.

[7] G. Ströhlein, Y. Assunção, N. Dube, A. Bardow, M. Mazzotti, M. Morbidelli, Esterification of acrylic acid with methanol by reactive chromatography: Experiments and simulations, Chem. Eng. Sci. 61 (2006) 5296–5306. https://doi.org/10.1016/j.ces.2006.04.004.

[8] E. Sert, F.S. Atalay, Esterification of acrylic acid with different alcohols catalyzed by zirconia supported tungstophosphoric acid, Ind. Eng. Chem. Res. 51 (2012) 6666–6671. https://doi.org/10.1021/ie202609f.

[9] Z. Hussain, R. Kumar, Kinetics & simulation of non-catalytic esterification, Mater. Today Proc. 5 (2018) 18287–18296. https://doi.org/10.1016/j.matpr.2018.06.167.

[10] K. Yates, R.A. McClelland, Mechanisms Of Ester Hydrolysis In Aqueous Sulfuric Acids, J. Am. Chem. Soc. 89 (1967) 2686–2692. https://doi.org/10.1021/ja00987a033.

[11] R.S. Tipson, [CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON OW ESTERS OF p-TOLUENESULFONIC ACID, (n.d.) 235–241.

[12] A. Srivastava, N. Pal, S. Agarwal, J.S.P. Rai, Kinetics and mechanism of esterification of epoxy resin with methacrylic acid in the presence of tertiary amines, Adv. Polym. Technol. 24 (2005) 1–13. https://doi.org/10.1002/adv.20026.

[13] S. Ostrowski, M.E. Jamróz, J.C. Dobrowolski, Formation of heavy adducts in esterification of acrylic acid: A DFT study, Comput. Theor. Chem. 974 (2011) 100–108. https://doi.org/10.1016/j.comptc.2011.07.016.