

Production of Cyclohexyl Acetate using Batch Reactor and Reactive Chromatography



Rajendra B. Bhandare, Akash B. Bodekar

Abstract: Production of cyclohexyl acetate by reaction between acetic acid and cyclohexanol using ion exchange catalyst Amberlyst - 15 presented in this work. Batch experiments were carried in batch reactor using variables such as agitation speed, catalyst size, temperature, mole ratio, catalyst loading, moisture content, catalyst reusability. Simulation also carried out using ACM. Activation energy found to be 10000 J/g.mole. Reactive chromatographic reactor is also used for process intensification. Results obtained from batch and reactive chromatographic reactors were compared. More conversion obtained in reactive chromatographic reactor as compared to batch reactor.

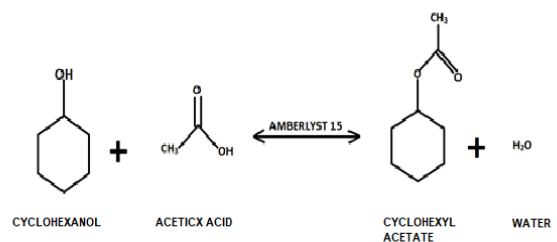
Keywords: Acetic acid, batch reactor, cyclohexyl acetate, modeling, reactive chromatography.

I. INTRODUCTION

Reaction between carboxylic acid and an alcohol produce esters in which water is a by-product. It is also produced by other reactions like using other ethers, acid anhydrides, unsaturated hydrocarbons, amides, esters, acid chlorides, nitriles, and alcohols etc. Esterification reaction carried out under mostly acid catalyst. Esterification reaction rate depends on the structure of the molecule, types of functional substituents. Primary alcohols reaction rate is fast and gives the highest yield. Secondary alcohols reaction rate slow and yields is also low. Reaction rate is also decreases due to branched chain in acid. Polymer industries, perfumery and pharmaceutical are those in which esterification reaction is used [1]. Products from these reactions are used in the pharmaceutical, dyestuff, fragrance, plastic and flavour industries [2]. The catalyst of these reaction are generally homogeneous, which create pollution and nature of catalyst is corrosive. Esterification reactions are reversible equilibrium limited and conversion is less. Conversions may increase by removing product like water. Reactive distillation can be used for this purpose [3]. Reactive extraction and reverse osmosis also used to increase the conversion.

Catalyst choice is depend upon several factors. Sulphuric acid and hydrochloric acid are homogeneous catalyst. Tin

and zinc salts, boron trifluoride, aluminium halides, and organo - titanates have been used. Zeolites and ion exchange resins are also used. By using acid and salt catalyst there was formation of side reactions and also reaction required higher temperature. Reference [4] studied production of cyclohexanol, the esterification of cyclohexene with formic acid. Reactive distillation column was used for this purpose. reaction kinetic study was also carried out. According to this study it was more difficult to measure the reaction kinetics due to extreme phase-splitting behavior of the liquid phase. Reference [5] studied the production of phenethyl acetate and cyclohexyl acetate using solid acids with experimental analysis. The list of catalysts employed is Filtrol-24, Amberlyst-15, sulphated zirconia, heteropoly acids (supported on silica and carbon and also unsupported), and concentrated sulfuric acid. Reference [6] studied equimolar cyclohexanol and acetic acid reaction, catalyzed by sulphuric acid with dioxane as the diluent, reaction carried out in a stirred batch reactor. Reversible reaction was also taken in to account. Reference [7] studied acetic acid esterification with *n*-butanol. Ion-exchange resin catalysts used such as Amberlyst-15 and determined the intrinsic reaction kinetics. Reference [8] studied the production of triacetine, starting from glycerol and acetic acid using acidic polymeric resins is explored. Reference [9] studied acetic acid recovery from dilute aqueous solutions which is creating problem in chemical industries. 30% acetic acid recovered by reaction with *n*-butanol and *iso*-amyl alcohol in a reactive distillation column (RDC) using Indion 130 as a catalyst. Reference [10] studied the catalytic distillation in process were carried out in column for recovery of dilute acetic acid. Amberlyst 15 was used as a catalyst for this purpose. Reference [11] studied the reaction of acetic acid with *n*-butanol and *iso*-butanol using Amberlyst-15. Present work selected esterification of cyclohexanol with acetic acid to produce cyclohexyl acetate by using Amberlyst 15 as catalyst in batch reactor followed by reactive chromatographic reactor (Scheme 1):



Scheme 1. Esterification of Acetic Acid and Cyclohexanol

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II. MATERIALS AND METHODS OF ANALYSIS

Acetic acid (99.5% purity), Cyclohexanol (99.5% purity) and cyclohexyl acetate (99.9% purity) were purchased from s.d. fine-chem. Ltd. India and were used without purification. Amberlyst-15 was used as heterogeneous catalyst. The solvent, Propan-2-ol was also purchased from s.d. fine - chem India Ltd. For analysis, both titration as well as gas chromatography (GC) was employed. In order to obtain butyric acid content, titration of the samples with NaOH (standardized with oxalic acid) was performed using phenolphthalein as indicator. It was observed that with titration, the accuracy was ~ 98 %. The concentrations of reactant and product were measured using gas chromatograph (Chemito with Flame Ionization Detector). The oven temp was consisted at 150°C constant for 1 min and ramp at 20°C/min to get oven temp 230°C. Total run is 30 min. The injector and detector maintained at 240°C. Calibration done using Propan - 2 - ol was used as standard. The accuracy of the results obtained with GC was ~ 99%. The results obtained from titration and GC analysis were matched wherein a match of about $\geq 97\%$ was observed.

III. EXPERIMENTAL WORK

3.1 Batch kinetics

For batch experiments, three necked glass batch reactor having capacity of 750 ml with mechanically agitated stirrer was used (figure 1).

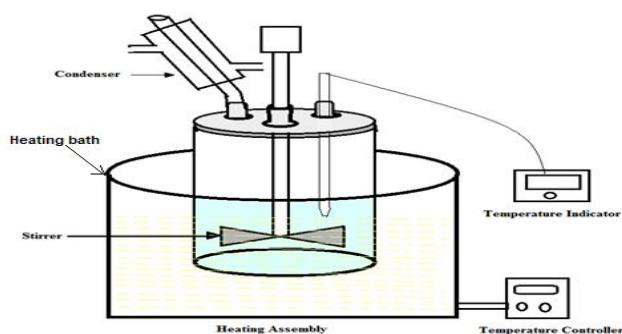


Fig.1: Schematic Diagram of Batch Reactor assembly

Out of these three necks, one neck is used for measuring the temperature of the mixture, second is used for the charging of feed and removal of product with the help of sampler while third is used for condenser arrangement. For heating system, we have provided an oil bath consisting of silicone oil. Condenser arrangement is also made for the condensation of vapours. To control the temperature, constant temperature bath was used (accuracy $\pm 1^\circ\text{C}$). Initially a known amount of acetic acid was placed in reactor. With side by side heated calculated quantity of cyclohexanol with catalyst in separate container. Then acetic acid and cyclohexanol were mixed when reaction temperature reached. This time counted as 'zero time' The samples were taken out with the help of sampler this time and then at regular time intervals and analysed as detailed above. Conversion was calculated using equation 1 given below.

$$\% \text{ Conversion} = \frac{\text{amount of acid converted}}{\text{amount of acid initially taken}} \times 100 \quad (1)$$

Various experiments were conducted to investigate the effect of different parameter.

IV. RESULT AND DISCUSSION

4.1 Effect of agitation speed

Batch runs carried out runs using different RPM of stirrer like 600,700,800 and 900 keeping other parameters constant. From figure 2 observed that there is no effect on the % conversion with change in RPM of stirrer.

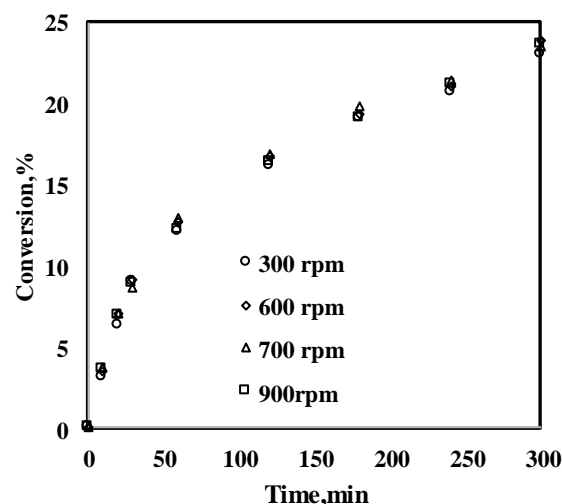


Fig. 2: Effect of rpm of agitator on conversion (70°C, A -15 catalyst, loading 5%, mole ratio1:1)

4.2 Effect of size of catalyst

Catalyst size effect on conversion shown in figure 3 . Batch runs carried by varying the size of the catalyst (A -15) like 0.51mm, 0.263mm and 0.0875mm by keeping all other parameters constant. This is done by using different mesh and by taking average of two mesh screening sizes. From figure 3, observed that as there is no effect of catalyst size on conversion, which prove that the reaction is intrinsically kinetically controlled.

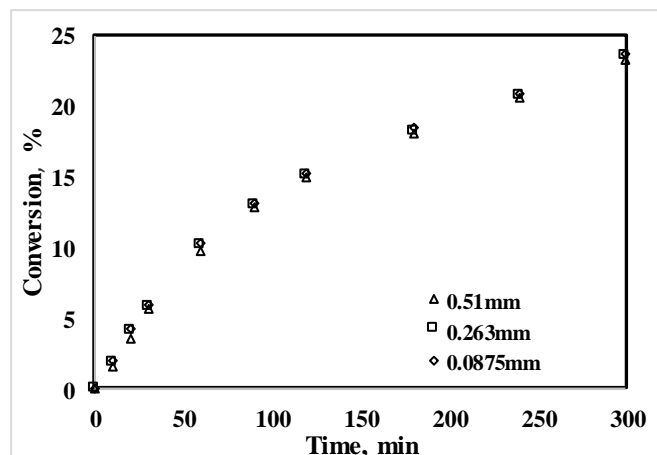


Fig. 3: Effect of catalyst size on conversion (70°C, A -15 catalyst, loading 5%, mole 1:1)

4.3 Effect of temperature effects

Figure 4 shows effects of various temperatures on conversion. After all, runs we observed that as we increase the temperature % conversion also increases which is proved according to reaction kinetics in which rate constant is directly proportional to temperature

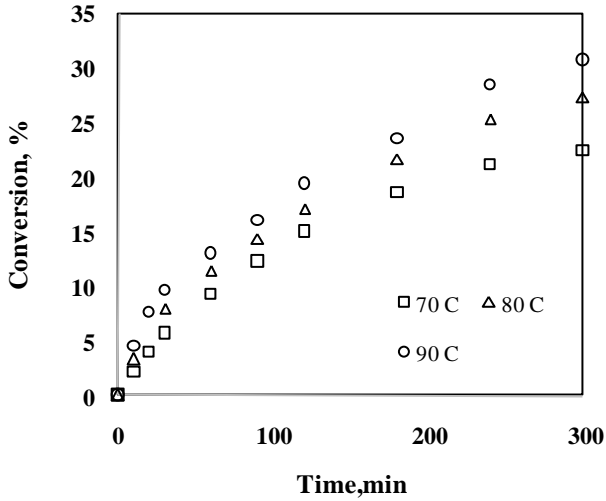


Fig. 4: Effect of temperature on conversion
(A -15 catalyst, loading 5%, mole ratio 1:1, 700 rpm)

4.4 Effect of ratio of mole

Mole ratio effect on conversion shown in figure 5. Here batch runs carried out at various mole ratio like 1:1, 1:2, 1:3 (Acetic acid to Cyclohexanol), with other parameters kept constant. So, we observed that as we increase the mole ratio % conversion also increases.

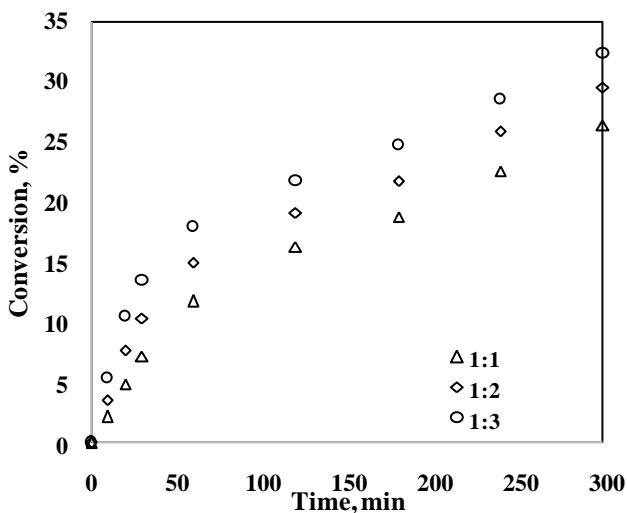


Fig. 5: Effect of mole ratio on conversion
(70°C, A -15 catalyst, loading 5%, mole ratio 1:1, 700 rpm)

4.5 Effect of catalyst loading

Catalyst loading effect on conversion shown in figure 6 and also the shows effect on conversion without catalyst. We observed that as we increase the amount of catalyst, the conversion also increases

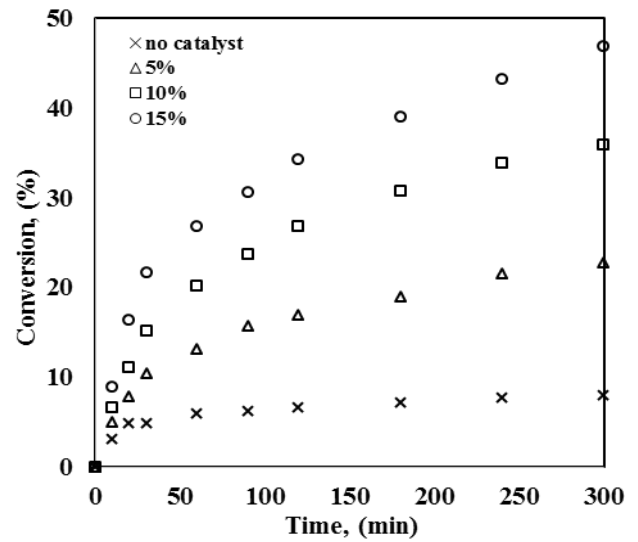


Fig. 6: Effect of catalyst loading on Conversion
(A -15 catalyst, mole ratio 1:1, 700 rpm)

4.6 Effect of moisture content

As reaction is reversible thus, to check the effect of moisture (water) content which is product in the esterification reaction. So, batch runs carried out reactions using moisture content 25%, 50%, 75% and 100% (w/w water). After these runs, concluded that as we increase the moisture content the % conversion decreases which is the effect of reversible reaction as shown in figure 7.

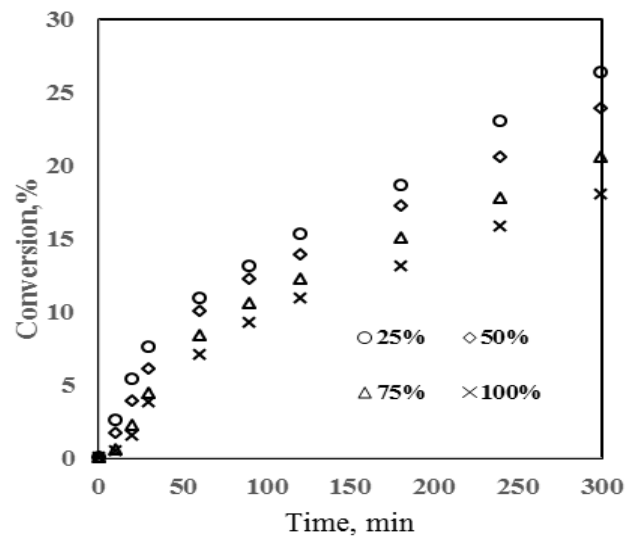


Figure 7: Effect of moisture on conversion
(70°C, A -15 catalyst, loading 5%, mole ratio 1:1, 700 rpm)

4.7 Effect of catalyst reusability

Batch runs carried out by using fresh and reused catalyst. We take out catalyst first time and then wash with water several times and then we put the catalyst in the oven at 200°C for 5 hours. Same procedure is repeated for second time. By these runs we observed that if we reuse the catalyst it shows almost the same effect (figure 8), hence catalyst can be reused.



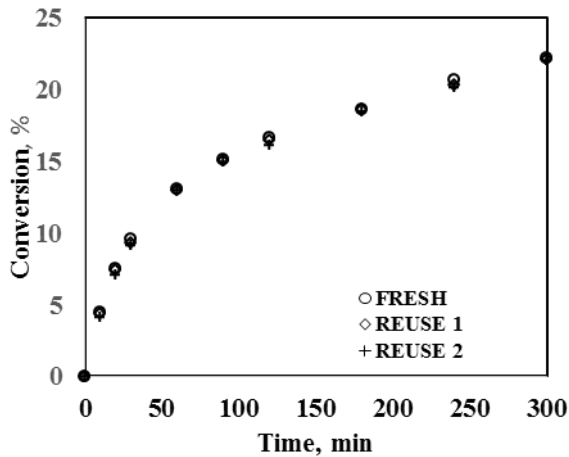


Fig. 8: Plot of catalyst reusability (70°C, A -15 catalyst, loading 5%, mole ratio1:1, 700 rpm)

4. 8 Long run

Long run carried out for to know the equilibrium conversion. Reaction carried out at 70°C, 1:1 mole ratio, 5% catalyst, and 700 rpm and without moisture (figure 9). Equilibrium conversion obtained at 36%.

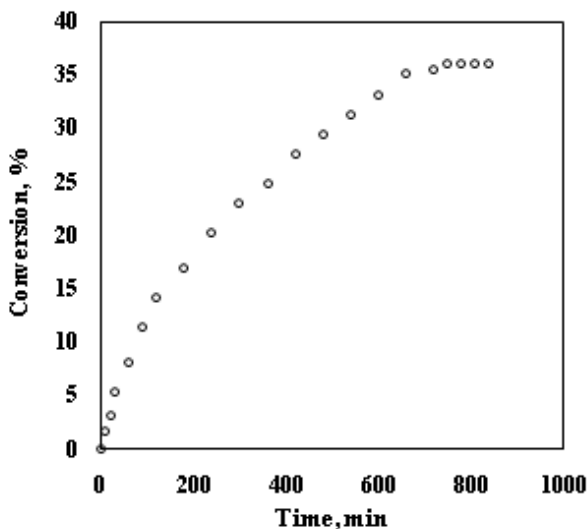


Fig. 9: Long run (70°C, A -15 catalyst, loading 5%, mole ratio1:1, 700 rpm)

V. REGRESSION

5.1 Kinetic model and parameter Estimation

The batch kinetics data thus obtained was utilized further for the regression of parameters in batch kinetics. For a reaction to occur in the presence of a heterogeneous catalyst, the reactants first need to diffuse from bulk fluid to surface of the catalyst; from here reactants still need to diffuse into the pores of the catalyst and lastly adsorb onto the catalyst surface. The simulation was done using ASPEN CUSTOM MODELER (ACM) with estimation mode. In ACM, the batch kinetic data was converted into mole fractions and these mole fractions were used to predict the data.

Considering the literature data for simulation we assumed some values for rate constants and activation energies.

The modeling can be done by using pseudo homogeneous model (PH) or Langmuir- Hinshelwood - Hougen-Watson (LHHW) or Elay Rideal (ER) for the catalytic reaction [12]. Model is preferred LHHW to clarify the kinetic data produced in the current work. Assumption was, all the reactants and products are supposed to be adsorbed on the catalyst surface. Based on this statement, rate expression for the reaction can be given as below (equation 2 - 4).

$$r_{\text{cyclohexylacetate}} = \frac{1}{M_{\text{cat}}} \frac{dn}{dt} = C^2 \frac{(K_f \cdot X_2 \cdot X_1) - (K_b \cdot X_3 \cdot X_4)}{(1 + K_c \cdot C \cdot X_1 + K_w \cdot C \cdot X_4)^2} \quad (2)$$

$$K_f = k_{10} e^{\frac{-E_1}{RT}} \quad (3)$$

$$K_b = k_{20} e^{\frac{-E_2}{RT}} \quad (4)$$

It is a liquid phase reaction, adsorption constants can be considered to be constant with respect to temperature. Reaction is expected to take place only in the liquid phase due to the fact that negligible amount of reactants are existing in the vapour phase, which does not react due to the nonappearance of catalyst. The kinetic parameters of the model, such as rate and adsorption constants with activation energy, are expectable by reducing the sum of squares of error between the simulated values of mole fractions of different components and that experiential value. In such a way, we have obtained the rate constants and activation energies as given below (Table1):

Table 1: Values of kinetics parameter

parameters	values
E_1 (J/g-mole)	10000
E_2 (J/g-mole)	150000
K_f (Lit/gmol. s)	30.4776
K_b (Lit/gmol. s)	24.5664
K_c (g-mol/gm)	15612.6
K_w (g-mol/gm)	246195.0

Here, we specify experimental and predicted data graphically in terms of concentration of acetic acid for various molar ratios and remaining effects. Figures 11 to 14 shows plots for experimental data of acetic acid (Concentration) for various effects.

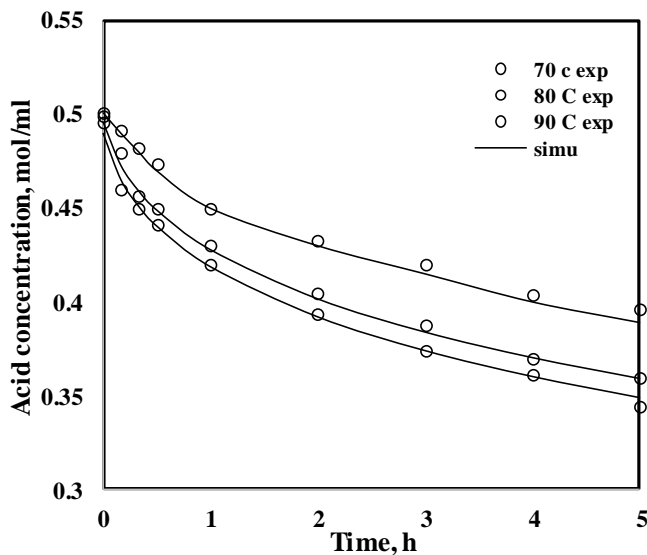


Fig. 11: Kinetic model performance for change in the reaction temperature

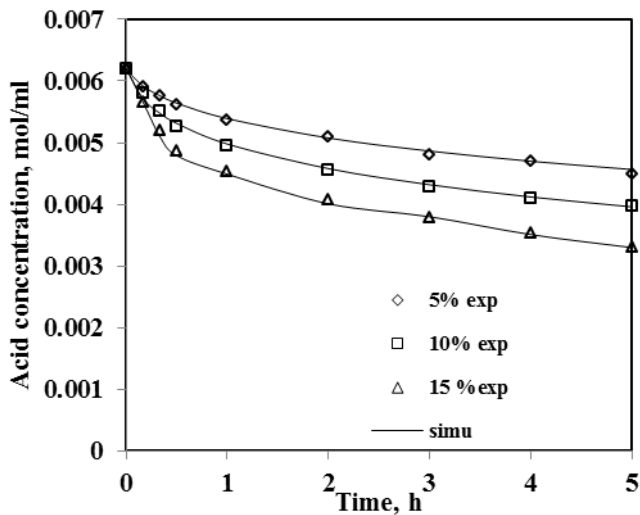


Fig. 12: Kinetic model performance for change in catalyst loading

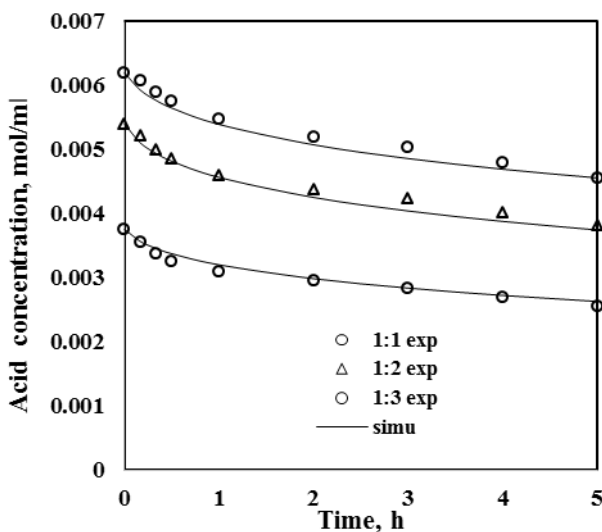


Fig. 13: Kinetic model performance for change in the initial mole ratio of reactants

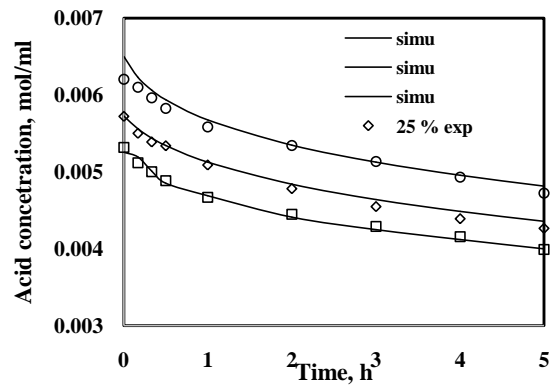


Fig. 14: Kinetic model performance for effect of moisture content.

Figure 15 is parity plot, which shows the linear consistency between experimental and simulated data (R^2 of 0.9858). This make LHHW model is appropriate for various downstream processing.

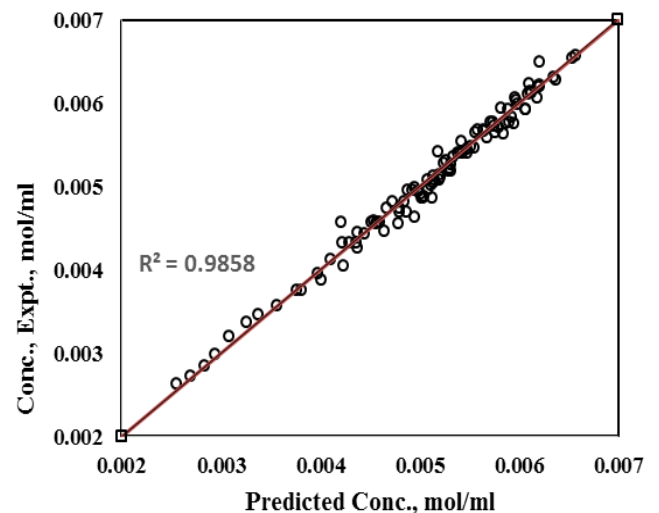


Fig. 15: Parity plot of simulated vs. experimental data

VI. REACTIVE CHROMATOGRAPHY (RC)

The reactive chromatography process is a combination of reaction and chromatographic separation in a single column. RC is an adsorptive separation process, where the components are separated based on their different affinity towards the adsorbent [13]. A chromatographic reactor combines a chemical reaction or biochemical reaction with a chromatographic separation. Therefore, the conversion of equilibrium limited reversible reactions can be increased by a shifting of the chemical equilibrium to product side due to simultaneous separation of the products. Basset and Habgood are the presumed authors of first experimental study on a fixed-bed chromatographic reactor[14]. Generally, chromatographic reactors involves a stationary phase and a movable phase in constant contact. Reactant are treated continuously or periodically into the reactor as per mode of operation [15].

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Stationary phase acts as adsorbent and catalyst, the reaction and the separation take place simultaneously inside the reactor [16].

6.1 Reactive Chromatography set up and experiments

A column of 3 cm diameter, 70 cm height was used for the experimental work (figure16). The thermocouples are used for measuring a temperature at different location in column. The sintered plate is used for a retaining porous ring packing (ceramic) and Catalyst A -15 also used.

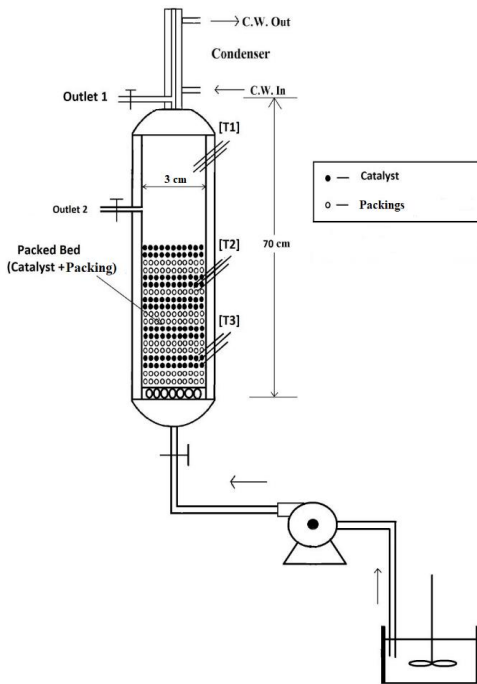


Fig. 16: Schematic diagram of Reactive chromatographic reactor setup

30 grams of packing was packed over the sintered plate. Thermocouples were used for measuring a temperature at different location in column. A calibrated peristaltic pump was used for feeding (mixture of Acetic Acid and Cyclohexanol in a proportional quantity i.e. feed mixture). The electric heating coil was wrapped around the column. After reaching a desired temperature, the feed mixture was passed through the column with constant flow rate (1 ml/min). As feed comes in contact with the catalyst (A - 15) bed, reaction takes place rapidly. The Exist samples were taken at regular intervals of time. Then samples were analysed with titration as well as by GC to find out composition. The purpose was to show that Reactive chromatography gives better results than batch reactor. Thus, Batch kinetics and Reactive chromatography runs were compared and as shown in figure17. With the help of above results, we can say that Reactive Chromatographic reactor gives better conversion than batch reactor. As we increase the amount of catalyst, the % conversion also increases as compared to the batch reactor. That's why we can use reactive chromatographic reactor over batch reactor for this reaction without any hesitation.

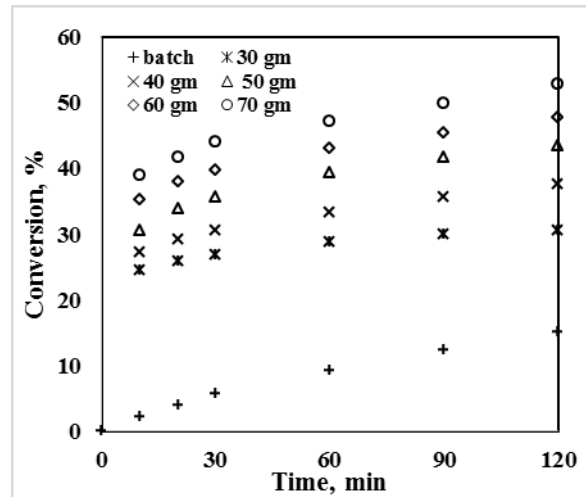


Fig. 17: Batch versus Reactive Chromatography Run comparison (70^o C, mole ratio 1:1, flow rate 1ml/min)

VII. CONCLUSION

Esterification of Acetic Acid with Cyclohexanol was studied using Amberlyst-15 catalyst. Batch experiments runs carried to study effect of different parameters on conversion. Also runs were carried out in reactive chromatographic reactor at different conditions. Comparison has done with batch reactor. In batch reactor 15% conversion obtained for same condition maximum @53 % conversion was obtained in reactive chromatographic reactor. This way process intensification was explored by reactive chromatographic reactor.

NOMENCLATURE

- M_{cat} - Weight of catalyst in kg
- X_1, X_2 - Mole fractions of Reactants
- X_3, X_4 - Mole fractions of products
- K_f, K_b - Rate constants of forward and backward reactions
- K_c, K_w - Adsorption constants for cyclohexanol and water resp.

ABBREVIATIONS

- A - 15 - Amberlyst -15
- CW in - cold water inlet
- CW out - cold water outlet
- ER - Elay Rideal
- GC - gas chromatography
- IER - ion exchange resin
- LHHW - Langmuir Hinshelwood Houghen Watson
- PH - Pseudo- homogeneous
- RC - Reactive chromatography
- T_1, T_2, T_3 - temperature

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