Available online at BCREC website: https://bcrec.id

Bulletin of Chemical Reaction Engineering & Catalysis, 17 (4) 2022, 811-820

Research Article

Manufacture of n-Propyl Propionate Using Ion Exchange Resins: Reaction Kinetics and Feasibility of Reactive Distillation

Reshma R. Devale, Bipin S. Deogharkar, Yogesh S. Mahajan*

Department of Chemical Engineering, Dr. Babasaheb Ambedkar Technological University, Lonere, Maharashtra 402103, India.

Received: 22nd September 2022; Revised: 18th November 2022; Accepted: 25th November 2022
Available online: 5th December 2022; Published regularly: December 2022

Abstract

Reaction kinetics of esterification of propionic acid with 1-propanol to produce n-propyl propionate using Amberlyst-15 as a catalyst was investigated in this work. Effect of various parameters was studied. Initially, the efficacy of different catalysts was investigated which revealed that Amberlyst-15 can be suitably used for the reaction. This was followed by mass transfer exclusion which included effect of agitation speed, catalyst size and calculation of Weisz-Prater Criterion. Parameters selected for kinetic study were mole ratio of propionic acid to 1-propanol, temperature, catalyst loading and initial water concentration. Catalyst reusability was also verified. Aspen Custom Modeler (ACM) was used to regress kinetic parameters and a good match was obtained. Reactive Distillation (RD) runs in the batch mode were performed which showed that RD is a better option for process intensification (PI) for this reaction.

Keywords: Ion exchange resins; Intrinsic kinetics; Effect of parameters; Regression; Feasibility of Reactive Distillation

How to Cite: R.R. Devale, B.S. Deogharkar, Y.S. Mahajan. (2022). Manufacture of n-Propyl Propionate Using Ion Exchange Resins: Reaction Kinetics and Feasibility of Reactive Distillation. *Bulletin of Chemical Reaction Engineering & Catalysis*, 17(4), 811-820 (doi: 10.9767/bcrec.17.4.15928.811-820)

Permalink/DOI: https://doi.org/10.9767/bcrec.17.4.15928.811-820

1. Introduction

There is an increasing demand of chemical industries towards new processes or techniques that can meet requirements like generation of nearly zero waste, using less energy, while producing chemicals for variety of applications. The flavour and fragrance industry mostly uses small, volatile organic compounds to create pleasant odours or tastes, many of which are mixtures of naturally-occurring substances. These sense to our olfactory or taste receptors like a single organic molecule. Some molecules are synthetic substitutes that cheat our brain into having sampled natural compounds. These artificial flavours and odours are used because these are easier and cheaper to obtain and that these can retain the aromatic character of natural compounds. Process industry has developed the artificial spice, soap and perfumery industries with these compounds as their foundation.

Best examples of synthetic flavour and odour compounds are esters. An ester is the condensation product resulting when a carboxylic acid reacts with an alcohol. Many carboxylic acids have

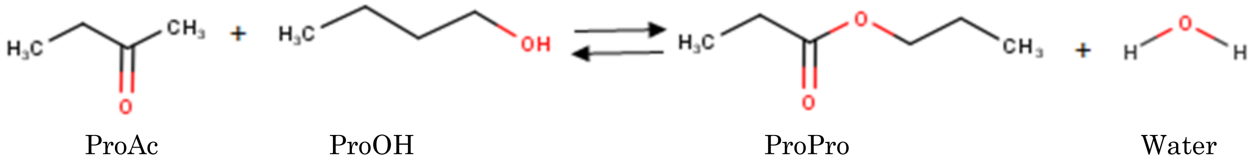
---

* Corresponding Author.
Email: ysmahajan@dbatu.ac.in (Y.S. Mahajan);
Telp: Telp: +91-99-23188748, Fax: 021-40-275142

foul smell, but when these react with an alcohol, these can produce wide-ranging flavours and fragrances. Esterification of carboxylic acids with alcohols is catalyzed by either homogeneous or heterogeneous catalysts [1]. Sulphuric acid (H_2SO_4) is the most common homogeneous catalyst because of its effectiveness [2], but a small increase in concentration or temperature can cause dehydration of alcohol to ethers or olefins. Acidic catalysts like ion exchange resins (IERs) can also be used as an alternative [3]. IERs possess good catalytic activity and generally cause less side reactions than H_2SO_4. IERs have received better attention than H_2SO_4 because of several advantages: recovery of the catalyst by filtration [4-5]; possible continuous operation; higher purity products due to higher selectivity [4]; reduced waste disposal problems and possibility of isolation of reaction intermediates [5]. IERs like Amberlyst-15 (A-15) have played an important role in organic synthesis and its applications include: esterification, transesterification, addition, cyclization, alkylation, acylation, etc. [6-11].

Dakshinamurty *et al.* studied the esterification of 1-propanol (ProOH) with propionic acid (ProAc) using Dowex-50W (Scheme 1) [12]. Lilja *et al.* studied this reaction using fibrous polymer supported sulfonic acid catalyst (Smopex-101) [13]. Ali *et al.* studied esterification of this reaction using different catalysts (namely Dowex 50Wx8-400, A-15, Amberlite IR-120, and H_2SO_4). Among the three IERs, Dowex offered highest conversion of ProAc (~58 %) whereas still more conversion was obtained with H_2SO_4 (~64 %), Ali *et al.* selected Dowex 50Wx8-400 for their work [4]. Buchaly *et al.* studied modelling, simulation and process analysis of synthesis of n-propyl propionate (ProPro) by using RD with membrane separation in a hybrid process. Catalyst used in reactive zone was Amberlyst-46 (A-46). Membrane was located after distillate to remove reaction water without using entrainer [14]. Altman *et al.* studied synthesis of ProPro using reactive distillation (RD) with decanter separator for reactant recovery using A-46 [15]. Keller *et al.* studied ProPro synthesis in a RD column (RDC) coupled with a liquid–liquid phase separator using A-46 [16]. Cruz-Diaz *et al.* studied synthesis of ProPro in a pilot-plant RDC using A-46 [17].

Bhandare *et al.* synthesized isoamyl propionate by esterification of ProAc with isoamyl alcohol in batch as well as packed bed reactor using A-15 [10]. Conversions obtained were 33 and 53 %, respectively, at 343 K and 1:3 mole ratio [10]. Tekale and Yadav carried out esterification of ProAc in a batch reactor with 1,2-propanediol using a clay supported heteropolyacid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 as the solid acid catalyst [18]. Conversion of ProAc was ~75 % at 180 ^{0}C [18]. Leyva *et al.* studied esterifica-



Scheme 1. Reaction of ProAc and ProOH to produce ProPro and water [12]

Table 1. Different catalysts used for the reaction under study

Sr. No.	Catalyst	Reaction Conditions	Results (Conv., %)	Ref.
1	Dowex-50W	Batch reactor: 343.15 K, mole ratio 1: 3, Cat. Conc. 3 %	~ 58	[12]
2	Smopex-101	Batch reactor: 343.15 K, Acid to alcohol mole ratio 1: 2, 550 rpm	~ 80	[13]
3	Dowex 50Wx8-400	Batch reactor: 323.15 K, 900 rpm, 1: 1 acid to alcohol mole ratio, Cat. Loading 60 g dry cat/L	~ 58	[4]
4	A-46	RD: Acid flow 1.52 kg/h, Alcohol flow 2.46 kg/h, Molar feed ratio 2, RR 2.48	~ 75	[20]
5	A-46	RD: Acid flow 1.5 kg/h, Alcohol flow 2 kg/h, Molar feed ratio 1.7, RR 2.156	~ 83	[15]
6	A-46	RD: Acid flow 0.99 kg/h, Alcohol flow 2.01 kg/h, Molar Feed Ratio 2.5, RR 2	~ 82	[17]

tion of ProAc with isoamyl alcohol in a batch reactor with Amberlyst-70 catalyst and obtained a conversion of 69 % [19]. Table 1 gives the instances of different IERs for the given reaction (ProAc reacting with ProOH to give ProPro).

2. Materials and Methods

2.1 Chemicals

Propionic acid (99%) and 1-propanol (99.5%) were supplied by Thomas Baker Pvt. Ltd. India and n-Propyl propionate by Merck Limited, India. A-15 was purchased from Rohm and Haas, USA, Tulsion-63 (T-63) and Tulsion-66 (T-66) from Thermax Limited, Pune, India and Indion 190 from Ion exchange (India) Ltd., Mumbai, India. Properties of IERs are given in Table 2. Double distilled water was used wherever needed.

2.2. Analysis

Samples taken out at regular time intervals were analyzed by titration as well as by gas chromatography. Samples were titrated with NaOH solution, standardized with 0.1 N oxalic acid solution. Liquid samples were weighed and analyzed with a gas chromatograph (NUCON) using thermal conductivity detector. Porapack-Q packed column (length 1.82 m, O.D. 1/8 inch, made up of S.S.) was used for separation. For preparation of the GC samples, mixture of collected samples with known amount of ethyl alcohol (EtOH, used as internal standard) was used for analysis. From the prepared sample, 0.5 µL was injected into the column through a syringe. Oven temperature was 150 °C constant for 1 min with a ramp of 5 °C/min up to 230 °C. Injector and detector temperatures were maintained at 230 °C. Using standard calibration curves prepared for all components, the integrated areas were converted to weight % of each component in the sample. Back calculation of samples showed that the results obtained by GC were about 98 % accurate and those for titration were ~ 99 % accurate. Amount of sample withdrawn was very small so that it did not affect the material balance. Conversion of ProAc was calculated from Equation (1):

$$\%Conversion = \frac{Moles\ of\ propionicacid\ Reacted}{Moles\ of\ propionicacid\ fed} x100\% \quad (1)$$

2.3 Kinetic Experiments

When heterogeneous catalysts are used, a rather standardized methodology is adopted. First, the better catalyst among those available is selected. Secondly, experiments are conducted to ensure that mass transfer resistances are absent (for this, generally in order to assess the inter-particle and intra-particle diffusion, two experimental sets are evaluated: namely, effect of particle size and speed of agitation). Investigation of effect of various parameters on kinetics is evaluated after this (temperature, catalyst loading, mole ratio and initial water concentration). This is generally followed by catalyst reusability and reproducibility of results. An error bar analysis is also sometimes employed and reported. The procedure employed in the present study is exactly the same.

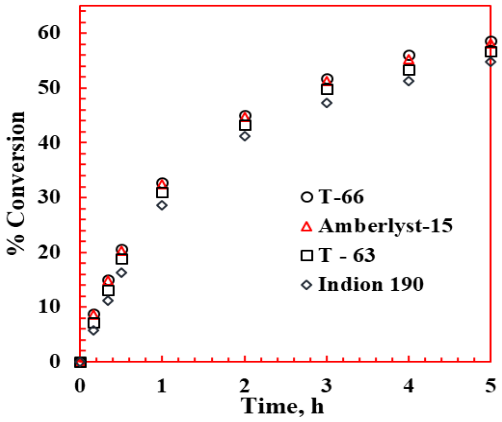


Figure 1. Selection of catalyst. (80 ^{o}C, Acid to alcohol mole ratio 1:1, Cat. Loading: 5% of ProAc, 900 rpm)

Table 2. Properties of catalysts used in the given study

Parameters	A-15	T-66	T-63	Indion 190
Particle size mm	0.355 - 1.180	0.3 - 1.2	0.3 - 1.2	0.42 - 1.2
Concentration of active sites (m_{eq}/dry g)	~ 4.7	5.0	5.0	4.7
Max. operating temp. (^{o}C)	120	130	130	130
Pore diameter (A^o)	300	NA	NA	NA
Surface area (m^2/g)	53	NA	NA	NA
Ref.	[21]	[22]	[22]	[23]

Laboratory batch reactor with 4 necks, 500 mL volume (~ 330 mL of reaction mixture) with condenser, oil bath (accuracy ±1°C) with stirrer and sampler was used. ProOH was taken in reactor and was heated till desired temperature was obtained. After the desired temperature was attained, separately preheated required quantities of ProAc and catalyst maintained at same temperature were added to the batch reactor and this was taken as "zero" time. Liquid sample was pipetted out from the reactor at regular intervals for analysis. All experiments were performed at least twice to ensure authenticity of the results.

3. Results and Discussion

Effect of different parameters including catalyst selection, molar ratio, temperature, catalyst loading, water concentration, particle size, catalyst reusability and stirrer speed on the reaction rate was studied.

3.1 Selection of Catalyst

The reaction was studied using different IER catalysts (T-66, T-63, A-15, and Indion-190). Figure 1 shows that A-15, T-66, and T-63 offered almost similar conversion. The well-known A-15 catalyst was used in this work [7-8,10-11].

3.2. Effect of Speed of Agitation

Effect of mass transfer on the kinetics was studied by performing the reaction at various agitation speeds. Figure 2(a) shows that speed of agitation does not affect conversion. Hence, all the experiments were conducted at 900 rpm.

3.3. Effect of Catalyst Particle Size

Figure 2(b) shows the effect of catalyst particle size on conversion. There is not much change in conversion of ProAc. Also, calculation of Weisz-Prater coefficient (C_{WP}) was performed [24] which represents the ratio of the intrinsic reaction rate to intra-particle diffusion rate. This can be evaluated from the observed rate of reaction ($-r'_{A(obs)}$), the average particle radius (R_P), the effective diffusivity of the limiting reactant (D_e) and concentration of the reactant at the external surface of the particle (C_{AS}):

$$C_{WP} = \frac{-r'_{A(obs)}\,\rho_c R_p^{\,2}}{D_e C_{AS}} \tag{2}$$

If $C_{WP} << 1$ then there are no diffusion limitations and consequently no concentration gradients exist within the pellet. In the present case, the value of C_{WP} was calculated to be 0.00231, which is much less than 1, therefore the reaction is seen to be intrinsically kinetically controlled.

3.4. Effect of Temperature

The reaction was conducted at four different temperatures (70-100 ^{0}C) with mole ratio 1:1 (acid to alcohol) and catalyst 5% of limiting reactant. From Figure 3(a), the conversion of ProAC is observed to increase with temperature. 80 ^{0}C was the chosen temperature at which ~ 58 % conversion was obtained.

3.5. Effect of Molar Ratio of Reactants

An increase in alcohol concentration leads to an increase in conversion as seen in Figure 3 (b). Use of excess alcohol is typical in order to shift equilibrium. It is seen that the effect is

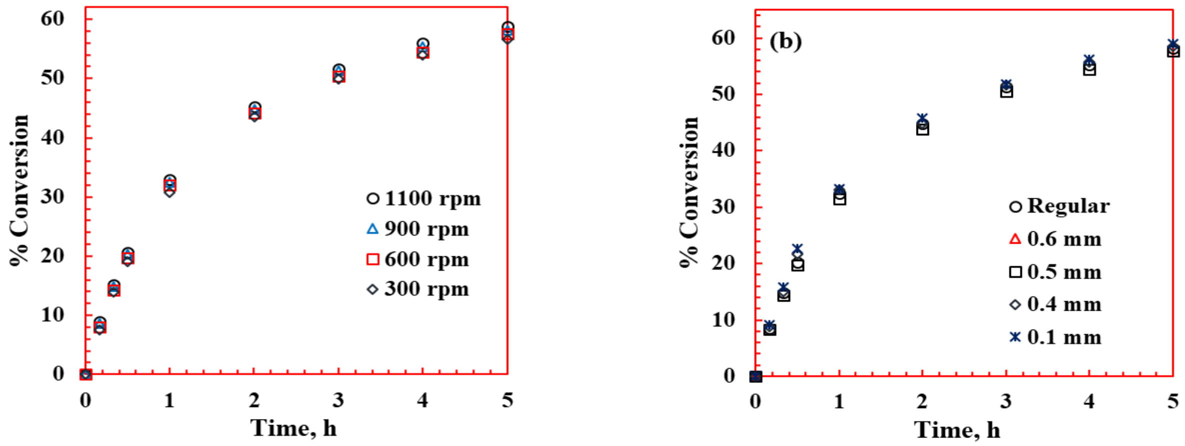


Figure 2. Effect of (a) speed of agitation (80 ^{o}C, acid to alcohol mole ratio 1:1, cat. 5 % of ProAc), (b) catalyst particle size (80 ^{o}C, acid to alcohol mole ratio 1:1, cat. 5 % of ProAc)

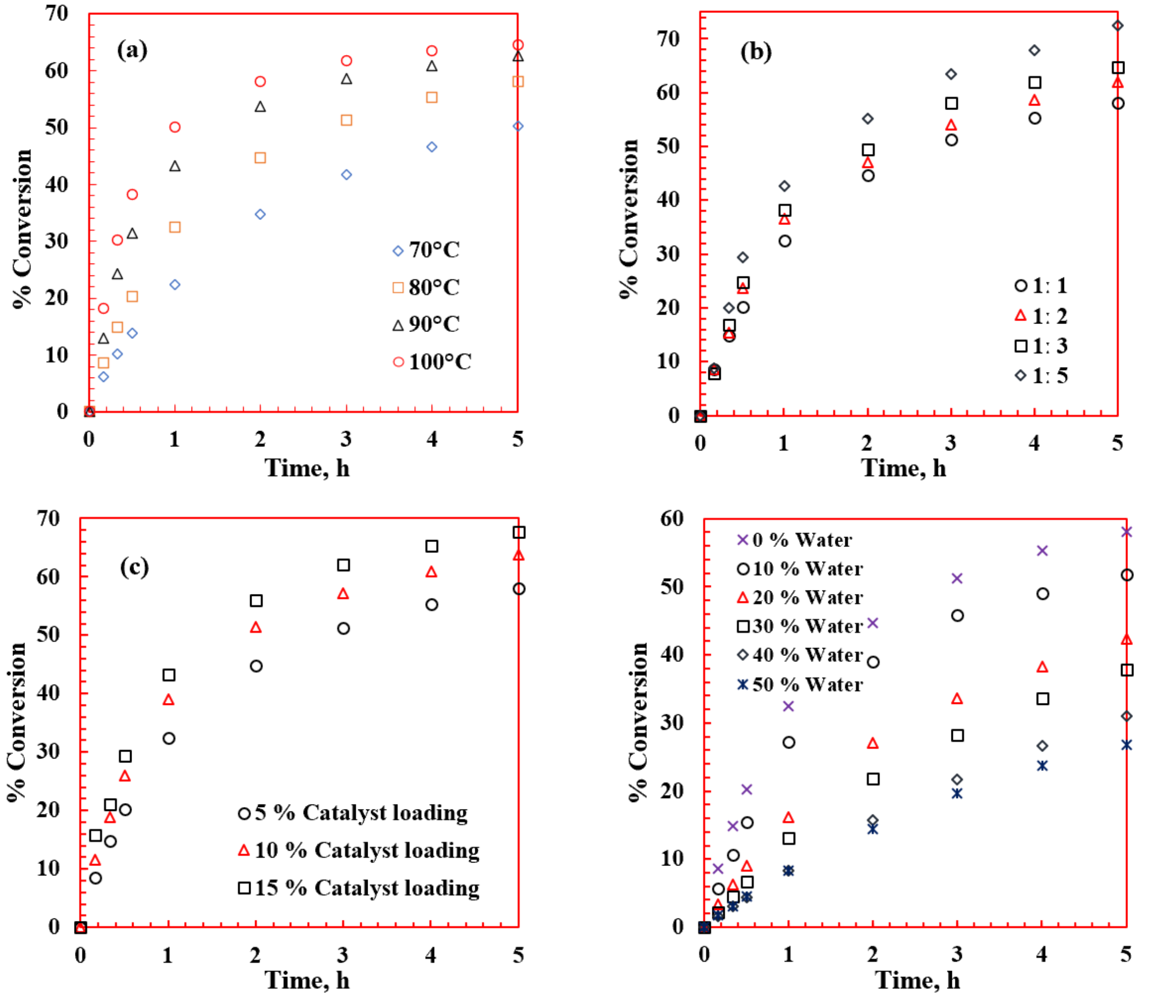


Figure 3. Effect of (a) Temperature (acid to alcohol mole ratio 1:1, cat. 5% of ProAc, 900 rpm), (b) molar ratio of acid to alcohol (80 °C, cat. 5% of ProAc, 900 rpm), (c) catalyst loading (80 °C, acid to alcohol mole ratio 1:1, 900 rpm), (d) Water concentration (80 °C, acid to alcohol mole ratio 1:1, cat. 5% of ProAc, 900 rpm)

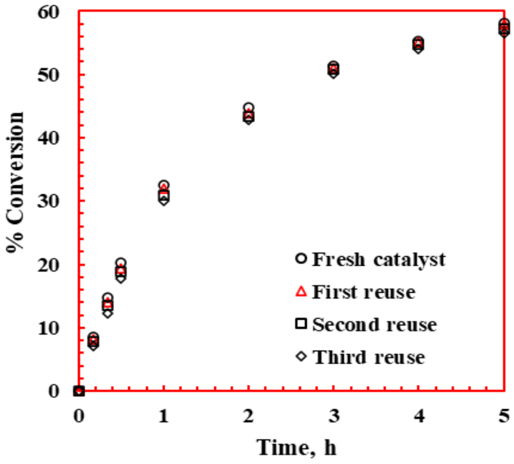


Figure 4. Effect of catalyst reusability. (80 °C, Acid to alcohol mole ratio 1:1, cat. 5% of ProAc, 900 rpm)

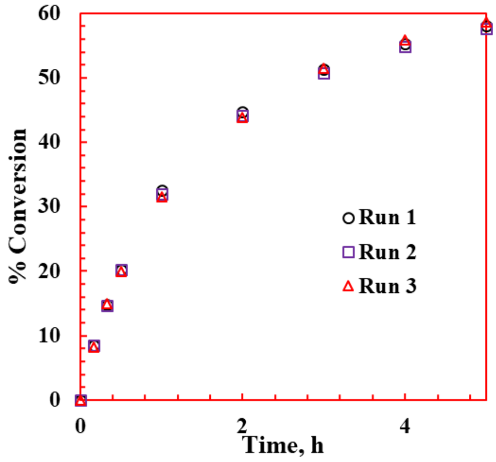


Figure 5. Reproducibility runs. (80 °C, Acid to alcohol mole ratio 1:1, cat. 5% of ProAc, 900 rpm)

not very prominent after mole ratio of 1:2, hence the mole ratio of 1:2 was chosen for future runs.

3.6. Effect of Catalyst Loading

Reaction was carried out by varying the catalyst amount at 80 °C and mole ratio 1:1 (acid to alcohol). It is seen from Figure 3(c) that as the catalyst loading is increased, conversion of ProAc increases. The 5 % catalyst loading was chosen for further runs.

3.7. Effect of Water Concentration

Reaction was carried out with initial addition of water (Figure 3(d)). As the initial concentration of water was increased, the % conversion of ProAc decreased.

3.8. Catalyst Reusability

There is no significant decrease in catalyst activity when the same catalyst is reused even up to 3 times as seen from Figure 4. This proves the capability of IERs and also of A-15 to be reused several times.

3.9. Reproducibility of Results (Error Bar)

Figure 5 shows the results of the run (80 ^{0}C, Acid to alcohol mole ratio 1:1, cat. 5 % of ProAc, 900 rpm) when conducted three times. It is seen that almost unchanged results were obtained.

3.10. Regression of Kinetic Parameters

Heterogeneously catalyzed reactions (and especially those where IERs are used), are generally represented in terms of either of the following: (a) Pseudohomogeneous (PH) (b) Eley Rideal (ER) and (c) Langmuir-Hinshelwood-Hougen-Watson (LHHW) models [25,26]. For most esterification reactions catalyzed by A-15, the LHHW type model has been found applicable. Concentration based or activity based models can be used. The present reaction scheme is a typical esterification system in which A-15 is employed. Different forms of ER and LHHW were tested and the LHHW type equation (Equation 3) using concentration was seen to provide best fit.

For regression, i.e. estimation of kinetic parameters, the following are needed: kinetic data in prescribed form (time vs. concentration of all the species involved), range of parameters covered (temperature, catalyst amount, moles, water concentration), objective function and initial guesses. There are various methods for solving estimation problems, but two are commonly employed are: weighted least square method and maximum log likelihood method, the former being generally employed. For a chosen model, parameter estimation is done based on several criteria like accuracy of the fit, parameter accuracy, etc. The given model is either accepted as such, is altered or is replaced by another model until the chosen criteria are fulfilled. Optimization methods are used to move the model parameters from initial guesses to their optimal destination by way of minimizing the objective function. The accuracy is measured using standard deviation of estimation parameter with the help of a confidence interval and certainty values.

Batch kinetics was utilized for the regression of parameters of kinetics. Following Equation (3) was utilized for this purpose:

$$r_{\text{ProAc}} = \frac{C^2[k_f.x_2.x_1 - k_b.x_3.x_4]}{[1 + k_p.C.x_1 + k_w.C.x_4]^2} \tag{3}$$

where, C is total concentration, k_{f} is forward rate constant, k_{b} is backward rate constant, k_{p} is adsorption constant of ProAc, k_{w} is adsorption constant of water and x_1, x_2, x_3, x_4 are mole fractions of ProAc, ProOH, ProPro and water, respectively. ACM was used for regression. Data related to mole ratio, temperature, catalyst loading and initial water concentration was used for regression. Table 3 shows the kinetic parameters obtained from regression. Figure 6 (a) to (d) shows the predicted concentration of ProAc compared with the experimentally observed concentration of ProAc. A good fit is indicated by R^2 value which is close to unity (Figure 7).

3.11. Reactive Distillation

RD is a combination of reaction and distillation in a single vessel which can offer many ad-

Table 3. Kinetic parameters for LHHW model

Kinetic Parameters	Values
k_{f} (L/gmol.s)	2.5 x 10^{15}
k_{b} (L/gmol.s)	148.41
k_{w} (gmole/g)	113.70
k_{m} (gmole/g)	13.99
E_1 (J/gmol)	74752.1
E_2 (J/gmol)	48925.7

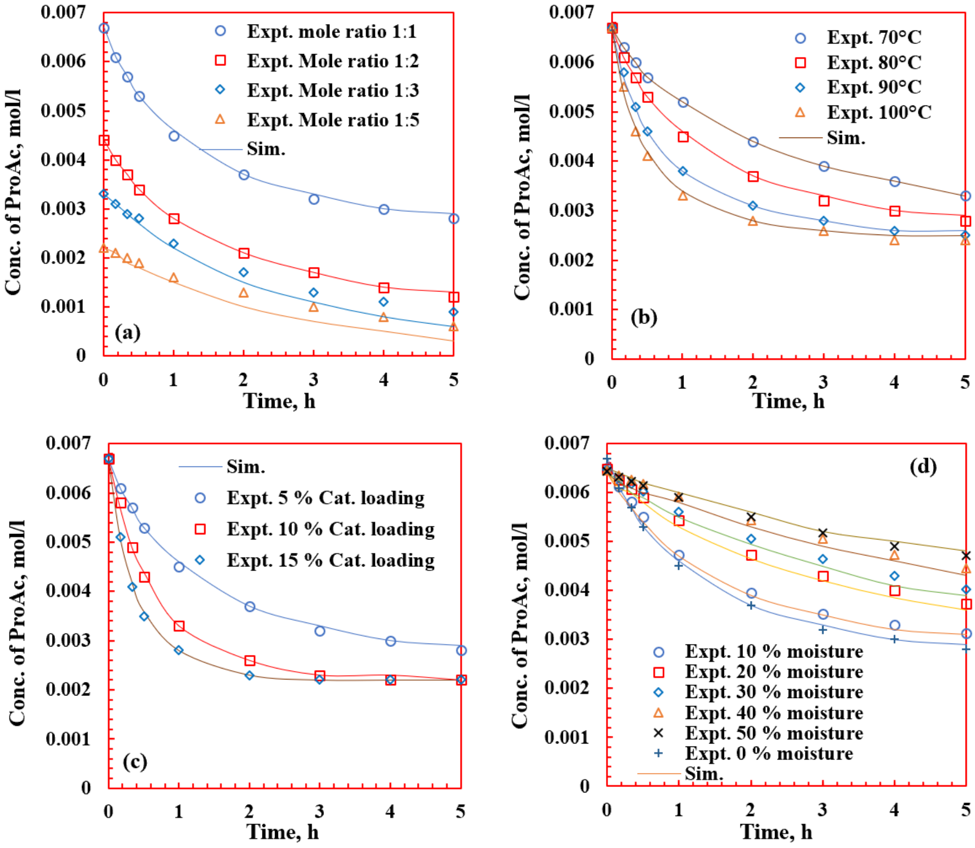


Figure 6. Simulation results for effect of (a) Molar ratio, (b) Temperature, (c) Catalyst loading, (d) Initial water concentration

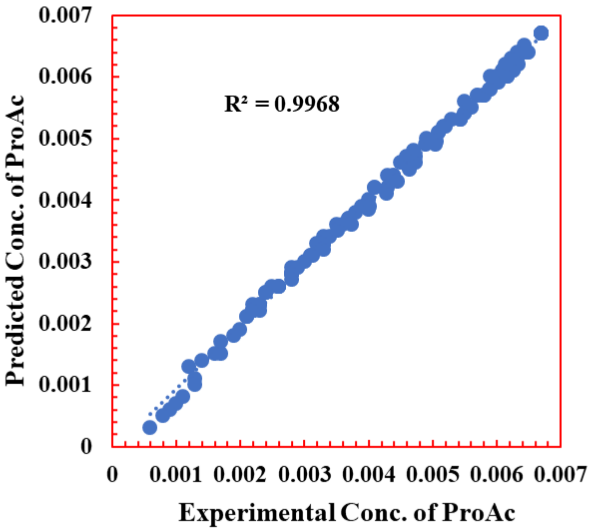


Figure 7. Parity plot of simulated and experimental data.

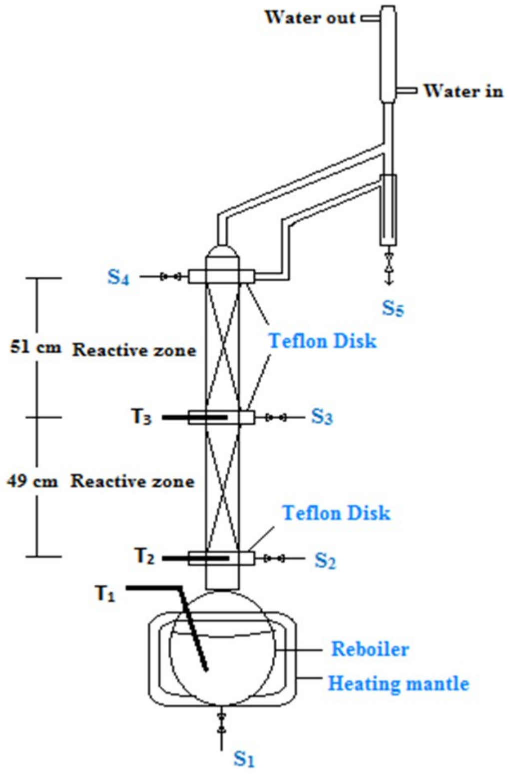


Figure 8. Schematic diagram of laboratory scale Batch Reactive Distillation Column

vantages over conventional method of reaction followed by separation. RD offers advantages like increased conversion, improved selectivity, better heat control and effective utilization of reaction heat [27]. Although invented in 1921, the industrial application of RD mostly took place after the 1980s [7,27-29]. RD is especially useful for equilibrium limited reactions such as esterification and hydrolysis. Due to continuous removal of reaction products from the reaction zone, conversion increases beyond the equilibrium value in RD. Thus RD helps for lower consumption of resources thereby reducing capital and investment cost. Use of RD may not be feasible for every reaction, as the suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products, reaction and distillation temperatures, etc. RD can be useful for process intensification (PI). The present work has aimed at establishing the feasibility of use of RD using A-15 for this important manufacturing processes.

3.11.1 Laboratory reactive distillation set up

Esterification of ProAc with ProOH was studied in batch RD setup shown in Figure 8, which consists of a reaction vessel (2000 mL capacity) fitted with stop cock and thermocouple for temperature measurement. The setup consists of two glass columns of lengths 49 cm (0.49 m) and 51 cm (0.51 m) and each of diameter 51 mm (0.051 m). Teflon disks were used to facilitate sample collection, to input the reactants and for temperature indication. Catalytic reactive packings were used (Katapack, Sulzer, 30) which contained the catalysts. Dean and Stark assembly was fitted at the top along with condenser as shown (Figure 8).

3.11.2 Batch reactive distillation

In a batch RD run, initially 700 mL of ProOH (1:1 mole ratio) was taken in reboiler and 500 mL ProOH in Dean and Stark assembly and then heating was started. Catalyst packings were fitted in the column, with screened A-15 catalyst (110 gm, washed and dried) with a particle size > 600 µm filled in the packing. When the reboiler temperature reached the boiling temperature, vapor rose through column. Vapors condensed in Dean and Stark assembly, which supplied the reflux to the column. ProAc was added through sample point S_4 using peristaltic pump. Total 1200 mL of ProAc was added to the reactor. Column was operated with total reflux. Temperatures at intermediate stages and reboiler were noted. Samples were withdrawn from sample points S_1 to S_5 and were analyzed. Temperature and composition profile thus obtained was plotted as shown in Figure 9 (a) and (b), respectively. In about 5 h, 72 % conversion was achieved. In batch runs under similar conditions, conversion was about 58% in 5 h. Obviously, this is a better way of carrying out the reaction. Probably due to insufficient separation stages, sharp separation was not achieved. But it is seen that RD helps to enhance the conversion.

Figures 9 (a) and (b) show the temperature and composition profile along the height of column at 5 h. It is clear that as ProAc flows towards the bottom, the temperature of top portion decreases and the bottom temperature increases. It is thus seen that use of RD helps as follows: (a). the conversion was increased in lesser time; (b). the process can be converted into a continuous one, thereby helping for PI; (c). about 70 % pure product was obtained from the bottom with ~ 24 % of acid and less alcohol and water; (d). this can be improved in a continuous RD column.

A genuine design of RD column can help to increase conversion and also separation and purification of products. Continuous RD runs are planned. A 51 mm (0.051 m) diameter, 3 meter high RD column is presently being commissioned. Detailed experimental data will be obtained and reported. Vapor liquid equilibrium (VLE) data for the different binaries in the system is being compiled and modeled and the design of continuous RD sequence will be done as a natural course of action using modelling and simulation. Experimental validation of the predictions from simulations will be done and will be communicated for consequent publication.

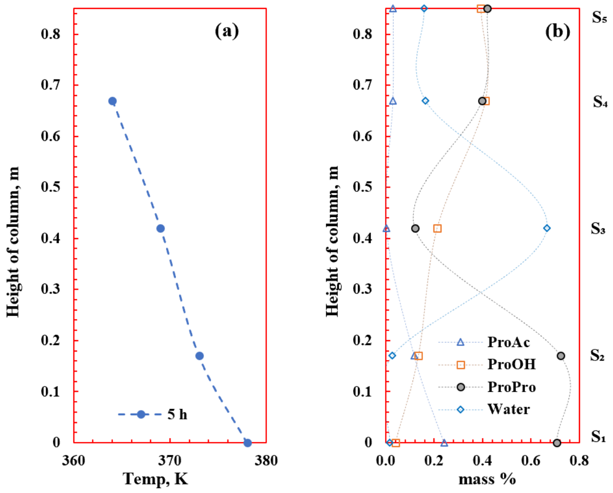


Figure 9. (a) Temperature profile, (b) Composition profile for BRD at 5 h

4. Conclusions

Esterification of ProAc with ProOH was carried out in this work in a batch reactor and in batch reactive distillation column. Kinetic data was obtained in batch reactor by variation of parameters like temperature, mole ratio, catalyst loading. A kinetic model was proposed and was validated through regression. Experimentation using batch reactive distillation shows its applicability. The conversions obtained were: ~ 58 % in batch reactor and ~ 72 % in RD. Genuine design and operation of RD column can help in process intensification.

Abbreviations

ACM	Aspen Custom Modeler
RD	Reactive Distillation
PI	Process Intensification
H2SO4	Sulphuric acid
IERs	ion exchange resins
A-15	Amberlyst-15
ProOH	1 - propanol
ProAc	Propionic acid
ProPro	n-propyl propionate
A-46	Amberlyst-46
RDC	Reactive Distillation Column
T-63	Tulsion-63
T-66	Tulsion-66
EtOH	Ethyl alcohol

CRediT Author Statement

Yogesh S. Mahajan: Conceptualization, methodology, investigation, resources, data curation, writing, review and editing, supervision; Reshma R. Devale: Partly helped in experimental investigation and in regression. She is also responsible for writing, draft preparation, Review and Editing etc.; Bipin S. Deogharkar: Experimental and simulation work, validation and initial draft of the article. All authors have read and agreed to the published version of the manuscript.

References

[1] Liu, Y., Liu, J., Yan, H., Zhou, Z., Zhou, A. (2019). Kinetic Study on Esterification of Acetic Acid with Isopropyl Alcohol Catalyzed by Ion Exchange Resin. *ACS Omega,* 4, 19462 - 19468. DOI: 10.1021/acsomega.9b02994.

[2] Beula, C., Sai, P. (2015). Kinetics of Esterification of Acetic Acid and Ethanol with a Homogeneous Acid Catalyst. *Indian Chemical Engineer,* 57, 177 - 196. DOI: 10.1080/00194506.2014.975761.

[3] JagadeeshBabu, P., Sandesh, K., Saidutta, M. (2011). Kinetics of Esterification of Acetic Acid with Methanol in the Presence of Ion Exchange Resin Catalysts. *Industrial and Engineering Chemistry Research,* 50, 12, 7155 - 7160. DOI: 10.1021/ie101755r.

[4] Ali, S., Tarakmah, A., Merchant, S., Al-Sahhaf, T. (2007). Synthesis of esters: Development of the rate expression for the Dowex 50 Wx8-400 catalyzed esterification of propionic acid with 1-propanol. *Chemical Engineering Science,* 3197 - 3217. DOI: 10.1016/j.ces.2007.03.017.

[5] El-Nassan, H. (2021). Amberlyst 15®: An Efficient Green Catalyst for the Synthesis of Heterocyclic Compounds. *Russian Journal of Organic Chemistry,* 57, 1109 - 1134. DOI: 10.1134/S1070428021070125.

[6] Pande, M., Samant S. (2012). Amberlyst-15 catalyzed acetylation of phenols and alcohols under solvent free conditions. *Recyclable Catalysis,* 1, 6 - 9. DOI: 10.2478/recat-2012-0002.

[7] Shinde, V., Patil, G., Katariya, A., Mahajan, Y. (2015). Production of tetrahydrofuran by dehydration of 1, 4-butanediol using Amberlyst-15: batch kinetics and batch reactive distillation. *Chemical Engineering and Processing: Process Intensification,* 95, 241 - 248. DOI: 10.1016/j.cep.2015.06.016.

[8] Talnikar, V., Deorukhkar, O., Katariya, A., Mahajan, Y. (2018). Intensification of the Production of 2-Ethyl-Hexyl Acrylate: Batch Kinetics and Reactive Distillation. *International Journal of Chemical Reactor Engineering*, 16, 20170134. DOI: 10.1515/ijcre-2017-0134.

[9] Zarei, N., Golmakani, M., Keramat, M., Majdinasab, M., Karami, A. (2021). Process intensification for the autocatalytic esterification of citronellol using microwave radiation. *LWT - Food Science and Technology,* 145, DOI: 10.1016/j.lwt.2021.111358.

[10] Bhandare, R., Katariya, A., Mahajan, Y. (2021). Production of isoamyl propionate: use of Amberlyst-15 in batch reactor and packed bed reactor. *Journal of the Chinese Institute of Engineers*, 44, 509 - 518. DOI: 10.1080/02533839.2021.1933597.

[11] Bhandare, R., Katariya, A., Mahajan, Y. (2022). Ion exchange resin catalyzed synthesis of methyl butyrate: Batch reactor and packed bed reactor studies. *Journal of the Chinese Institute of Engineers*, 187 - 194. DOI: 10.1080/02533839.2021.2012521.

[12] Dakshinamurty, P., Ramarao, M., Ramachandramurty, C. (1984). Kinetics of catalytic esterification of propan-1-ol with propanoic acid using cation exchange resin. *Journal of Chemical Technology and Biotechnology*, 34A, 257 - 261. DOI: 10.1002/jctb.5040340510.

[13] Lilja, J., Warna, J., Salmi, T., Pettersson, L., Ahlkvist, J., Grenman, H., Ronnholm, M., Murzin, D. (2005). Esterification of propanoic acid with ethanol, 1-propanol and butanol over a heterogeneous fiber catalyst. *Chemical Engineering Journal,* 115, 1 - 12. DOI: 10.1016/j.cej.2005.08.012.

[14] Buchaly C., Kreis, P., Gorak, A. (2007). Hybrid separation processes-Combination of reactive distillation with membrane separation. *Chemical Engineering and Processing: Process Intensification,* 46, 790 - 799. DOI: 10.1016/j.cep.2007.05.023.

[15] Altman, E., Kreis, P., Gerven, T., Stefanidis, G., Stankiewicz, A., Gorak, A. (2010). Pilot plant synthesis of n-propyl propionate via reactive distillation withdecanter separator for reactant recovery. Experimental model validation and simulation studies. *Chemical Engineering and Processing: Process Intensification*, 49, 965 - 972. DOI: 10.1016/j.cep.2010.04.008.

[16] Keller, T., Muendges, J., Jantharasuk, A., Gonzalez-Rugerio, C., Moritz, H., Kreis, P., Gorak, A. (2011). Experimental model validation for n-propyl propionate synthesis in a reactive distillation column coupled with a liquid - liquid phase separator. *Chemical Engineering Science,* 66, 4889 - 4900. DOI: 10.1016/j.ces.2011.06.056.

[17] Cruz-Diaz, M., Buchaly, C., Kreis, P., Perez-Cisneros, E., Lobo-Oehmichen, R., Gorak, A. (2012). Synthesis of n-propyl propionate in a pilot-plant reactive distillation column: Experimental study and simulation. *Computers and Chemical Engineering,* 39, 118 - 128. DOI: 10.1016/j.compchemeng.2012.01.004.

[18] Tekale, D., Yadav, G. (2021). Esterification of propanoic acid with 1, 2-propanediol: catalysis by cesium exchanged heteropoly acid on K-10 clay and kinetic modelling. *Reaction Chemistry and Engineering,* 6, 313. DOI: 10.1039/d0re00337a.

[19] Leyva, F., Orjuela, A., Miller, D., Vargas, J., Rodriguez, J. (2013). Kinetics of Propionic Acid and Isoamyl Alcohol Liquid Esterification with Amberlyst 70 as Catalyst. *Industrial & Engineering Chemistry Research,* 52, 18153 - 18161. DOI: 10.1021/ie402349t.

[20] Kotora, M., Buchaly, C., Kreis, P., Gorak, A., Markos, J. (2008). Reactive distillation - experimental data for propyl propionate synthesis. *Chemical Papers*, 62, 65 - 69. DOI: 10.2478/s11696-007-0080-x.

[21] Amberlyst-15 (21 September 2022) Citing Internet sources URL https://www.lenntech.com/Data-sheets/Rohm-&-Haas-Amberlyst-15wet-L.pdf.

[22] Tulsion-63 and Tulsion-66 (21 September 2022) Citing Internet sources URL https://www.thermaxglobal.com/wp-content/uploads/2020/03/Thermax-Resins-Catalogue.pdf.

[23] Indion 190 (21 September 2022) Citing Internet sources URL https://ionresins.com/pdf/pds/INDION%20190%20PDS.pdf.

[24] Fogler, H. (2016). *Elements of Chemical Reaction Engineering.* 5th ed. Philadelphia, PA: Prentice Hall.

[25] Popken, T., Gotze, L., Gmehling, J. (2000). Reaction Kinetics and Chemical Equilibrium of Homogeneously and Heterogeneously Catalyzed Acetic Acid Esterification with Methanol and Methyl Acetate Hydrolysis. *Industrial & Engineering Chemistry Research*, 39, 2601 - 2611, DOI: 10.1021/ie000063q.

[26] Calvar, N., Gonzalez, B., Dominguez A. (2007). Esterification of acetic acid with ethanol: Reaction kinetics and operation in a packed bed reactive distillation column. *Chemical Engineering and Processing*, 46, 1317-1323. DOI: 10.1016/j.cep.2006.10.007.

[27] Hiwale, R., Bhate, N., Mahajan, Y., Mahajani, S. (2004). Industrial Applications of Reactive Distillation: Recent Trends. *International Journal of Chemical Reactor Engineering,* 2, 1 - 54. DOI: 10.2202/1542-6580.1109.

[28] Taylor, R., Krishna, R. (2000). Modeling reactive distillation. *Chemical Engineering Science,* 55, 5183 - 5229. DOI: 10.1016/S0009-2509(00)00120-2.

[29] Mahajan, Y., Kamath, R., Kumbhar, P., Mahajani, S. (2008). Self-condensation of cyclohexanone over ion exchange resin catalysts: Kinetics and selectivity aspects. *Industrial and engineering chemistry research,* 47, 25 - 33. DOI: 10.1021/ie061275b.

[30] Katapack, Sulzer (21 September 2022) Citing Internet sources URL https://www.sulzer.com/-/media/files/products/separation-technology/distillation-and-absorption/brochures/structured_packings.ashx