

HEAT AND MASS TRANSFER LIMITATIONS IN ESTERIFICATION OF PROPIONIC ACID OVER ION EXCHANGE RESIN

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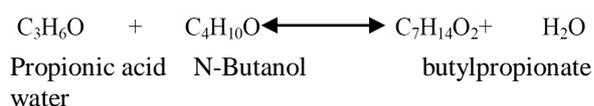
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Abstract - In heterogeneous synergist responses the warmth and mass exchange assume an indispensable part in influencing the rate of a response. Mass exchange confinements incorporate both the inner and outside dispersion of segments into and out of the impetus while warm exchange confinements incorporate whether the response occurring is isothermal in nature and to discover most extreme temperature inside the impetus molecule throughout response. In the present investigation of inherent rates of reaction both the dissemination component ought to be insignificant before the active catalyst investigations. Esterification of propionic acid over Indion 190 utilizing n-butanol as an entrainer was studied in a batch reactor. Considering the order of the esterification reaction to be one and the inner and outer dissemination is studied by Weisz Prater and Mears criteria. Temperature contrast (363 to 413^oK) with in the impetus molecule calculated to check the effect of heat transfer.

Keywords - Heterogeneous synergist, Indion-190, weisz prater, mears criteria.

I. INTRODUCTION

Esters are essential chemicals which have numerous applications in an assortment of regions, for example, solvents, plasticizers, pharmaceuticals and middle of the road for some enterprises¹. The impact recuperate of propionic corrosive from a waste stream in caprolactom a responsive refining was utilized to change over the waste acids and butanol into butyl propionate². At the same time the active and thermodynamic models are fundamental expected to the procedures reproduction squander corrosive recuperate framework³. The regular strategy for working balance restricted responses is to utilize an abundances of one reactant keeping in mind the end goal to build the transformation of constraining reactant⁴. Homogeneous and heterogeneous acids acts chemically in the esterification, in light of the fact that the restricting strides in the response component is the protonation of the carboxylic acid⁵. Propionic corrosive n-butanol and butyl propionate. The rate of heterogeneous response is regularly identified with inside/outer dissemination. Diverse models have been produced to speak to the active model to speak to the dynamic conduct of the heterogeneous impetuses of esterification.



Diffusion of reactants into the catalyst play vital role while determining the kinetics of the reaction. Prior to kinetic studies it is important to study the diffusion of reactants from the bulk phase to the surface of the catalyst particle, and subsequently from the surface to the inside of the particle. Internal and external diffusion play a major role in the transfer rate of reactants to heterogeneous catalysts. In order to

estimate the internal diffusion effect, Weisz modulus for catalytic reactions in solid catalyst particles could be quantified. Esterification reaction using ion exchange resin catalyst particles. Instead, the contribution of heterogeneous and homogeneous reactions towards conversion is represented by first and second terms respectively. The conversion X_A contributed by homogeneous part and heterogeneous part can be compared.

It is assumed that the equilibrium constant K_{eq} is same for both homogeneous reaction as well as for reaction inside the catalyst particle. It is also assumed that the diffusion constant of propionic acid is similar in magnitude to that of other reactants and products. The variation of Diffusion constant with temperature is also assumed to be negligible in the range of operating Temperature which otherwise would complicate the reaction-diffusion

The diffusivity of the propionic acid is dependent on temperature through Wilke-Chang

Equation in the form of

$$D_{AB} = 1.173 \times 10^{-16} (\Phi M B) T / (\mu B v A^{0.6})$$

Which predicts the diffusivity of the limiting reactant that is propionic acid in other species namely butanol, water and butyl propionate (Treybal et. al., 1981). An average value of the diffusivity is taken at 10⁻⁹ m²/s inside the pores of the catalyst. This is arrived at after taking the effect of porosity also into consideration (Ju et al., 2011).

In this kinetic model, it is considered that the void volume inside the catalyst particles is also utilized for the reaction. The liquid species can penetrate into the pore volume of the catalyst particle by diffusion. The reaction rate constant could be much higher in the

Volume of the catalyst particle since active sites are dense. In other words, the H^+ ion concentration that catalyzes the reaction is higher in the pores than in the bulk liquid outside the particle. Due to the constraint of charge neutrality, the entire H^+ ion content of the catalyst particle would not be dissolved into the bulk reactant liquid. Nevertheless, the presence of catalyst increases the homogeneous rate constant as well because the liberated H^+ ions from the catalyst. Hence, in this catalytic reaction, both the homogeneous and heterogeneous rate constants are fitted simultaneously from the initial reaction rate data. In view of the above condition, the net reaction rate due to catalytic activity substantially occurs inside the catalyst particles. In addition to it, there is the homogeneous reaction occurring in the bulk reactant solution. Hence there are two rate constants and one equilibrium constant as parameters in the model.

The contributions of heterogeneous and homogeneous reactions towards conversion are represented by first and second terms respectively the model parameters are fitted using only the initial reaction rate and equilibrium conversion. The rest of the kinetics is predicted using those parameters. The experiment provides the overall conversion of acetic acid due to homogeneous and heterogeneous reactions. The individual rate constants can be determined in a coupled model only rather than individually. There are few homogeneous models like in the case of H_2SO_4 catalyzed esterification of acetic acid with methanol. But those rate constants cannot be applied for the ion exchange resin catalyzed esterification.

In this study the esterification of the propionic acid using the n-butanol to synthesize the butyl propionate by the catalyst Indion 190, which the effect of the temperature and investigated the effect of heat for the synthesis of butyl propionate by the catalyst Indion-190, the behavior of the catalyst towards the reactants which are the internal or the external diffusion to be found.

II. EXPERIMENTAL DETAILS

2.1. Materials and Methods:

Commercially available catalyst Indion 190 is used for the reaction of propionic acid with the n-butanol for the synthesis of butyl propionate in a batch reactor setup.

Nomenclature

R	Radius of catalyst particle
N_A	Mass flux of A
$D_{A,mix}$	Diffusivity of A in gas mixture
D_e	Effective diffusivity
C_{Ab}	Bulk concentration of gas A
C_{Ac}	Concentration of A at the centre of catalyst

C_{As}	Concentration of A at the surface of catalyst
C_A	Exit concentration of A
Φ_1	Thiele modulus
C_{wp}	Weisz prater parameter
$-r_A'$	Rate of the reaction per unit weight of catalyst
C_m	Mears parameter
k_1''	Rate constant per unit surface area of catalyst

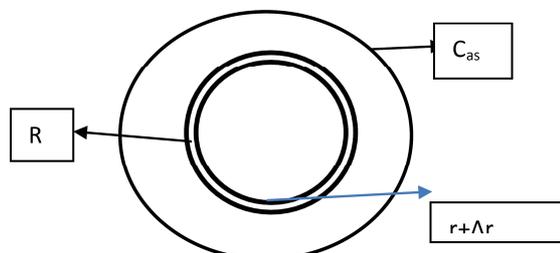


Figure 1: Shell mass balance on catalyst Pellet

2.2. Catalyst characteristics:

The properties of the catalyst used for the esterification process for the synthesis of butyl propionate is given below :

Appearance:	Opaque grey to dark grey beads
Matrix:	Styrene divinylbenzene copolymer
Functional Group:	Sulphonic acid
Ionic form as supplied:	Hydrogen
Moisture content:	3 %
Maximum Particle size range:	0.42 to 1.2 mm
	> 1.2 mm : 5.0%, maximum
	< 0.42 mm : 5.0%, maximum
Maximum operating temperature:	150 C
Operating pH range:	0 to 7

III. RESULTS AND DISCUSSION

3.1 Temperature Effect

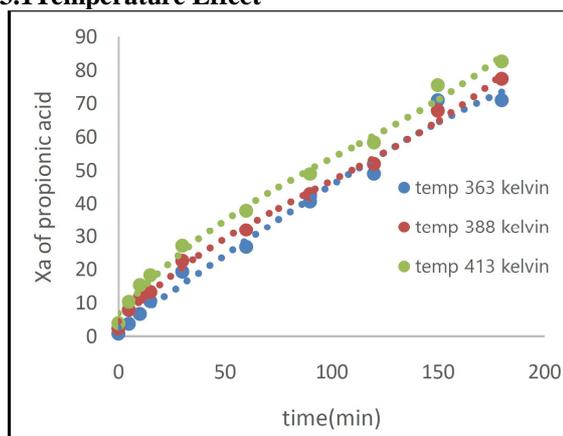


Fig 2: Impact of transformation w.r.t temperature

The impact of temperature on transformations of propionic acid at ideal loading (1 wt% ,2wt% and 3wt% Indion 190) of catalyst is shown in Fig 2. The transformation of propionic acid increases with

increment in temperature, however the variation is very minimum from 368 to 388 °K when compared to the difference from 388 to 413°K. The maximum conversion of propionic acid i.e 82.7% was observed at higher temperature after 180 minutes of operation.

PROPERTIES		
	Propionic acid	N-butanol
Chemical formulae	C ₃ H ₆ O ₂	C ₄ H ₁₀ O
Molecular weight	74.08 g·mol ⁻¹	74.12 g·mol ⁻¹
Appearance	Colorless, oily liquid	Colorless, refractive liquid
density	0.978g/cc	0.81 g cm ⁻³
Boiling point	141.15°C	117.7 °C
Acidity (pK _a)	4.88	16.10

3.2 Dissemination Effects on Heterogeneous responses:

In heterogeneous synergist responses the dissemination of gas from the mass to impetus surface (External dispersion) and from the surface to the inside of impetus (Internal dissemination) assumes an imperative part in rate of response. These dissemination instrument go about as protections which influences the rate of response and it ought to be dismissed. The figure beneath gives the means occurring in a permeable synergist molecule

3.2. a Internal diffusion:

For a round impetus molecule of range R in which first request response happens at consistent express the mass balance for A is given by

[Rate of mass A in]-[Rate of mass A out]+[rate of disappearance of A in the element Δr]=0

$$[4\pi R^2 N_A]r - [4\pi R^2 N_A]r + \Delta r + [-r_A' \rho 4\pi R^2 \Delta r] = 0 \dots (1)$$

$$\frac{d(NAr^2)}{dr} - rA' \rho r^2 = 0 \dots (2)$$

The molar flux of A by molecular diffusion is given by

$$N_A = -D_e \frac{dC_A}{dr} \dots (3)$$

Where D_e is effective diffusivity given by

$$D_e = \frac{D_{AB} \phi}{\tau} \dots (4)$$

Where D_{AB} is diffusivity of A in B, τ is the pellet porosity and φ is the constriction factor.

The value is taken as 1 for many cases and the tortuosity [16] of catalyst is calculated from porosity by

$$T = 1 - 0.5 \ln \Phi \dots (5)$$

Thiele modulus 1 of 1st reaction order is given by

$$\Phi_1 = \frac{\text{surface reaction rate}}{\text{diffusion rate}} = R \sqrt{\frac{K_1' S_{apc}}{D_e}} \dots (6)$$

In the event that Thiele modulus is high the mass exchange controls the response and in the event that it is low at that point surface response is the rate constraining advance. The inner adequacy factor can likewise be utilized to check whether interior dispersion is the rate restricting advance. The inside viability factor relies upon response arrange and also impetus shape. For a first request response on a circular impetus the inward viability factor is given by

$$n = \frac{3}{\Phi_1} (\Phi_1 \coth \Phi_1 - 1) \dots (7)$$

Weisz Prater criterion [17] is used to check whether the reaction is diffusion limited.

$$C_{w-p} = r_A' \text{obs} \rho_p R_p^2 / (D_A C_{A0}) \dots (8)$$

Parameters	values
r _{A'} (obs)	3.26*10 ⁻⁷ (mol/Kg cat.s)
ρ _c	0.6 (g/cm ³)
R	225 (μm)
D _e	6*10 ⁻⁸ (m ² /s)
C _{A0}	10.24 (mol/ml)
Φ	0.68
τ	1.1

C_{w-p}<1 diffusion limitations and concentration difference exists within the pellet

C_{w-p}>1 internal diffusion limits the reaction severely

3.2b External Diffusion:

Under relentless state conditions the outside dissemination of the reactants into heterogeneous impetus from main part of liquid is equal to the rate at which reactants are expended both inside the impetus and the surface. Mears Criterion is utilized to check whether the response is restricted by outside dispersion which is given underneath

$$C_m = \frac{-r_A' \rho_b R_n}{K_c C_{Ab}} < 0.15 \dots (9)$$

Since the Reynolds number is low crawling stream of liquid exists and the mass exchange coefficient is computed from the relationship (Sh-Sherwood number)

$$Sh = (4 + 1.21 Pe^{2/3})^{1/2} \dots (10)$$

Where Pe is the Pectlet number, Pe = Reynolds number (Re)* Schmidt number (Sc). For estimation of Re and Sc

$$Kc = \frac{Da_{mix} Sh(1-\Phi)}{dp\Phi} \dots\dots\dots (11)$$

Parameters	values
rA' (obs)	6×10^{-9} (mol/Kg cat.s)
ρ_c	0.6 (g/cm ³)
R	225 (μ m)
n	1
CAs	10.24 (mol/ml)
Φ	0.58
Kc	0.486

The value of C_m is 0.000206

CONCLUSION

In this the dissemination impacts were explored for the conversion of propionic acid response over Indion 190 impetus. The estimation of Mears rule demonstrates the significance of mass exchange protection over an impetus. With respect to the outcomes for the impetus with $C_m = 0.000206$, the outside mass exchange is especially unimportant at the given working conditions. The Thiele modulus esteem diminishes as size of impetus molecule diminishes and the adequacy factor keeps an eye on

an esteem about equivalent to 1. For a viability factor esteem equivalent to 1 the interior dispersion is insignificant. Likewise the outside dispersion is immaterial at the working food stream rate and thus both dispersion protections are insignificant. As the viability factor approaches 1 the surface response is said to be the controlling instrument and from the warmth exchange ponders the response is observed to be isothermal in nature.

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