

The Kinetic Comparison Study of Catalytic Esterification of Butyric Acid and Ethanol over Amberlyst 15 and Indion-190 Resins

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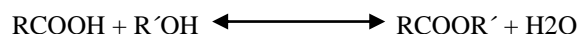
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ABSTRACT: Esters are an important class of chemicals that find use in a number of fields in the chemical industry. Esters are responsible for the aroma of many fruits, including apples, durians, pears, bananas, pineapples, and strawberries. However, the conventional method of production using homogeneous catalysts faces some problems with respect to efficiency and economic feasibility. Therefore, the development of an efficient process for the manufacture is the need of the hour in which the use of a solid acidic catalyst is highly desirable. In the present study, the reaction kinetics of heterogeneous esterification reaction is found out by a series of experimental analysis involving varying parameters like catalyst loading, initial molar ratio of alcohol to acid and temperature. The kinetic modelling was done for the production of ethyl butyrate from ethanol and butyric acid using dioxane as a solvent and two sulphonic acid resin solid catalysts namely Amberlyst 15 and Indion-190. A pragmatic kinetic model based on the pseudo homogeneous model was used for the analysis. Indion-190 proved to be the better catalyst.

KEYWORDS: Heterogeneous Esterification, Amberlyst-15, Indion-190, Ethyl Butyrate, Reactive distillation.

I. INTRODUCTION

Esters are important classes of chemicals that have many applications in a variety of areas such as solvents, plasticizers, pharmaceuticals and intermediates for many industries. Esters are compounds of the chemical structure R-COOR', where R and R' are either alkyl or aryl groups. The most common method for preparing esters is to heat a carboxylic acid, R-CO-OH, with an alcohol, R'-OH, while removing water that is formed. The limiting conversion of the reactants is determined by the equilibrium. The general reaction is as given below:



The esterification reactions are second order reactions and are highly reversible in nature due to the presence of water as by-product. This water reacts with the ester and again forms the acid and alcohol thus reducing the conversion. This problem is in practice surmounted by continuous removal of the entire product – especially water – from the reaction mixture through distillation or any other separation technique like reactive distillation. Esterification reactions are catalysed by an acidic medium because the reaction requires the presence of H⁺ ions to proceed. The esterification can be either carried out in the presence of a liquid catalyst like concentrated sulphuric acid or solid catalyst like polymeric sulphonic acid resins like Amberlyst 15. The traditional industrial process of synthesizing esters using homogeneous acid catalyst is conveniently replaced by solid acid catalyst, ion exchange resins, clay, and so forth [10]. Heterogeneous catalysts have many advantages over their homogeneous counter parts like being highly selective, less corrosive and

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ease of separation. P.F. Siril et al. [1] gave a detailed analysis of the various sulphonic acid resins used recently along with their acidic properties. Nisha Singh et al. [5] performed a similar study of kinetics of esterification of ethanol and butyric acid over Amberlyst-15. Their work showed the high conversions that can be achieved using solid sulphonic acid resins. To the best of our knowledge, no research has been done using Indion-190.

The ester of butyric acid and ethanol, namely, ethyl butyrate, finds wide applications. It is commonly used as artificial flavouring resembling orange juice or pineapple in alcoholic beverages (e.g. martinis, daiquiris etc.), as a solvent in perfumery products, and as a plasticizer for cellulose. In industrial use, it is also one of the cheapest chemicals, which only adds to its popularity.

II. MATERIALS AND METHODS

1. MATERIALS

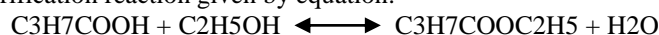
Absolute ethanol of >99.5% purity (AR, Chemco Chemicals) and butyric acid of 99.5% purity (AR, Chemco Chemicals) are used as the reactants. The reaction was carried out in the solution of dioxane of 99.0% purity (AR, Chemco Chemicals). Aqueous solutions were prepared in distilled water. Sodium Hydroxide (SD Fine chemicals) and phenolphthalein (SD Fine chemicals) were used for titration purposes. Amberlyst-15 H⁺ ion form catalytic ion exchange resin (IR, Rohm and Hass) and Indion-190 H⁺ ion form catalytic ion exchange resin (IR, Ion Exchange India Ltd.) were used as catalysts. Both are styrene-divinyl benzene cross linking resins.

2. METHOD

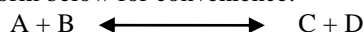
Any one of the parameter is varied whereas the remaining parameters are kept constant. This constitutes one experiment or one "run". A parameter (temperature, molar ratio, catalyst loading or catalyst type) is varied for that particular set. A set may typically consist of three runs. Based on the solution densities and molecular weights the volumes of ethanol and butyric acid were decided. The remaining volume was filled in by dioxane such that the total volume of the reaction mixture was 150mL. The glycerine bath is heated to the required temperature. As the temperature becomes constant the reactants are added and then the catalyst is fed with a help of a funnel. The stirrer is started and over the time samples are withdrawn using a syringe and needle arrangement. The sample withdrawn is considered to be negligible in comparison to the total reaction mixture volume. All samples were measured in a syringe of 5 mL, taken periodically, and titrated against 0.5 N standard NaOH solution using phenolphthalein as an indicator.

III. KINETIC MODELLING

The kinetics of esterification reaction can be expressed using a simple Pseudo-homogenous model or more complicated models based on the Langmuir-Hinshelwood Hougen-Watson (LHHW) mechanism or Eley-Rideal (ER) mechanism in the absence of any intraparticle diffusional limitations. Pseudo-homogenous first and second order models are applicable to many ion-exchange resin catalysed esterification reactions and highly polar reaction medium. In the present case, the reactants used are ethanol and butyric acid in dioxane. All the three components are highly polar. The integrated rate equation for second order reversible esterification reaction based on the pseudo-homogeneous model is as follows. Consider the esterification reaction given by equation:



The above equation can be written in the form below for convenience:



Where A is Butyric Acid, B is Ethanol, C is ethyl butyrate and D is water.

The rate expression for this reaction is given by

$$-r_A = \frac{dC_A}{dt} = k_f C_A C_B - k_b C_C C_D$$

Substituting and rearranging in integrated form, we get

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)(M-X_A) - \frac{(1-X_{Ae})(M-X_{Ae})X_A^2}{X_{Ae}^2}} = \int_0^t k_f C_{A0} dt$$

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The integrated rate equation is

$$\ln \frac{(M - X_{Ae} - M X_{Ae}) X_A + M X_{Ae}}{M(X_{Ae} - X_A)} = \frac{2M - X_{Ae}(1+M)}{X_{Ae}} k_f C_{A0} t$$

Here,

M is the initial concentration ratios of B to A; X_{Ae} is the equilibrium conversion of A.

X_A is the conversion of A at any time t, k_f is the forward rate constant.

IV. RESULTS

1. EFFECT OF CATALYST LOADING

Experiment work was carried out by varying the catalyst loading from 33.33 kg/m³ of the solution to 100 kg/m³ of the solution, keeping the molar ratio of butyric acid to ethanol constant at 1:10 and the temperature at 75 degrees Celsius. It is found out that with an increase in catalyst loading, the conversion of butyric acid increased with proportional increase in the number of active sites. At higher catalyst loading, the rate of mass transfer is high, and therefore, there is no significant increase in rate. The observations of the set are plotted on a graph as shown below..

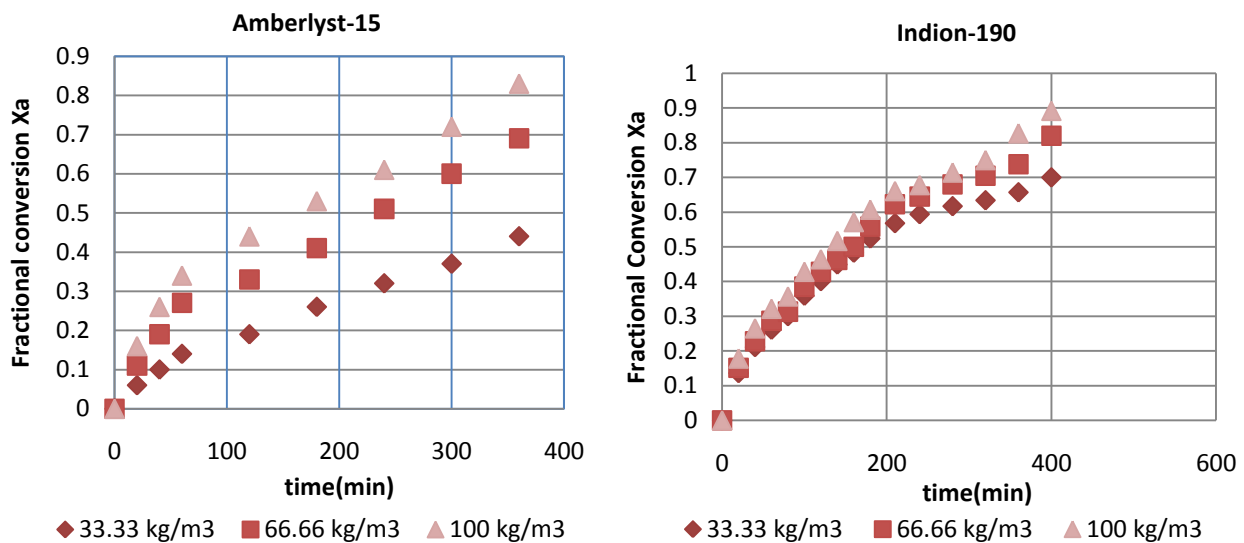


Figure 1: Graph comparing the effect of catalyst loading on conversion with constant molar ratio of 10:1 and temperature of 75 degrees Celsius.

2. EFFECT OF INITIAL MOLAR RATIO (ETHANOL TO BUTYRIC ACID)

The concentration of ethanol had an influence on the reaction rate and the conversion. The results are given in the figure below. It can be seen that the conversion of acid increases with increasing initial molar ratio of ethanol to butyric acid. For esterification with ethanol over Amberlyst-15, the conversion of butyric acid increases from 57% to 88% as the molar ratio was increased from 5:1 to 15:1 for a catalyst loading of 100 kg/m³ and a temperature of 75 degrees Celsius at a time of 360 minutes. It can be seen that the conversion of acid increases with increasing initial molar ratio of ethanol to butyric acid. For esterification with ethanol over Indion-190, the conversion of butyric acid increases from 81.4% to 89.2% as the molar ratio was increased from 5:1 to 10:1 for a catalyst loading of 100 kg/m³ and a temperature of 75 degrees Celsius at a time of 400 minutes. However, it was noticed that the conversion for a molar ratio of 15:1 was slightly lower than 10:1. This may be indicative of the fact that 10:1 may be the optimum molar ratio for Indion-190. The result observed for the effect of initial molar ratio of ethanol to butyric acid indicated that the equilibrium conversion of butyric acid can be effectively enhanced by using a large excess of ethanol. The results are plotted on a graph below.

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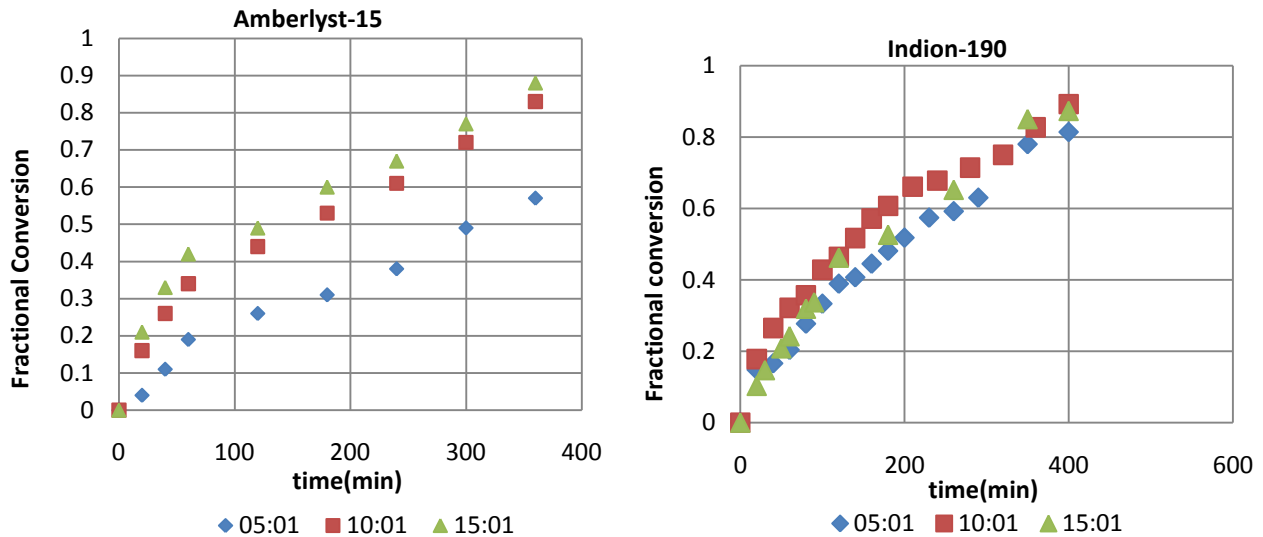


Figure 2: Graph comparing the effect of initial molar ratio of ethanol to butyric acid on conversion with constant catalyst loading of 100 kg/m³ and temperature of 75 degrees Celsius.

3. EFFECT OF TEMPERATURE

The study on the effect of temperature is extremely imperative for a heterogeneously catalysed reaction, as this information is helpful in calculating the activation energy for this reaction. Moreover, the intrinsic rate constants are strong functions of temperature. The figures shows the variation of fractional conversion with temperature. In order to investigate the effect of temperature, esterification reactions are carried out in the temperature region of 328K (55 degrees Celsius) to 348 (75 degrees Celsius) while keeping the catalyst loading at 100 kg/m³ and molar ratio of 10:1. With an increase in reaction temperature, the initial reaction rate or the conversion of butyric acid is found to increase substantially as shown in the figures. It shows that the higher temperature yields a greater conversion of the acid at fixed contact time. The data observed is shown in the graphs.

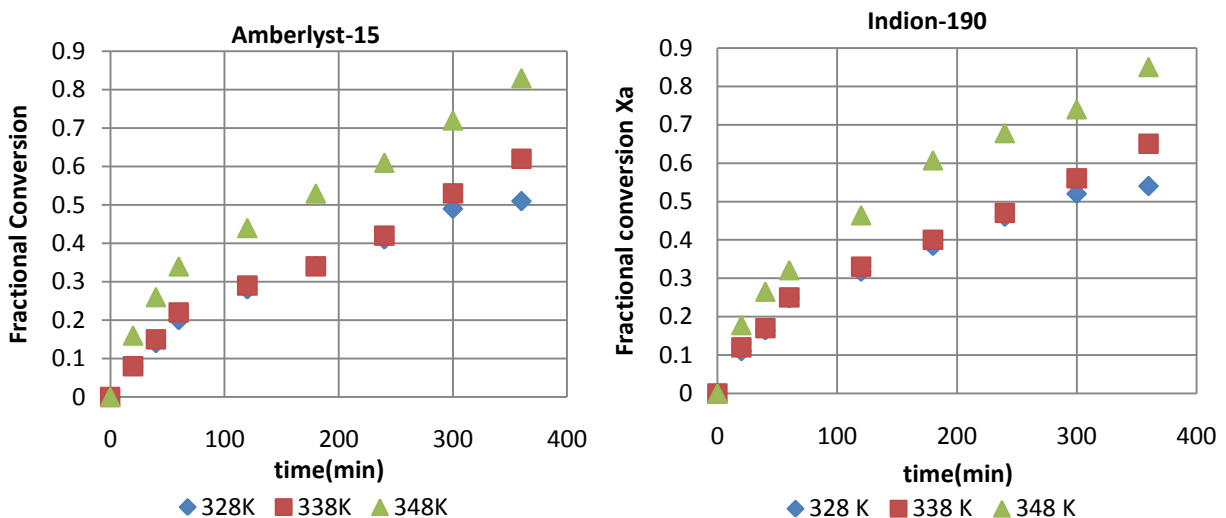


Figure 3: Graph comparing the effect of Temperature on conversion with constant catalyst loading of 100 kg/m³ and a molar ratio of 10:1.

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4. EVALUATION OF KINETIC PARAMETERS

Using the integrated rate equation and the equilibrium relation, the value of k_f is found out at three different temperatures. To determine the activation energy and frequency factors for forward and backward reactions, we plot the Arrhenius Plot as shown below. The slope of the plot gives the value of (E_a/R) and the exponential negative of the intercept gives the Arrhenius factor.

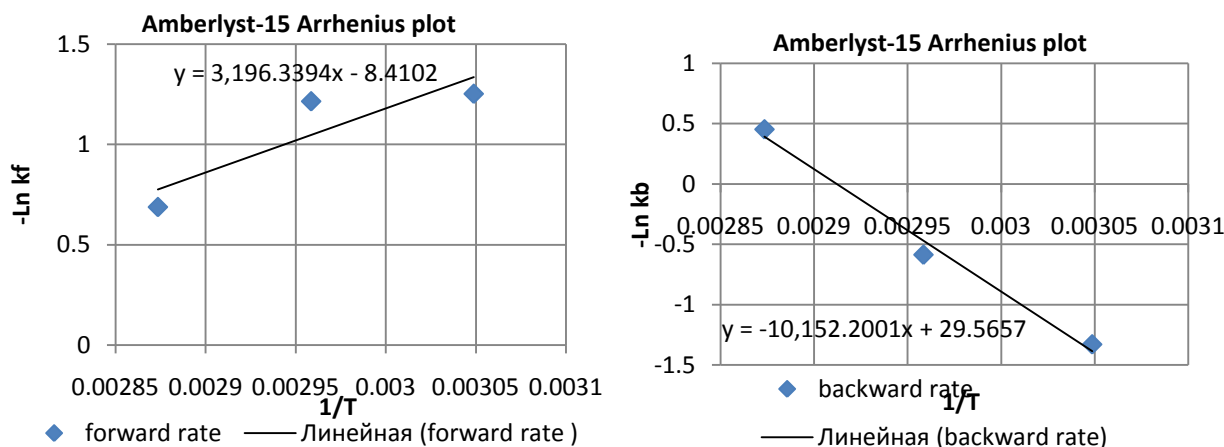


Figure 4: Arrhenius plots for forward and backward reactions for Amberlyst-15

From the graphs plotted above, the value of the activation energy for the forward reaction is 26.57 KJ/mol and the activation energy for the backward reaction is 84.403 KJ/mol. With the help of the intercepts, the forward and backward reaction Arrhenius factors is calculated as 4491.76 cc/mol.min and 1.45×10^{-13} cc/mol.min respectively. Also, taking the difference of the forward and backward activation energies gives us the enthalpy of the reaction. Therefore, the enthalpy of the reaction is 57.833 KJ/mol. The positive sign shows that the reaction is endothermic. From the graphs plotted below, the value of the activation energy for the forward reaction is 23.625 KJ/mol and the activation energy for the backward reaction is 88.602 KJ/mol. With the help of the intercepts, the forward and backward reaction Arrhenius factors is calculated as 1757.24 cc/mol.min and 3.92×10^{-14} cc/mol.min respectively. Also, taking the difference of the forward and backward activation energies gives us the enthalpy of the reaction. Therefore, the enthalpy of the reaction is 64.977 KJ/mol. The positive sign shows that the reaction is endothermic.

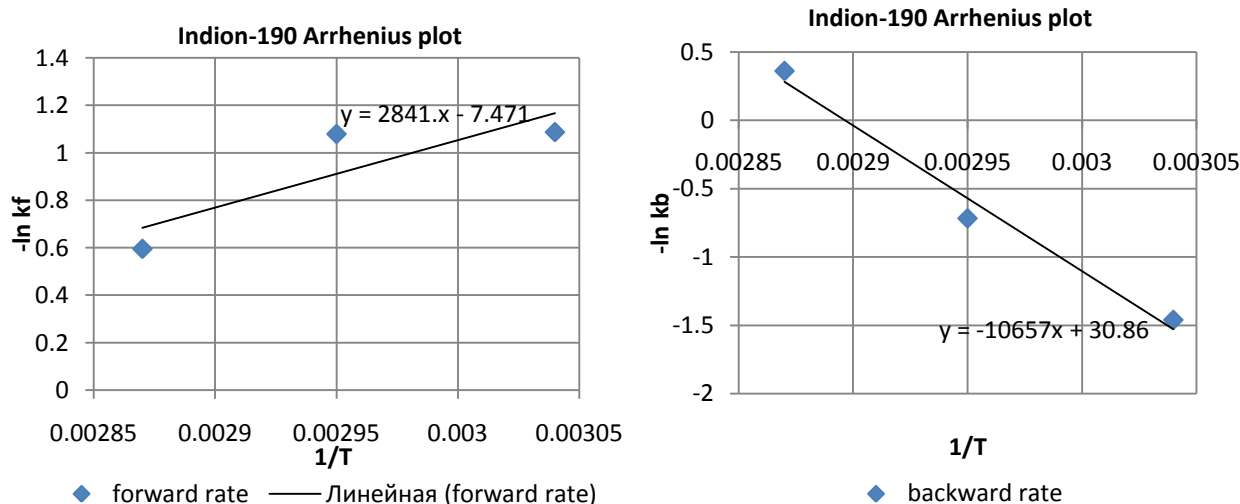


Figure 5: Arrhenius plots for forward and backward reactions for Indion-190.

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V. DISCUSSIONS

1. PHYSICAL COMPARISON OF THE CATALYSTS

Table 1: Physical comparison of the two catalysts

	INDION-190	AMBERLYST 15
Physical form	Grey Opaque beads	Opaque beads
Ionic form as shipped	H+	H+
Concentration of active sites	≥ 1.7 eq/L	≥ 1.7 eq/L, ≤ 4.7 eq/kg
Moisture holding capacity	$\leq 1\%$	52-57%
Surface area of the catalyst	NA	53 m ² /gram
Average pore diameter	NA	300Å
Operating pH	0-7	0-14
Operating Temperature	$\leq 150^{\circ}\text{C}$	$\leq 120^{\circ}\text{C}$
Cost(Rs./gram)	4.3	13.5
Regenerability (without significant loss in catalytic activity)	3	3

2. KINETIC COMPARISON OF THE CATALYSTS

Table 2: Kinetic comparison of the two catalysts

KINETIC PARAMETERS		AMBERLYST-15	INDION 190
Equilibrium constants	328 K	0.0755	0.0755
	338 K	0.1649	0.1649
	348 K	0.7904	0.7904
Forward reaction rate constant	328K	0.2857 cc/gmol.min	0.3366 cc/gmol.min
	338K	0.2966 cc/gmol.min	0.3395 cc/gmol.min
	348K	0.502 cc/gmol.min	0.5513 cc/gmol.min
Backward reaction rate constant	328K	3.78 cc/gmol.min	4.485 cc/gmol.min
	338K	1.789 cc/gmol.min	2.05 cc/gmol.min
	348K	0.636 cc/gmol.min	0.6974 cc/gmol.min
Activation energy	Forward	26.57 kJ/mol	23.625 kJ/mol
	Backward	84.403 kJ/mol	88.602 kJ/mol
Arrhenius factor	Forward	4491.46 cc/gmol.min	1757.24 cc/gmol.min
	Backward	1.45×10^{-13} cc/gmol.min	3.92×10^{-14} cc/gmol.min

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From the above table we get the comparison of activation energies and Arrhenius factors for both the reaction sets consisting of different catalysts. The value of k_f (forward reaction) rate constant increases with temperature and k_b (backward reaction) rate constant decreases with increase in the temperature. The activation energy in the forward direction of Indion 190 catalyst is less than that of the Amberlyst 15 and the activation energy in the backward reaction is more than that of Amberlyst 15. This shows that Indion 190 favours the forward direction more and the backward reaction less (greater activation energies mean greater difficulty for the molecules to react and cross the energy barrier). Clearly, the value of the forward rate constants for Indion 190 are also greater than Amberlyst-15, this means that given sufficient amount of time, Indion 190 will help attain equilibrium faster than Amberlyst-15.

3. PARITY PLOT (FOR INDION-190)

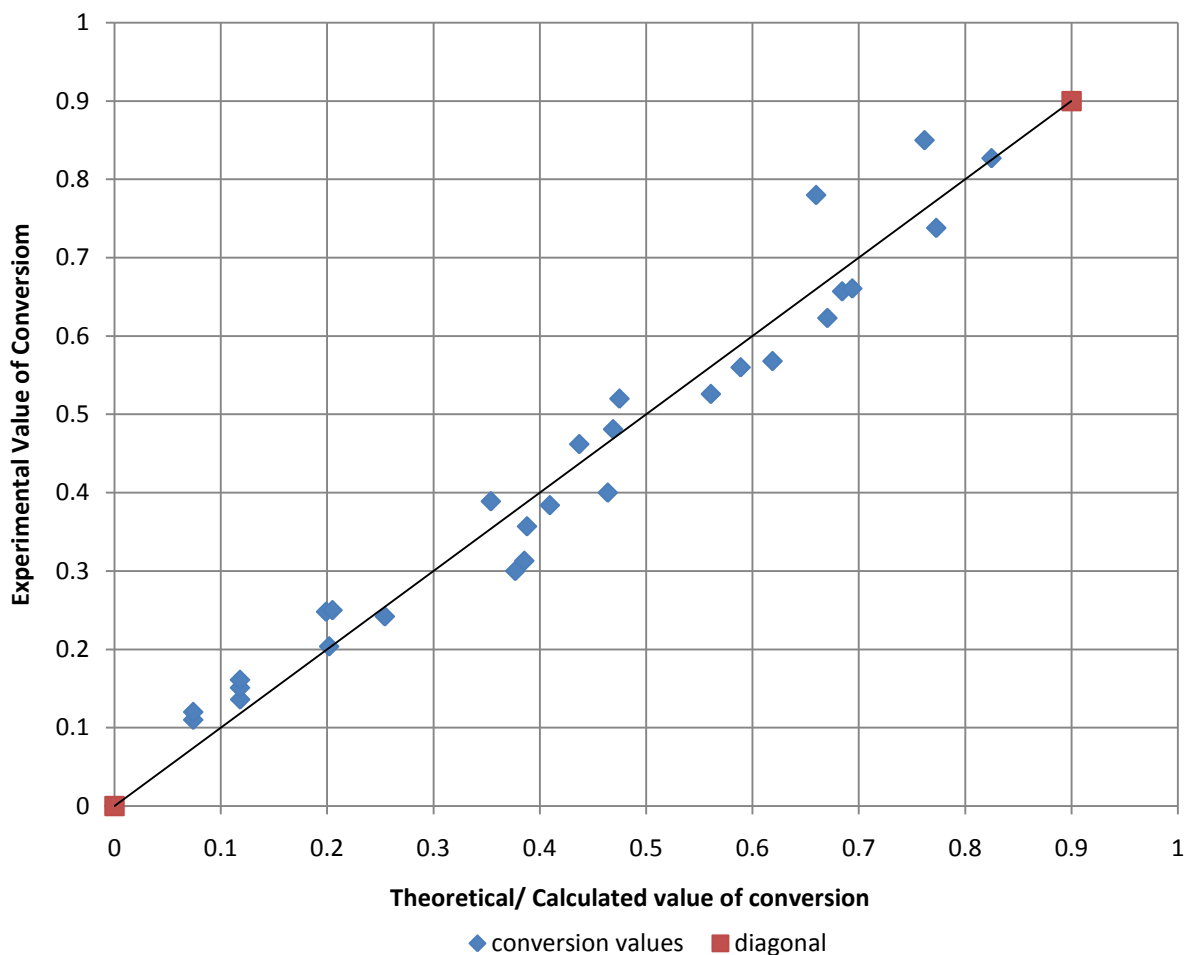


Figure 6: Parity plot comparing experimental and theoretical values for Indion-190.

VI. CONCLUSIONS

The behaviour of the catalyst was compared on the basis of temperature, initial molar ratio of alcohol to acid and catalyst loading. In each case, the conversion increased with operating temperature, catalyst loading and initial mole ratio of reactants. Optimum conditions were drawn out. The study focussed on comparing two acidic ion exchange resins, Amberlyst-15 and Indion-19, on the basis of their kinetic parameters. A pseudo-homogeneous model was

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applied and it was shown that Indion-190 was better than Amberlyst-15 as it helped in attaining equilibrium faster and also helped lowering the activation energy of the reaction to a larger extent in comparison to Amberlyst-15. Amberlyst-15 and Indion-190 could be utilised up to three times with negligible loss of catalytic activity.. After that they can be regenerated to full potential for further use. A parity plot shown in figure 6 confirms the accuracy of the experiment as a very large deviation from the diagonal wasn't observed. To achieve near to 100% conversion we will have to make use of an in situ separation technique such as reactive distillation or reactive adsorption. A brief comparison shows that reactive adsorption is relatively new and has its own design complexities. Thus reactive distillation is chosen to increase the conversion of the acid.

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