Reaction Kinetics of Tert-Butanol Esterification

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ABSTRACT

In this study, the kinetics for the reaction of tert-butanol esterification with acetic acid in the presence of Dowex 50Wx8 catalyst was investigated. The reaction kinetic experiments were conducted in 1000 milliliter vessel at temperatures ranged from 50 - 80 ^{o}C, catalyst loading 25-50 g/L, and the molar ratios of acetic acid to tert-butanol from 1/3 – 3/1. The reaction rate was found to increase with increasing temperature and catalyst loading. It was also found the conversion of the tert-butanol increases as the molar ratio of acid to alcohol increases from 1/3 – 3/1. The Non-ideality of the liquid phase was taken into account by using activities instead of molar fractions. The activity coefficients were calculated according to the group contribution UNIFAC method. The results show that the activation energy of tert-butanol esterification with acetic acid was found to be 1.09 kJ/mol.

Key words: esterification, reaction kinetic, tert-butanol, tert-butyl acetate, dowex 50wx8.

دراسة حركية تفاعل الاسترة المحفزه لكحول البيوتانول الرباعي

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الخلاصة

تم دراسة حركية تفاعل الاستره لحامض الخليك مع كحول البيوتانول الرباعي باستخدام عامل مساعد من نوع ديواكس 50. تم اجراء التجارب العمليه عند درجة حراره تتراوح بين (50-80) درجه مئويه وكميات من العامل المساعد تتراوح بين (25-50) غم ونسبه موليه (حامض/كحول) للمواد المتفاعله بين (3-1/3). تم التوصل الى ان زيادة درجة الحراره وكمية العامل المساعد تؤدي الى زيادة معدل التفاعل. وكذلك وجد ان نسبة التحول من كحول البيوتيل الرباعي تزداد مع زيادة النسبه الموليه (حامض/كحول) من (3-1/3). ولكون السائل غير مثالي تم حساب معامل التنشيط بطريقة اليونيفاك. من خلال النتائج العمليه في تفاعل الاستره لحامض الخليك مع كحول البيوتيل الرباعي تم التوصل الى ان طاقة التنشيط للتفاعل تساوي 1.09 كيلوجول/مول.

1. INTRODUCTION:

Esterification is a chemically reversible reaction producing ester and water from two reactants of acid and alcohol; it's an important reaction in the chemical engineering industry. The desired product (ester) plays a major role in the production of flavors and fragrances, solvents, plasticizers, pesticides and herbicides, medicinal and surface-active agents, **Ali, et al., 2007**.

Butyl acetates are used primarily as solvents in the lacquer and enamel industries. It is used in coatings, where its solvent capacity and its low relative volatility make it useful for adjustment of evaporation rate and viscosity. It is particularly useful as a solvent or thinner for acrylic polymers, vinyl resins, as reaction medium for adhesives, as solvent for leather dressings, and a process solvent in various applications and in cosmetic formulations **, Liu, et al., 2005**.

A general method is presented for the preparation of tert-butyl esters by the gentle warming of the carboxylic acid in the presence of excess of tert-butyl acetoacetate and a catalytic amount of acid. This method generates only low pressures, and is therefore suitable for laboratory scale pressure glassware **, Taber, et al., 2006**.

There are two catalysts to accelerate the rate of esterification reaction, that is, homogeneous and heterogeneous catalyst **, Lilja, et al., 2002**. Homogeneous catalysts provide distinguished performance in terms of reaction rate, the benefit of those catalysts is diminished since separation and recovery of catalyst are difficult due to the miscibility between liquid acid catalyst and reaction medium**, Ali, et al., 2007and Lilja, et al., 2002** . In addition, the homogeneous acid catalysts cause the occurrence of side reactions, corrosion of the equipment and the need to deal with acidic wastes, **Liu and Tan, 2001**.

Heterogeneous catalyst (ion-exchange resin) is a promising material for the replacement of the homogeneous acid catalysts. The solid type of material has good physical and chemical properties, and shows excellent performance as a heterogeneous catalyst in esterification reaction. The mechanical separation by filtering is possible, the ion exchange resin is reusable, guaranteeing the continuous operation, waste or disposal problems are eliminated, and isolation of reaction intermediates is possible **, Ali, et al., 2007** and **Sanz, et al., 2002**. Moreover, catalysts in the solid type preclude corrosion as well as pollution, and show both high selectivity and thermal stability**, Gangadwala, et al., 2003**.

The significance of external mass transfer limitation which is directly related to stirrer speed in batch systems depends on several factors such as the viscosity of the system, reactions conditions, in addition to the type and properties of catalyst used. The effect of internal diffusion on the rate of the reaction catalyzed by a solid catalyst (ion-exchange resin) is dependent on many parameters such as catalyst composition, particle size, reaction medium and temperature **, Ali, et al., 2007**.

Several works on esterification with heterogeneous catalyst have been studied with various reactants.

Nagasawa et al., 1994, used activated basic alumina for the esterification of tert-butanol by acid chlorides or acid bromides. They got a good yield for tert-butyl ester; the amount of catalyst relative to the reactants used by them was very large.

Altiokka and Çıtak 2003, studied the kinetics of esterification of acetic acid with isobutanol with and without catalyst. They found the initial reaction rate decreases with alcohol and water concentration as it linearly increases with that of acid.

Niasari et al., 2005, studied the esterification of tert-butanol by acetic anhydride to tert-butyl acetate over $InCl_3/Al_2O_3$, $GaCl_3/Al_2O_3$, $FeCl_3/Al_2O_3$, $MnCl_2/Al_2O_3$, $CoCl_2/Al_2O_3$, $NiCl_2/Al_2O_3$, $CuCl_2/Al_2O_3$ and $ZnCl_2/Al_2O_3$ catalysts. They reported that the homogeneous indium chloride, gave lower conversions than to the supported catalyst, and in the presence of an acid catalyst, tert-butanol undergoes dehydration to iso-butylene even at room temperature.

Blagov et al. 2006, studied the kinetics of side reactions of the formation of *n* butyl acetate in the heterogeneous catalyst. They were reported that the reaction rate is practically equal for their catalysts and the side reactions occur primarily on the active sites inside the pores of catalysts.

Izci and Bodur 2007, observed that initial reaction rate increases with increasing of reaction temperature and catalyst loading and Dowex 50 Wx2 ion exchange resin has very high activity in the synthesis of isobutyl acetate.

Ali et al., 2007, studied the kinetics of the esterification reaction of propionic acid with 1-propanol over the ion-exchange resin Dowex 50Wx8-400. They were found that both external and internal diffusion limitations did not affect the overall reaction rate, the conversion of propionic acid increased with increasing temperature and catalyst loading and decreased with increasing initial mole fraction of acid.

Korkmaz et al., 2009, used PDMS (Polydimethylsioxane) membrane with two different catalysts for isobutyl acetate production. It was observed that increasing the catalyst concentration and using the thinner membranes increase the conversion, and that while the reaction occurs slowly in Dowex 50W-X8 catalyzed PVMR, the conversion obtained is higher for longer reaction times than the one using H_2SO_4.

Bhorodwaj and Dutta, 2011, studied the esterification of acetic acid with primary (n-), secondary (sec-) and tertiary (ter-) butanol catalyzed by supported heteropoly acids (HPAs), they were reported that the conversions of different alcohols into the corresponding esters decrease in the following order: n-butanol>sec-butanol>ter-butanol. The selectivities for the corresponding esters are nearly 100%.

Tsai et al., .2011, studied the heterogeneous esterification of glutaric acid with methanol over acidic cation exchange resin beads, Amberlyst 35, were investigated through a packed-bed reactor. They were found that the equilibrium conversion of glutaric acid increases slightly as the molar ratio of feed increases from 15 to 20. The same observation was found with **Tsai et al.,** for the esterification of acetic acid with methanol.

Akbay and Altiokka, 2011, found that Amberlyst-36 has slightly higher activities for esterification of acetic acid with amyl alcohol.

Ju et al., 2011, studied the experimental parameters were reaction temperatures (100–110 ◦C), molar ratios of reactants (butyric acid/n-butanol = 0.25–4) and catalyst loading (10–40 g/L), they found that the conversion increased with temperature and catalyst loading whereas it decreased as the molar ratio of reactants increased.

The present work was undertaken to find the reaction kinetic representing the esterification of acetic acid with tert-butanol in the presence of Dowex 50Wx8. The effect of the significance of both external and internal diffusion limitations on the esterification system, reaction temperature, catalyst amendment with HCl, catalyst loading, and initial reactants mole ratio on the reaction kinetics were investigated. To take into consideration, the nonideality of the liquid mixture, activities of the species in liquid phase, estimated by the group contribution method UNIFAC, were used instead of molar fractions.

2. EXPERIMENTAL WORK

2.1 Apparatus

Fig. 1 shows the schematic diagram of the experimental which was used to carry out the esterification reaction. The reaction was carried out in a round-bottomed QVF flask with two necks with capacity of 1000 ml. A reflux condenser was placed on the top of the reactor in order to prevent the escape of volatile compounds. A thermocouple immersed in the flask and was used to control the temperature within ±0.1K by Digital temperature controller. The mixture was mixed using a magnetic stirrer, with speed 1000 rpm.1 cm^3 of liquid sample was withdrawn from the reactor at regular intervals for analysis and immediately transferred to a crucible in refrigerator at 5 ^oC to ensure that no further reaction took place.

2.2 Materials

Tert-butanol of 99% purity was manufactured by Riedel-de Haën Ag Seelze-Hannover (Germany); acetic acid of 99% purity was manufactured by Rioel-de Haën chemicals (Germany) were used as the reactants. Among various cation exchange resins, Dowex 50Wx8 with a particle size range of 0.04–0.07 mm was obtained from Fluka which is a strong acid ion-exchange resin.

2.3 Procedure

In the experiments, the catalyst was prepared by treatment with (1N) HCl to increase acidity. Each 100 gm of catalyst was stirred for 2 hrs with 500 ml HCl (1N).The chloride ions were washed three times with distilled water to remove it. After that the catalyst was dried at 60 ^oC for 12 hours to remove the moisture. The dried catalyst was stored in a desiccator before further use. Dowex 50Wx8 and tert-butanol were placed in the reactor. A known weight of the catalyst was added at the same time the reactor contents well mixed. After a steady value of the desired temperature was attained, the acetic acid at the same temperature was added and this was taken as zero time for a run. 1 cm^3 of liquid sample was withdrawn from the reactor at regular intervals for analysis. The operating conditions of the present study are given in **Table 1**.

Before any experiment the reactants were prepared in the vessel maintaining the required molar ratio with overall volume of 800 ml.

3. GC ANALYSIS

At a certain time, 0.1ml of liquid product sample was extracted through a syringe filter and analyzed with a gas chromatograph (GC type Shimadzu, Model 2014) equipped with a flame ionization detector (FID) at temperature 180 °C, column (30 m length, 0.35 mm inner diameter and 1.15 cm^3/min column flow), N_2 as carrier gas at 50 kpa, split ratio 50 at temperature 150 °C, 61.8 cm^3/min total flow,6 min total time, 24.5 cm/sec linear velocity and temperature program 110 ^oC hold for 1 min, heat at 10 K/min to 130 C hold for 1 min.

4. KINETIC MODEL

4.1 Reaction kinetics

The kinetic model for the esterification reaction was developed using the obtained concentration over a temperature range of 50-80 ^oC a catalyst loading between 25-50 gm of catalyst for feed (tert-butanol + acetic acid) and a tert-butanol/acetic acid mole ratio of 1:1, 1:3, and 3:1. The reaction kinetic model has the following form **, Altiokka and Çıtak, 2003.**

$CH_3COOH + C_4H_9OH \leftrightarrow CH_3COOC_4H_9 + H_2O$

$$r_j = m_H \frac{dx_j}{dt} = \delta_j M_{cat} K_f \left(a_{HAc} a_{TBuOH} - \frac{1}{K_a} a_{TBuAc} a_{H2O} \right) \qquad \ldots (1)$$

The initial reaction rates in the carried experiments are calculated by the following expression:

$$-r_i = \frac{\Delta C_i}{\Delta t} = C_T \frac{\Delta x_i}{\Delta t} \qquad \ldots.(2)$$

Experimental reaction rate data was fitted using a nonlinear regression method. Seven data points were used to calculate the parameters.

The following steps are used to calculate parameters of reaction kinetics:

1) Determining the rate constant of the reaction by using Eq. (1).
2) Depending on assumed forward and reversible reaction rate constant, simulation of the kinetic reactions is performed by using MATLAB R 2010b program.
3) The simulation results are compared with experimental results at each point. All deviations between experimental and calculated values are squared and summed up to form an objective function F**:**
4)

$$F = \sum (exp.conc. - cal.conc.)^2 \qquad \ldots (3)$$

5) For each experimental data, the concentration-time data and seven new values for F is calculated. The rate constants corresponding to the minimum F are stored and considered improved rate constants for final or next iteration.
6) The iteration proceeds until the absolute difference between two successive objective functions is less than a predefined tolerance ε. The final obtained values of K_f and K_a will be the optimal rate and equilibrium constants respectively.

The study of the effect of temperature is very important since it is useful to calculate activation energy of the reaction. The observed reaction rate constants (k) data at different temperatures were fitted to the Arrhenius-type equation Eq. (4) and the model parameters, k^o (frequency factor) and (EA) (activation energy), were determined using linear regression technique **, Altiokka and Çıtak, 2003.**

$$K = K^0 exp\left[-\frac{E_A}{R.T}\right] \qquad \ldots..(4)$$

4.2 Estimation of Activity Coefficient

The determination of the activity coefficient can be done without the need for actual data, by assembling the pure component from individual groups and assessing the contributions of their interactions. One of these methods is the UNIFAC (universal functional activity coefficient) model. UNIFAC was used to account for system non-ideality.

The expression for the activity coefficient is written as the sum of combinatorial and residual terms:

$$\ln \gamma_i = \ln \gamma_i^C + ln\gamma_i^R \qquad \ldots..(5)$$

Table 2 contains all UNIFAC model parameters that used in this study to calculate liquid phase activity coefficient.

5. DIFFUSION

It is necessary to eliminate both external and internal diffusion limitations.

The effect of external diffusion limitation on the esterification reaction rate was studied by earlier workers **, Ali, et al., 2007 and Ju, et al., 2011.**

If the production of the ester is independent of stirrer speed, this indicates that external diffusion is not the rate controlling step. Thus, to ensure that the reaction rate is not influenced by external diffusion; the experiments should be run at a high enough stirrer speed [1].

In general, external diffusion controls the overall rate in catalytic processes if the viscosity of the reactant mixture is very high or the stirrer speed is very low **, Othmer, 1994.**

To consider the effect of external mass transfer resistance on the rate of reaction, the Mears criterion for external diffusion was examined and the dimensionless Mears parameter (C_M) was calculated as follows:

$$C_M = \frac{r_{A.obs}\rho_c R_c n}{k_C C_{Ab}} < 0.15 \qquad \ldots.(6)$$

To estimate the mass transfer coefficient (k_C), the following equation was employed **,Geankoplis, 1993.**

$$k_C = \frac{2D_{AB}}{d_p} + 0.31 N_{Sc}^{-2/3}\left(\frac{\Delta\rho\mu_c g}{\rho_c^2}\right)^{1/3} \qquad \ldots..(7)$$

Note that k_C is dependent on the limiting reactant; as the limiting reactant is tert-butanol in all the cases.

The diffusivity (D_{AB}) was obtained from the multi-component diffusivity correlation, Perkin and Geankoplis method, as shown below **,Perry and Green, 1997.**

$$D_{AB}\mu_B^{0.8} = \sum_{\substack{j=1 \\ j\neq A}}^{n} x_j D_{Aj}\mu_j^{0.8} \qquad \ldots..(8),$$

The D_{Aj} can be obtained from the Wilke–Chang correlation [19]:

$$D_{Aj} = 7.4\times10^{-8}\left[\frac{(\emptyset Mwt_2)^{1/2}}{\mu_2}\times\frac{T}{V_1^{0.6}}\right] \qquad \ldots..(9)$$

If the value of left-hand side in **Eq. 6** is lower than 0.15, the external mass diffusion can be negligible in the kinetic study ,**Fogler, 1999**.

Table 3 shows that the calculated Mears parameters (C_M) are less than 0.15.

The effect of internal diffusion on the catalytic reaction can be studied by screening catalyst into different particle sizes or by calculating certain dimensionless parameters such as the well-known Weisz–Prater criterion.

The occurrence of any internal pore diffusion limitation is determined on the basis of the Weisz–Prater criterion, where the dimensionless Weisz–Prater parameter (C_{WP}) is calculated as follows:

$$C_{WP} = \frac{-r_{A.obs}\rho_c R_c^2}{D_{eff} C_A} \qquad \dots\dots(10)$$

The effective diffusivity (D_{eff}) can be expressed as:

$$D_{eff} = \xi_v^2 D_{lm} \qquad \dots\dots(11)$$

If $C_{WP} \ll\!\ll 1$ there are no internal diffusion limitations and no concentration gradient exists within the pellet, but if $C_{WP} \gg 1$ internal diffusion limits the reaction **, Fogler, 1999**. D_{eff} was calculated by applying finite difference approximation.

As listed in **Table 3**, the calculated Weisz–Prater parameters were less than 1, implying that the resistance to internal pore diffusion is sufficiently small and the internal diffusion can be negligible in the kinetic study.

6. RESULTS AND DISCUSSION

6.1 Effect of External and Internal Diffusions:

To study the kinetics of the esterification reaction, the effect of external and internal diffusion limitations should be eliminated.

It was found that values of the external diffusion and internal diffusion parameters are significantly less than 0.15 for external ($C_M \ll 0.15$) and one for internal ($C_{WP} \gg 1$). These results indicate that external and internal diffusion does not limit the reaction of acetic acid with tert-butanol over Dowex 50Wx8-400 for the reaction conditions implemented in this study. This is in agreement with the results obtained by **Ju, et al., 2011**.

The external diffusion limitation is negligible at stirrer speed of ≥ 200 rpm [1]. Therefore, a stirrer speed of 1000 rpm was maintained during all experiments to ensure that the measured reaction rate was free from external diffusion effects.

6.2 Effect of Temperature

In esterification reaction, the investigation on the effect of temperature is very important because this information is useful in calculating the activation energy. It was realized at different temperatures of 333, 348 and 358K under the constant reaction conditions: 1:1 mole ratio and the catalyst weight at 50 g. Results are given in **Fig. 2**. The reaction rate strongly depends on temperature. It can be seen that the reaction rate increases substantially with the increasing temperature. Moreover, the equilibrium conversion was nearly equal in the temperature range studied in this work. It shows that the higher temperature yields the greater conversion of t-butanol at a fixed contact time. This is in agreement with the results obtained by **Akbay and Altiokka 2011 and Ju, et al., 2011**.

6.3 Effect of catalyst amendment with HCl

In **Fig. 3** tert-butanol conversion was plotted by using Dowex-50 catalysts prepared with HCl while the other was Dowex-50 without amendment. From the **Fig.**, it can be concluded that this amendment with HCl catalyst has little effect on increasing the reaction rate and the reason for this is due to the activity of the resin catalyst used and a strong amendment with HCl has no significant effect on the increasing acidity of the catalyst. This is in agreement with the results obtained by **Bhorodwaj and Dutta, 2011**.

6.4 Effect of Catalyst Loading

The effect of catalyst loading on the conversion of tert-butanol and the initial reaction rates is represented in **Fig. 4**. Catalyst loading was varied from 25 g to 50 g at a temperature of 65 C, feed mole ratio of 1:1, and stirrer speed of 1000 rpm. It can be seen from **Fig. 4** that as the catalyst concentration increases, the reaction rate, conversion of acetic acid increases and thus the reaction time decreases. But the catalyst loading does not have any effect on the equilibrium conversion. This is in agreement with the results obtained by **Bhorodwaj and Dutta 2007**.

6.5 Effect of Initial Reactants Mole Ratio

The effect of acid to alcohol molar ratio was investigated by varying the acid to alcohol molar ratio (ranging from 1:3 to 3:1). As shown in **Fig. 5**, changing the molar ratio from 1:3 to 1:1 increases the conversion of the tert-butanol, and shows that the increasing of the molar ratio from 1:1 to 3:1 increases the conversion of the tert-butanol. **Fig. 5** shows that acid to alcohol molar ratio of 3:1 gives a higher conversion of the alcohol than 1:3. Moreover, a more significant increase in conversion was obtained at a ratio of 3:1 rather than 1:3. This is in agreement with the results obtained by **Ju, et al., 2011**.

7. REACTION KINETICS

Experimental reaction rate are fitted using a nonlinear regression method. Different values of the forward reaction rate constants K_f and equilibrium constant K_a are constructed and by applying Genetic Algorithm optimization method to predict the better constants that represent the minimum least square error between the experimental and predicted results.

$$K_f = K_f^0 exp\left(-E_f/RT\right) \qquad \ldots..(12)$$

$$K_f = 20.7654exp(3.68 \times 10^4/RT)$$

$$K_a = K_a^0 exp(-E_a/RT) \qquad \ldots..(13)$$

$$K_a = 1.5815exp(-1.09 \times 10^3/RT)$$

The activation energy of the esterification reaction is found to be (1.09 kJ/mol).

Figs. 6, 7, and 8 show that the model predictions for different operating conditions are compared with experimental data at temperatures 50 C, 65 C, and 80 C respectively. Depending on different initial condition and with the aid of 4th order (Rung-Kutta) integration method, the mathematical model was used to predict tert-butanol conversion respect with time can be predicted from **Eq. 1**. From these **Figs.**, it was concluded that the predicted kinetic model Correspond to a large degree with the experimental kinetics.

The lower line which is start from zero represents the experimental and model result for H_2O and tert-butel acetate concentration while the upper line is start from (0.5) mole fraction represent concentration of acetic acid and tert-butanol.

8. CONCLUSIONS

The reaction kinetic data have been determined experimentally for the esterification of acetic acid with tert-butanol over acidic ion exchange catalyst beads, Dowex 50Wx8, at temperatures from 50 C to 80 C, catalyst loading (25-50 gm), and the molar ratios of acetic acid to tert-butanol in the feed stream from 1 to3.The reaction rate was found to increase with increasing temperature, catalyst loading, and the conversion of the tert-butanol as the molar ratio of acid to alcohol increases from 1/3 – 3/1. Absence of resistance to external and internal diffusion was verified with theoretical criteria, the Mears ($C_M \ll 0.15$) and Weisz–Prater ($C_{WP} \ll 1$). The activation energy for the esterification reaction was estimated to be 1.09 kJ/mol. UNIFAC was used successfully to account for the non-ideal thermodynamic behavior of the reactants and the products.

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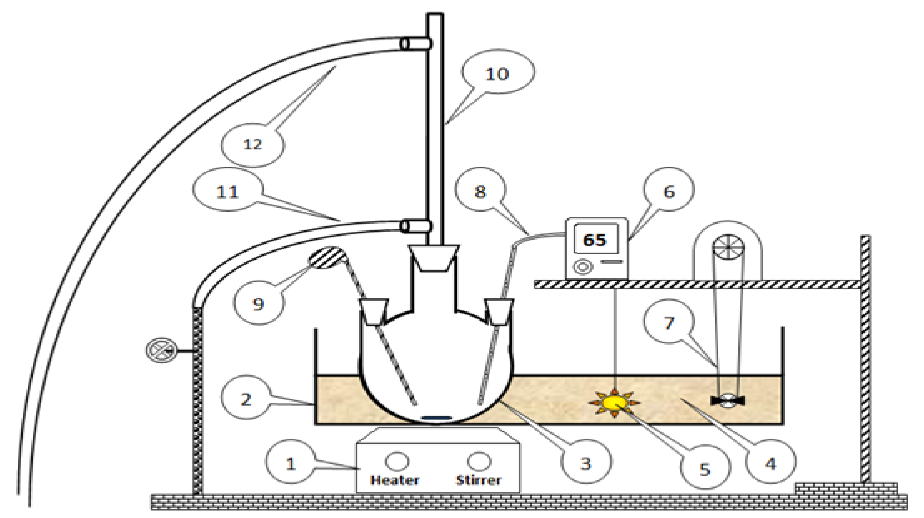
NOMENCLATURE

a_i	activity of component i
C_A	reactant concentration (mol/cm^3)
C_{ab}	bulk concentration (mol/cm^3)
C_i	concentration of component i (mol/cm^3)
C_{li}	bulk concentration of the limiting reactant (mol/cm^3)
C_M	mears parameter
C_{WP}	weisz–Prater parameter
D_{AB}	diffusivity of solute A (cm^2/s)
D_{Aj}	dilute binary diffusion coefficient of solute A in j (cm^2/s)

D_{Am}	dilute diffusion coefficient of solute A through the mixture (cm^2/s)
D_{eff}	effective diffusivity (cm^2/s)
D_{lm}	diffusivity of limiting reactant in the mixture (cm^2/s)
d_p	diameter of the catalyst particle (cm)
E_A	activation energy (J/mol)
g	gravitational acceleration (cm/s^2)
HAc	acetic acid
i	identifies species
j	dummy index running over all species
k	identifies subgroups
K_a	equilibrium constant (-)
K_a^0	preexponential factor for K_a(-)
k_C	mass transfer coefficient (cm/s)
K_f	forward reaction rate constant (mol/gm cat. hr)
K_f^0	preexponential factor for K_f(mol/gm cat.hr)
M	dummy index running over all subgroups
M.wt.	molecular Wight (g/mal)
m_H	molar holdup (mol) in equation (1)
M_{cat}	mass of the catalyst, gm.
n	reaction order
N_{Sc}	schmidt number
r	rate of reaction (mol/hr.gm catalyst)
$-r_{A,obs}$	observed reaction rate (mol/gcat s)
R_c	catalyst particle radius (cm)
r_i	relative molecular volume
R_k	relative volume
t	reaction time (s)
T	temperature (C)
TBuAc	tert-Butyl acetate
TBuOH	tert-Butanol
V	molar volume
W	water



1.	Heater & Magnetic stirrer	**2.**	Reaction Vessel
3.	QVF flask	**4.**	Paraffin Oil
5.	Heater	**6.**	Digital Temperature Control
7.	Mixing	**8.**	Thermocouple
9.	Absorbent	**10.**	Condenser
11	Water Inlet to Condenser	**12.**	Water Outlet from Condenser

Figure. 1 Schematic diagram of the experimental apparatus.

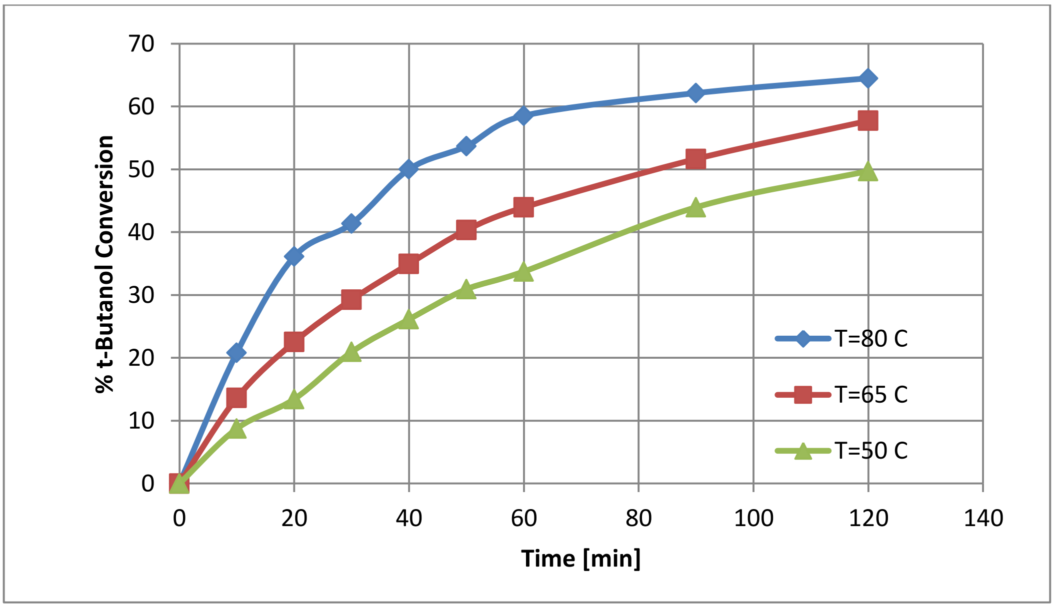


Figure. 2 Effect of temperature on t-butanol conversion (catalyst Dowex 50 modified with HCL, wt:50gm ,ACH:TBuOH=1:1).

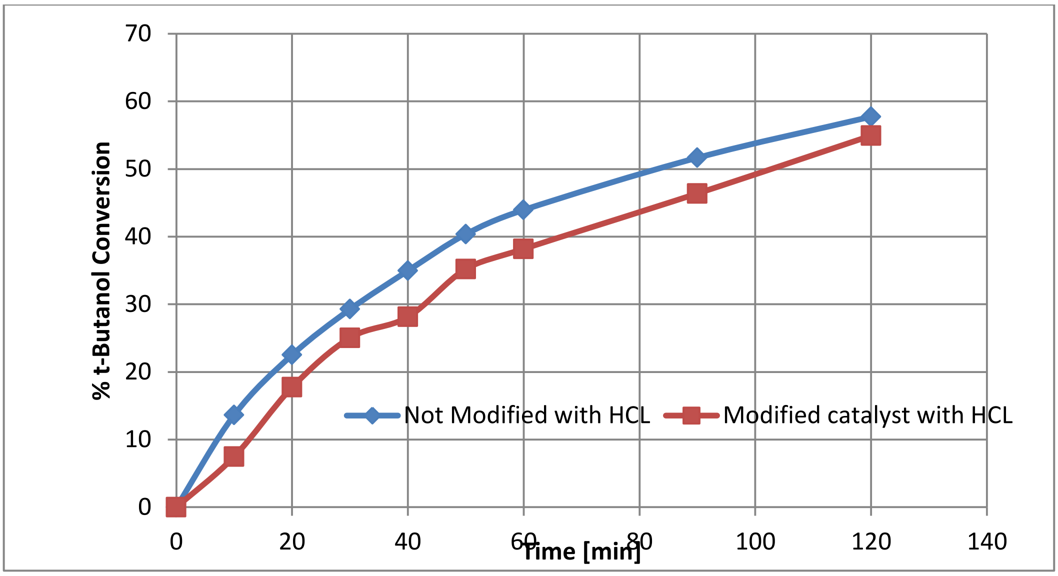


Figure. 3 Effect of catalyst modification on t-butanol conversion (catalyst dowex50 , wt:50gm,T=65 C ,HAc:TBuOH=1:1).

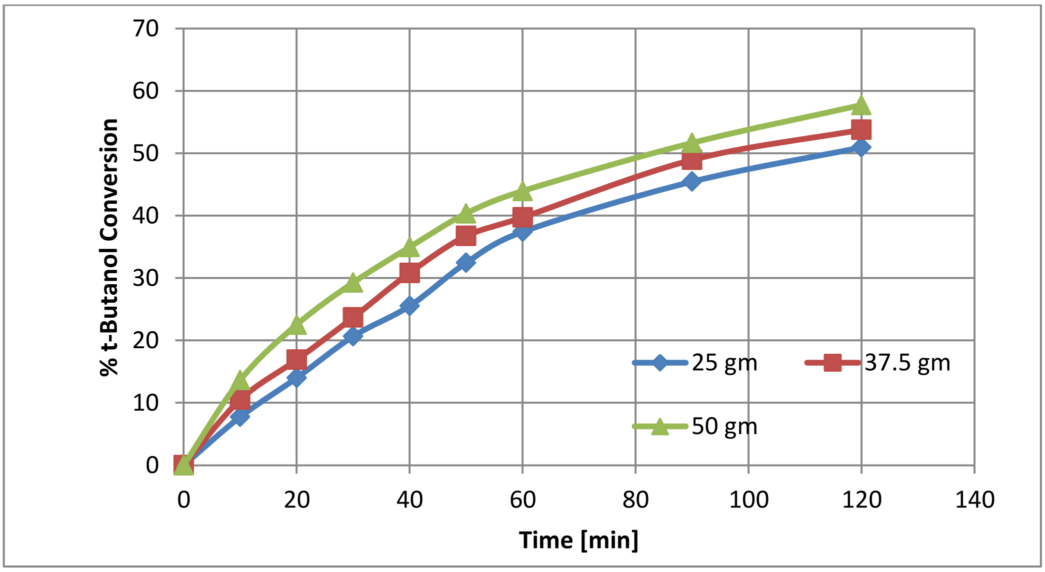


Figure. 4 Effect of catalyst weight on t-butanol conversion (catalyst Dowex 50 modified with HCL, T=65 C, HAc:TBuOH=1:1).

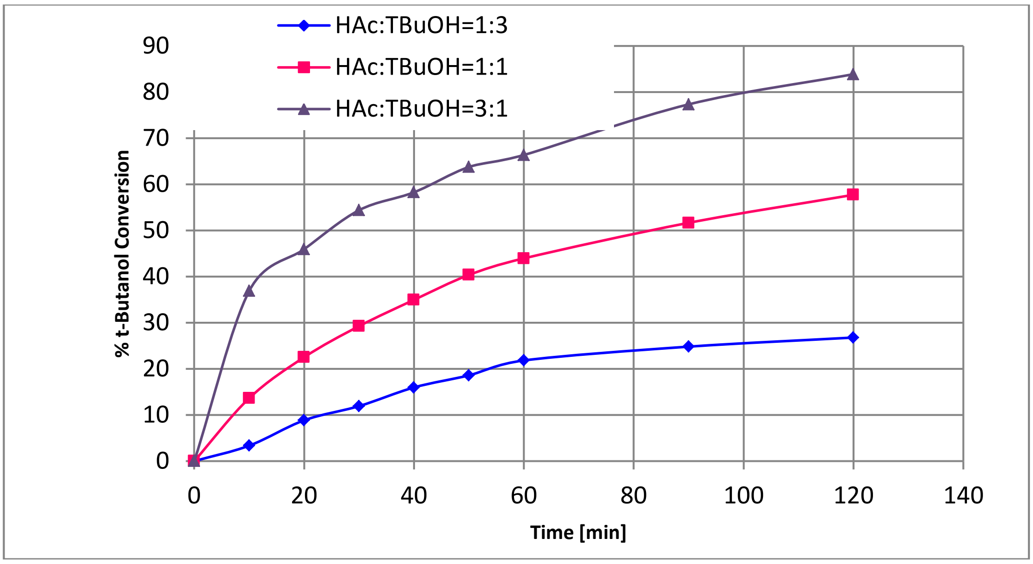


Figure. 5 Effect of feed mole ratio on t-butanol conversion (catalyst Dowex 50 modified with HCL, wt:50gm).

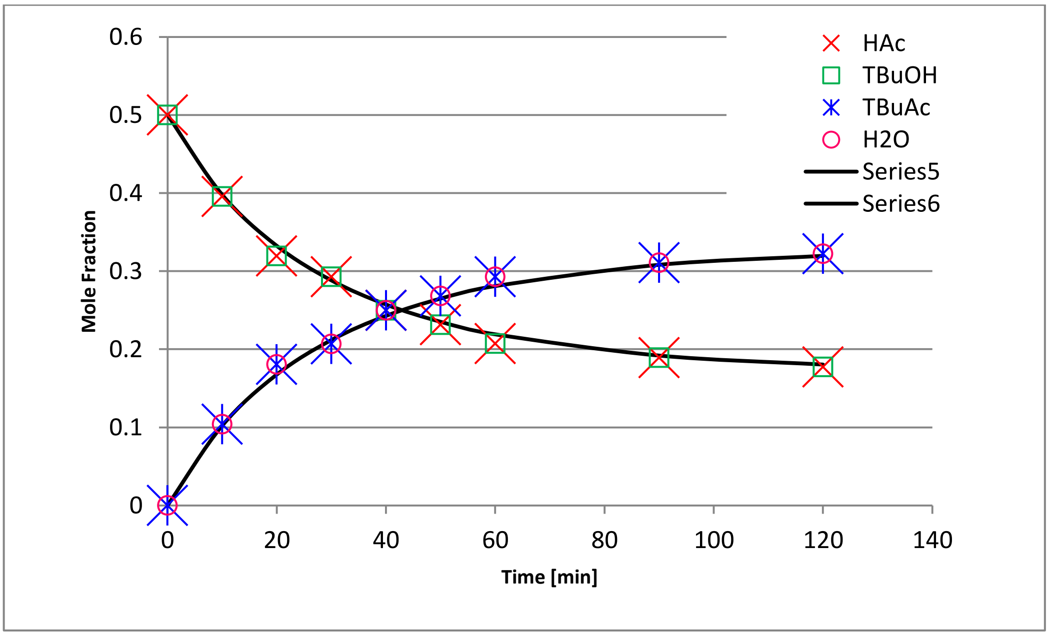


Figure. 6 Comparison between experimental data and rate equation results (catalyst Dowex 50 prepared with HCl, wt:50 gm, HAc:TBuOH=1:1, T=80 C), solid line represents rate equation results.

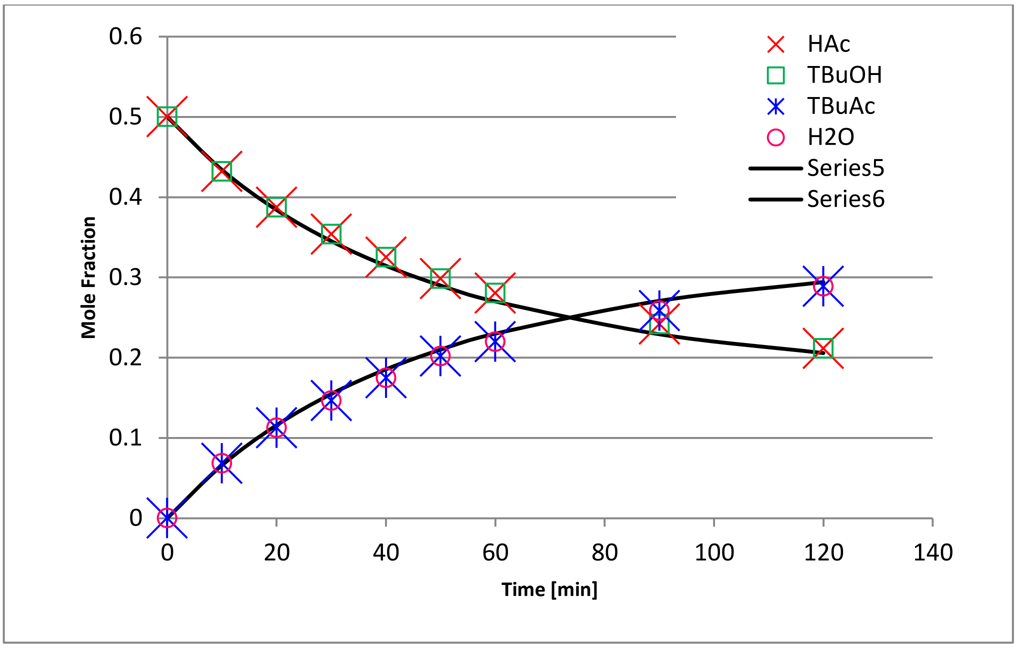


Figure. 7 Comparison between experimental data and rate equation results (catalyst Dowex 50 prepared with HCl, wt:50 gm, HAc:TBuOH=1:1, T=65 C), solid line represents rate equation results.

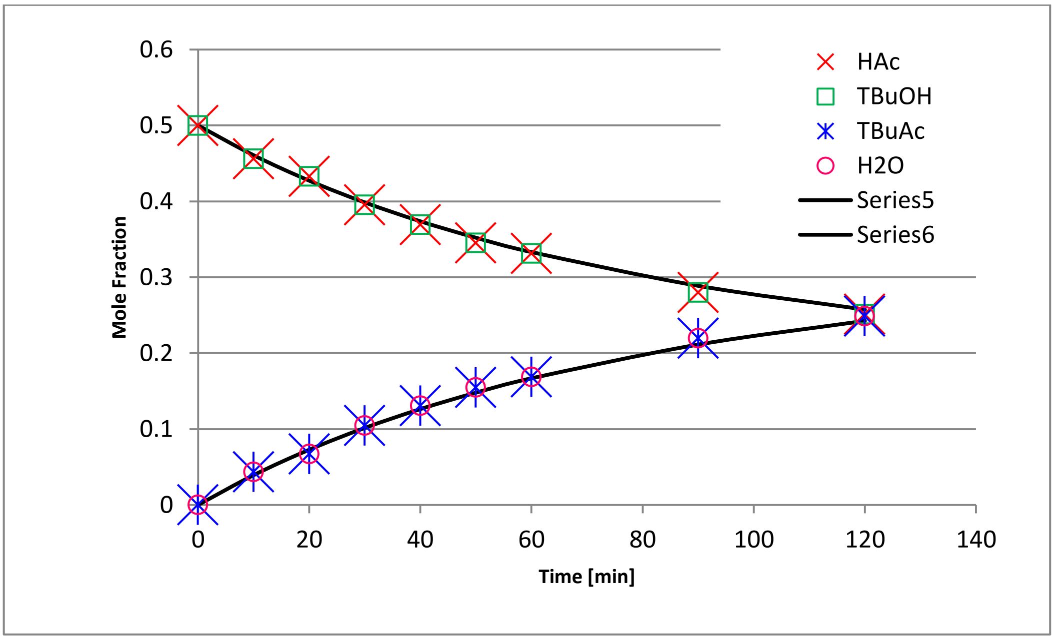


Figure. 8 Comparison between experimental data and rate equation results (catalyst Dowex 50 prepared with HCl, wt:50 gm, HAc:TBuOH=1:1, T=50 C), solid line represents rate equation results.

Table1. Reaction conditions**.**

Run	**Temperature (C)**	**Ratio of HAc:TBuOH**	**Catalyst loading (g/L)**	**amendment with HCl**
1	80	1:1	50	Yes
2	65	1:1	50	Yes
3	50	1:1	50	Yes
4	65	1:1	50	No
5	65	1:1	25	Yes
6	65	1:1	37.5	Yes
7	65	1:3	50	Yes
8	65	3:1	50	Yes

Table 2. The values of the various parameters for the UNIFAC model equations.

Component	**r**	**q**
Acetic acid	3.9243	3.668
tert-Butanol	2.6724	2.688
tert-Butyl acetate	5.3700	4.848
Water	0.92	1**.**
$a_{1,1}$=0	$a_{1,2}$=0	$a_{1,15}$=255.7
$a_{1,17}$=255.7	$a_{1,19}$=597	$a_{1,20}$=597
$a_{2,1}$=0	$a_{2,2}$=0	$a_{2,15}$=255.7
$a_{2,17}$=255.7	$a_{2,19}$=597	$a_{2,20}$=597
$a_{15,1}$=65.33	$a_{15,2}$=65.33	$a_{15,15}$=0
$a_{15,17}$=0	$a_{15,19}$=481.7	$a_{15,20}$=481.7
$a_{17,1}$=65.33	$a_{17,2}$=65.33	$a_{17,15}$=0
$a_{17,17}$=0	$a_{17,19}$=481.7	$a_{17,20}$=481.7
$a_{19,1}$=24.82	$a_{19,2}$=24.82	$a_{19,15}$=0
$a_{19,17}$=0	$a_{19,19}$=0	$a_{19,20}$=0
$a_{20,1}$=24.82	$a_{20,2}$=24.82	$a_{20,15}$=0
$a_{20,17}$=0	$a_{20,19}$=0	$a_{20,20}$=0

Table 3 The criteria for external and internal diffusion.

Run	**C_{li} at 30 min (mol/cm^3)**	**$r_{A.obs}$ at 30 min (mol/g$_{cat}$.sec)**	**Mears parameter**		**Weisz-prater parameter**	
			K_c (cm/sec)	**C_M**	**D_{eff} (cm^2/sec)**	**C_{WP}**
1	0.00386	6.85x10^{-8}	3.50x10^{-2}	3.90x10^{-6}	3.87x10^{-6}	1.93x10^{-4}
2	0.00466	3.39x10^{-6}	2.65x10^{-2}	2.90x10^{-4}	2.83x10^{-6}	1.10x10^{-2}
3	0.00521	3.03x10^{-6}	2.00x10^{-2}	2.22x10^{-4}	2.05x10^{-6}	1.20x10^{-2}
4	0.00494	4.53x10^{-6}	2.65x10^{-2}	2.65x10^{-4}	2.83x10^{-6}	1.40x10^{-2}
5	0.00523	5.66x10^{-6}	2.65x10^{-2}	3.12x10^{-4}	2.83x10^{-6}	1.60x10^{-2}
6	0.00503	4.89x10^{-6}	2.65x10^{-2}	2.80x10^{-4}	2.83x10^{-6}	1.45x10^{-2}
7	0.00846	6.39x10^{-6}	2.50x10^{-2}	2.31x10^{-4}	2.56x10^{-6}	1.24x10^{-2}
8	0.00171	1.69x10^{-6}	2.43x10^{-2}	3.11x10^{-4}	3.26x10^{-6}	1.27x10^{-2}