Reaction Kinetics of Acetic Acid and n-Butanol Esterification Catalyzed by Dowex 50 Catalyst

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Abstract

The reaction kinetics of the n-butanol esterification and acetic acid on acidic solid catalyst named Dowex 50 under atmospheric pressure was investagated in this work.

Reaction experiments were carried out in a stirred batch reactor at temperature range of 343 to 363 K, under various catalyst loads and various starting reactants feed ratios. The experimental data were fitted to estimate the kinetic parameters for reaction mechanisms by using MATLAB 7 software. The chemical equilibrium composition was measured and kinetic information was obtained at the same temperature range. The results show that the activation energy of n-butanol esterification reaction was found to be 39.975 kJ/mol.

Finally the results of produced reaction mechanisms were compared with experimental results to validate the reaction mechanism. Then it was conclud that the model results with the regressed kinetic parameters are in excellent agreement with the experimental results.

Keywords: Esterification, Heterogenous catalyst, n-butyl acetate, Reaction kinetic.

دراسة ميكانيكية تفاعل استرة حامض الخليك مع كحول البيوتانول باستخدام Dowex-50 كعامل مساعد
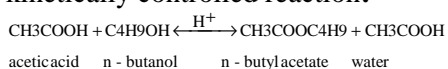
الخلاصة

في هذا البحث تمت دراسة ميكانيكية تفاعل الاسترة لحامض الخليك مع كحول البيوتانول باستخدام عامل مساعد صلب من نوع ديواكس 50.

تم اجراء التجارب العملية بمفاعل الوجبة في مدى واسع من الظروف التشغيلية. حيث كانت درجة الحرارة ضمن مدى 363-343 كلفن وكميات مختلفة من العامل المساعد ونسبة مولية مختلفة للمواد المتفاعلة وهي 0.5 و 1 و 2.

تم حساب الثوابت الخاصـــة للميكانيكيـة المقترحـة بالاعتمـاد علـى النتـائج العمليـة باستخدام برنـامج ماتلاب-7 . حيث تم حساب ثابت توازن التفاعل في نفس المدى من درجات الحرارة حيث كانت قيمتـه 39,975 كيلـو جـول\مـول. فـي النهايـة قورنـت النتـائج العمليـة مـع نتـائج المحاكـاة بالاعتمـاد علـى الميكانيكية المقترحة ولوحظ ان هنالك تطابق مذهل بين النتائج العملية والنظرية.

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Introduction

Esterification reaction is one of the most important industrial reactions. Esters are widely used in chemical industry such as a solvent for plastics, liquors, resins, gums, and coatings. Butyl acetate is commonly synthesized through esterification of acetic acid with n-butanol in the presence of a suitable acid catalyst by reversible and kinetically controlled reaction:

$$CH3COOH + C4H9OH \xleftrightarrow{H^+} CH3COOC4H9 + CH3COOH$$
$$\text{aceticacid} \quad \text{n - butanol} \quad \text{n - butylacetate} \quad \text{water}$$

Several works have reported the kinetics of the esterification reaction in the presence of ion exchange resin. Janowsky et al. (1997) studied the kinetics in the presence of Lewatit SPC 108 and 118 catalysts and proposed a pseudohomogeneous (PH) kinetic model for the esterification reaction. They proposed the expression to represent the following equilibrium constant.

$$Ka = 3.8207 \exp(3581.7 RT) \qquad (1)$$

Li et al. (1998) studied various types of zeolites, such as HX, HY, HM, and HZSM5, for esterification of butanol with acetic acid and found that HZSM5 acts as the best catalyst from all zeolites studied.

Zheng and Zeng (1997 and 2003) studied the kinetics of esterification in the presence of a strong cation-exchange resin. They investigated the influence of various parameters on reaction rate and proposed the rate equation.

Hanika et al. (1999) studied the esterification of butyl alcohol with acetic acid in a pilot plant reactive distillation column packed with commercial catalysts (KATPAK and CY). They found that butylacetate could be recovered in very high purity. On the other hand, the experimental

values of the equilibrium constant are reported by Loning et al. (2000).

Saha, et al. (2000) developed conventional methods of recovery of 30% acetic acid by reaction with n-butanol and isoamyl alcohol in a reactive distillation column using macroporous ion-exchange resin (Indion 30) as a catalyst bed. They found that recovery of acetic acid is enhanced by reactive distillation compared to the batch operation.

Gangadwala et al. (2003) studied the esterification of acetic acid with n-butanol in the presence of Amberlyst-15. They investigated the influence of various parameters such as temperature, mole ratio, catalyst loading, and particle size and they proposed the rate equation model.

Altiokka and Citak (2003) studied the kinetics of homogeneous and ion exchange resin (IR-120) catalyzed for esterification of acetic acid with butanol. They reported that presence of resin catalyst reduces the activation energy from 59.3 to 49 kJ/mol.

Blagova et al. (2006) studied the synthesis of n-butyl acetate by comparing three ion-exchange resin catalysts (Purolite CT 269, Amberlyst 46, and Amberlyst 48).

Bozek and Gmehling (2006) investigated the reaction kinetics and chemical equilibrium of transesterification of methyl acetate and *n*-butanol to *n*-butyl acetate and methanol in the temperature range of 313.15 to 330.15 K using acidic ion-exchange resin, Amberlyst 15. They studied the influence of the catalyst loading, initial reactant molar ratio, and temperature on the kinetics. They used two kinetic models, pseudohomogeneous (PH) and Langmuir-Hinshelwood (LH) to

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describe the reaction rate. They found that the chemical equilibrium constant obtained from kinetic experiments is in qualitative agreement with the calculated standard thermodynamic properties.

Izci et al (2009) studied the kinetics of esterification of acetic acid with isobutanol using Amberlite IR-122. Experiments were carried out in a stirred batch reactor at different temperatures (323 to 348 K) under atmospheric pressure. They found the equilibrium constant is equal to 4 in the temperature range. The possible mechanism of reaction is mathematically treated using the theories of the Eley-Rideal model. The reaction rate constants and the adsorption coefficients for isobutanol and water were determined from the experimental data at the same temperature intervals.

It was noted that, most of the previous studies performed in the literature have focused on the modification of catalysts and only a rather limited number of papers have focused on studying the influence of reaction conditions and the type of catalysts on the activity and selectivity. On the other hand, few studies were focused on production of butyl acetate [10–13]. Therefore, the main objectives of the present work are:

1-Provide the needed fundamental understanding of the reaction kinetics of esterfication of acetic aced and n-butyl alcohol through preparation and modification of more active, selective and stable catalysts for the reactionl.

2- Modify a kinetic model to describe the esterification reaction.

3-Compare the experimental results with model results to predict the validaty of the model.

Experimental Part

Apparatus

Figures (1) represent the schematic diagram of the experimental set-up.

Materials:

a) Chemicals:

The chemicals were of analytical grade (99%). Acetic acid was manufactured by Rioel-de Haën chemicals (Germany), n-butanol was manufactured by Gainland Chemical Company (U.K).

b) Catalyst:

Two types of catalysts (cation resins) were used in the present work, Dowex 50WX8, of size (16-40 mesh), supplied by Fluka, which is a strong acid ion-exchange resin, and Amberlite CG 50, of size (100-200 mesh) supplied by Hopkin & Williams

c) Catalysts preparation

Two types of catalysts were prepared by treatment with (1N) HCl to increase acidity of catalyst. Each 100 gm of catalyst was stirred for 3 hrs with 500 ml hydrochloric acid solution (1N) at 298 K. The prepared catalyst was filtered and washed several times with distilled water to remove of chloride ions. Then, the prepared catalyst was dried at 333.15 K for 6 hours.

Therefore, actually four types of catalysts were used in the present study (two original types and two prepared types).

The operating condition of the present study is given in Table 1.

Analysis

All samples analyzed by gas chromatograph (type Shimadzu GC, Model 2014) with a flame ionization

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detector (FID) with the follwing specification:

- N_2 as carrier gas at 50.0 KPa.
- Column length 30 m, Inner diameter 0.35 mm.
- Split ratio 50.
- Temperature program 383 K hold for 1 min, heat at 10 K/min to 413 K, hold for 1 min).

Parameter Identification

The kinetic model for the esterification reaction was developed using the obtained experimental data. The reaction kinetic model has the following form [11]:

$$r_j = m\frac{dx_j}{dt}$$

$$= \delta_j M_{cat} K_f (a_{HAc} a_{BuOH} - \frac{1}{Ka} a_{BuAc} a_{H_2O})$$

$$a_i = x_i \gamma_i$$

(2)

Where,

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

$$-r_i = \frac{\Delta C_i}{\Delta t} = C_{i,o}\frac{\Delta x_i}{\Delta t}$$

(3)

Experimental reaction rate data was fitted using a nonlinear regression method to predict the parameters of the reaction rate. For each reaction eight data points were used to calculate the parameters. All deviations between experimental and calculated values are squared and summed up to form an objective function F:

F = Σ (exp. conc. – calc. conc.)^2 (4)

The effect of temperature on reaction rate constants K is modeled using Arrhenius expression. The activation energy (E_A) of the reaction is calculated from two

measuring points at different temperatures [11]:

$$K = K_0 .\exp\left[-\frac{E_A}{R.T}\right]$$

(5)

The simulation result was compared with experimental results at each measured point. The UNIQUAC model was used to determine the activity coefficients in the liquid phase while the vapor phase was assumed ideal. This model distinguishes two contributions termed combinatorial Co and residual Rs. Table (2) contains the main equations of UNIQUAC model, while Table (3) contains the values of the various parameters for the UNIQUAC model equations.

Results and Discussion
Effect of Temperature

In Figure (2) the results of experiments 1, 2 and 3 are plotted, this figure represents the n-butanol conversion at three different temperatures (343, 353 and 363 K^o). According to this figure, the reaction rate is directly propertinal to the reaction temperature.

From these experiments with the aid of Matlab programs the forward reaction rate constants K_f and equilibrium constant K_a are constructed at different temperatures. The reaction rate constant increase directly with temperature increase. The Arrhenius equation was used to determine the apparent activation energy for forward reaction rate constant and equilibrium constant.

Effect of catalyst modification with HCl

In Figure (3) n-butanol conversion was plotted using two catalysts, the first one is Dowex-50

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catalyst prepared with HCl while the other was Dowex-50 without modification. It is clear from this figure that the catalyst modification with HCl a small effect on increasing the reaction rate and this result is due to the fact that the used catalyst is already strong acidic resin and modicication with HCl has a does not effect on the increasing the acidity of the catalyst.

In Figure (5) the n-butanol conversion is plotted using two catalysts, the first one is Amberlite CG catalyst prepared with HCl while the other is Amberlite CG without modification. In this figure, the catalyst modification with HCl decreases the reaction rate.

From the comparing of Figures (3) and (5), it is clear that the prepared Dowex-50 gives a better total conversion of n-butanol around 67 % while using Amberlite CG gives lower total conversion than Dowex-50 which is around 27.5 %.

Effect of Catalyst Loading and Size

The results of experiments (1, 5 and 6) are plotted in Figure (4), which represents the n-butanol conversion at various catalysts loading (24, 12 and 36 gm) respectively. It is clear from this figure that increasing the amount of catalyst loading will increase the reaction rate but does not have a significant effect on final n-butanol conversion.

Effect of Feed Ratio

The results of experiments (1, 9 and 10) are plotted in Figure (6), which contains the n-butanol conversion at various acetic acid to n-butanol feed ratos (1/1, 1/2 and 2/1) respectively. It is clear from this figure that using 100% excess amont of acetic acid will increase the n-

butanol conversion from 67 % to 86 %, while using 100% excess amount of n-butanol leads to decrease n-butanol conversion from 67 % to 40 %. Such as must of revesie reactants, the equilibrium conversion of n-butanol increases with increasing molar ratio of *n*-butanol to acetic acid.

Reaction Kinetics

Experimental reaction rate data for the experiments (1 ,2 ,3 ,4 ,5 ,6, 9, 10) are fitted using a nonlinear regression method. Different values of the forward reaction rate constants K_f and and equilibrium constant K_a are constructed and by applying the Arrhenius equation to the values obtained from experiments, the temperature dependency of the constants is found to be:

$$K_f = K_{fo} \exp(-E_f / RT)$$

$$= 8.824 \times 10^7 \times \exp(-52961 / RT)$$

$$K_a = K_{ao} \exp(-E_a / RT)$$

$$= 2.8 \times 10^{-5} \exp(-39975 / RT)$$

The activation energy of the esterification reaction is found to be 39.975 kJ/mol

By applying the predicted values of forward reaction rate constants K_f and equilibrium constant K_a to reaction rate equation 1, the model predictions for different operating conditions are compared with experimental data and the results are plotted in Figures (7), (8) and (9) for temperatures 363, 353 and 343 respectively. Using numerical integration (Runga-Kutta), n-butanol conversion at a given time can be predicted from Equation (1). The solid lines in Figures (7), (8) and (9) give the prediction of reaction conversion. Thus, the experimental

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results are compared with the results calculated from the model prediction. It was concluded from these three figures that the predicted kinetic model has amazing representation of n-butanol esterification with acetic acid on Dowex-50 catalyst.

Conclusions

The esterification of acetic acid with n-butanol to produce n-butyl acetate was carried out successfully using ion-exchange resin catalysts Dowex-50. The effect of various parameters such as temperature, catalyst loading and feed mole ratio on reaction kinetic parameters was studied. The best esterfication temperature which gives the highest n-butanol conversion is 90 C°.

From the experimental results a kintic model is developed for the heterogeneous reactions. From the temperature dependence of the rate constants, the values of activation energies for heterogeneous forward and backward reactions are found to be 52.9 and 39.975 kJ/mol respectively. It is noted that the model results with the regressed kinetic parameters are in excellent agreement with the experimental results.

Finally, the developed model could be used to determine the rate constants of any complex reaction at any operating conditions.

Notation

a_i : Activity of the ith component (-)
E_a: Activation energy for the equilibrium constant (J/mol)
E_f: Activation energy for the forward rate constant (J/mol)
K_a: Equilibrium constant (-)
K_f: Forward reaction rate constant (mol/gm cat. hr)
K_{a0}: Preexponential factor for K_a (-)

K_{f0}: Preexponential factor for K_f (mol/gm cat.hr)
C: Number of components (-)
C_i: Concentration of ith components (mol/m^3)
r:Rate of reaction (mol/hr.gm catalyst)
R: Gas law constant (8.314 J/mol·K)
t: Time (hr)
M: Molar holdup (mol)
M_{cat}: Mass of the catalyst, gm.
T: Temperature (K)
x_i: Liquid phase mole fraction of component i

Greek Letters

γ_i: Liquid activity coefficient of component i
φ_i^v: Vapor phase fugacity coefficient of component i
δi: Stoichiometric coefficient of ith component

List of Abbreviations

HAc: Acetic acid
BuAc: n-Butyl acetate
BuOH: n-Butanol
W: Water

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Table (1) Set of experiments

Catalyst type	Prepared with HCl	T(°C)	Feed Ratio	Catalyst weight (gm)	Initial molar holdup (mol)
Dowex-50	yes	90	1/1	24	5
Dowex-50	yes	80	1/1	24	5
Dowex-50	yes	70	1/1	24	5
Dowex-50	No	90	1/1	24	5
Dowex-50	yes	90	1/1	12	5
Dowex-50	yes	90	1/1	36	5
AmberliteCG	yes	90	1/1	24	5
AmberliteCG	No	90	1/1	24	5
Dowex-50	yes	90	1/2	24	7.5
Dowex-50	yes	90	2/1	24	3.75

Table (2) UNIQUAC model equations (Kathel and Amiya (2010)).

$$\ln \gamma_i = \ln \gamma_i^{Co} + \ln \gamma_i^{Rs}$$

$$\ln \gamma_i^{Co} = \ln \frac{\dot\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\dot\phi_i} + l_i - \frac{\dot\phi_i}{x_i} \sum_{j=1}^{c} x_j l_j$$

$$\ln \gamma_i^{Rs} = -q_i \ln \left(\sum_{j=1}^{c} \theta_i \tau_{ji} \right) + q_i - q_i \sum_{j=1}^{c} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{c} \theta_k \tau_{kj}}$$

$$\tau_{ij} = \exp \left(-\frac{u_{ji} - u_{ii}}{RT} \right)$$

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^{c} r_j x_j}$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{c} q_j x_j}$$

$$l_j = (\frac{z}{2})(r_i - q_j) - (r_j - 1) \text{ and } z = 10$$

Table (3) Binary interaction parameters for the UNIQUAC model (Kathel and Amiya (2010)).   (cal/mol)

Component		r	q
Acetic acid		2.2024	2.072
n-Butanol		3.4543	3.052
n-Butyl acetate		4.8274	4.196
Water		0.92	1.4
A11=0	A12=-131.7686	A13=-298.4344	A14=-343.593
A21=148.2833	A22=0	A23=82.5336	A24=68.0083
A31=712.2349	A32=24.6386	A33=0	A34=685.71
A41=527.9296	A42=581.1471	A43=461.4747	A44=0

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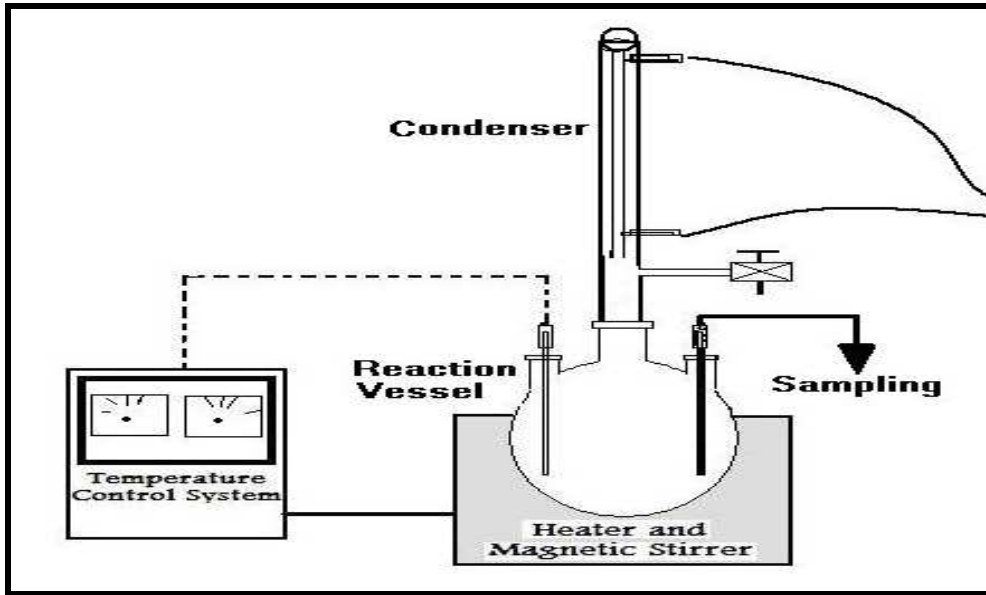n- Butanol Esterification Catalyzed
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Figure (1) Schematic diagram of the experimental apparatus.

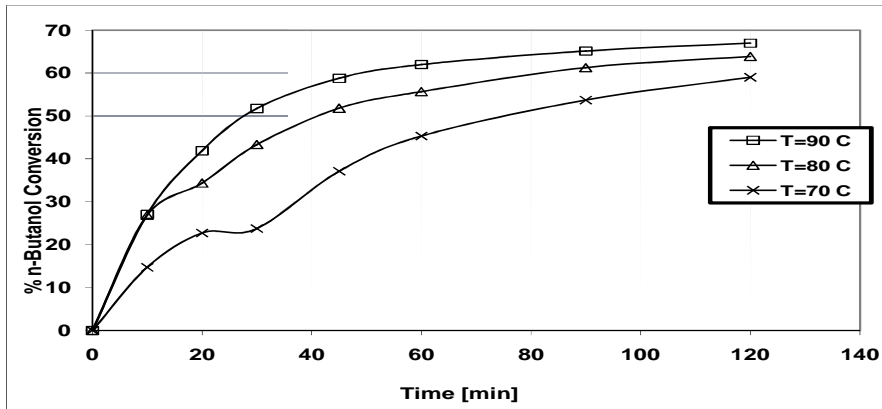**Figure (2) Effect of temperature on n-butanol conversion (catalyst
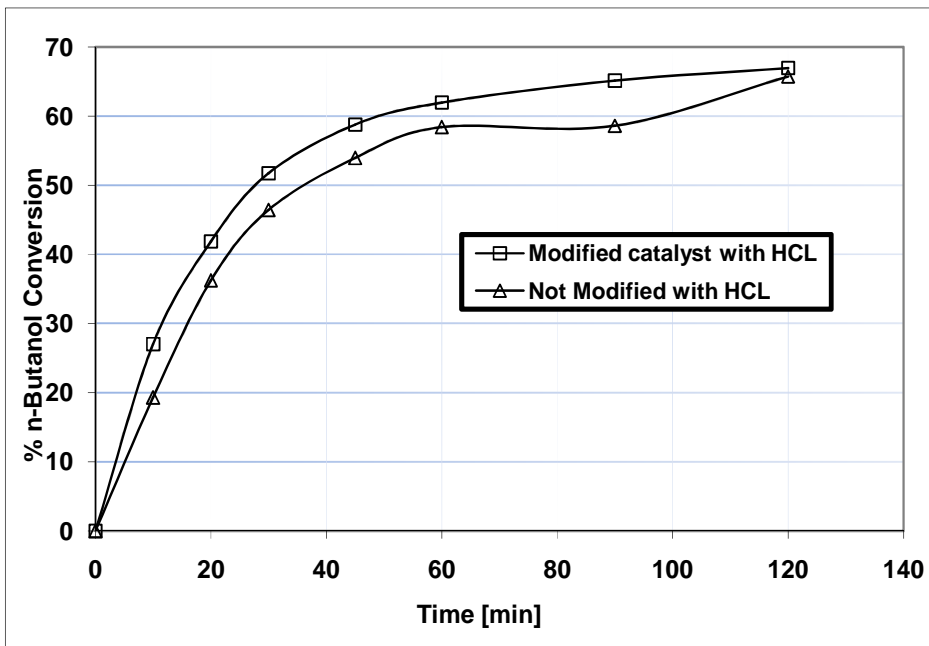Dowex 50 prepared with HCl, wt:24gm ,ACH:BuOH=1:1).**

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Figure (3) Effect of Catalyst Modification on n-butanol conversion (catalyst Dowex 50, wt:24 gm,T=90 C ,HAc:BuOH=1:1).
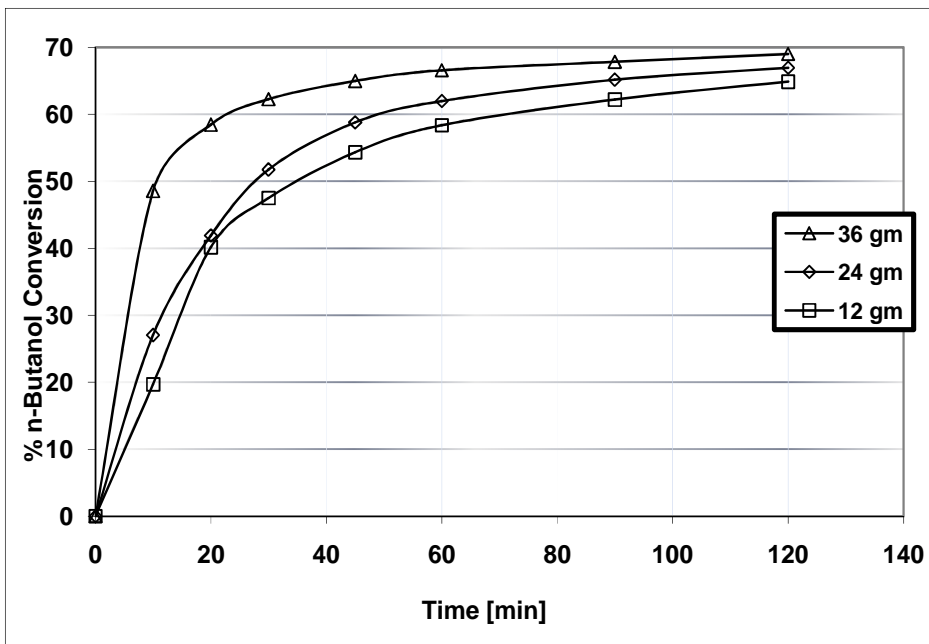
Figure (4) Effect of catalyst weight on n-butanol conversion (catalyst Dowex 50 prepared with HCl, T=90 C ,HAc:BuOH=1:1).
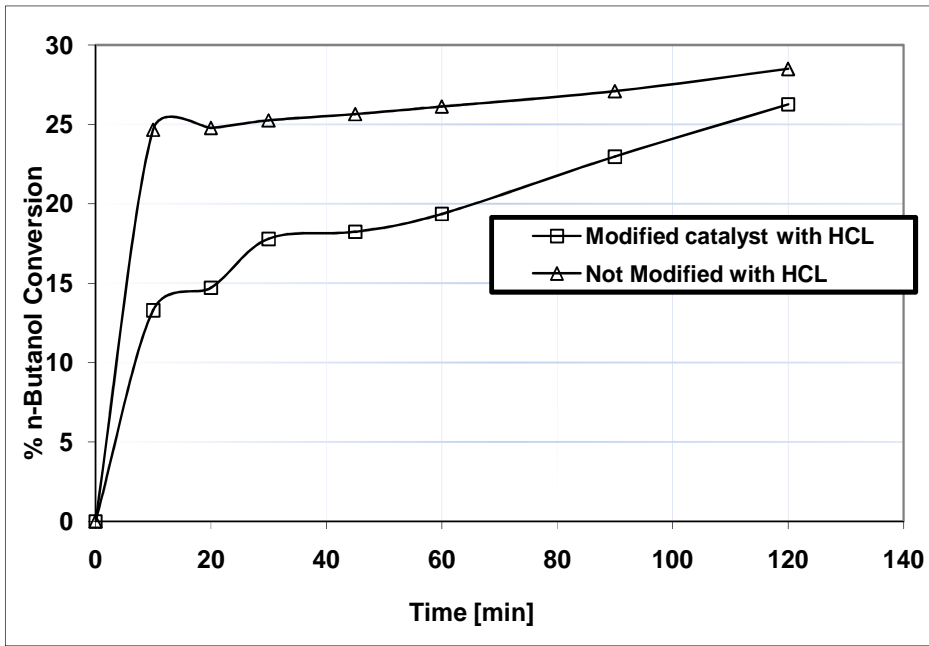
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**Figure (5) Effect of catalyst Modification on n-butanol conversion
(catalyst AmberliteCG , wt:24gm,T=90 C ,HAc:BuOH=1:1).**

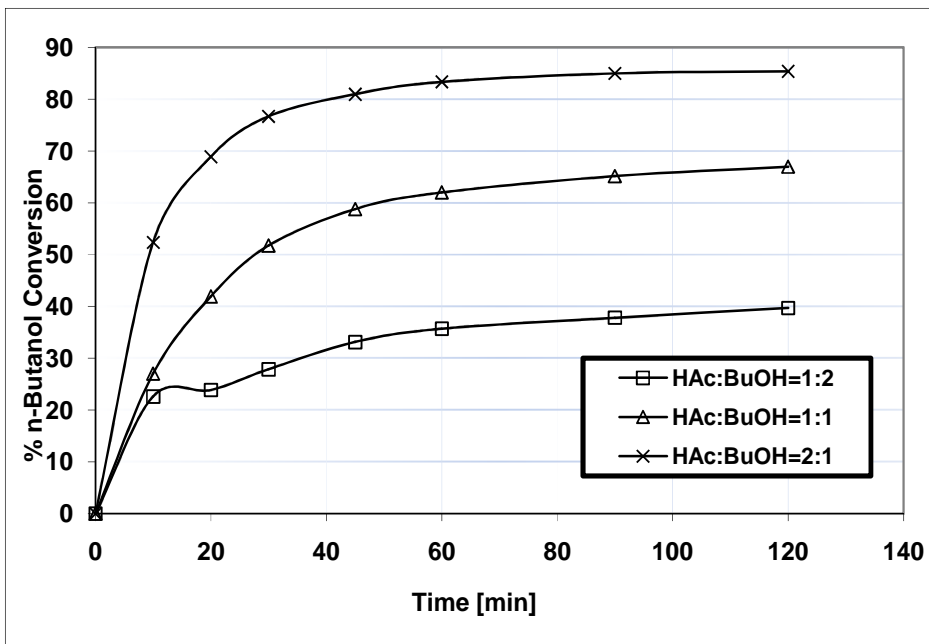**Figure (6) Effect of feed mole ratio on n-butanol conversion
(catalyst Dowex 50 prepared with HCL, wt:24gm).**

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Reaction Kinetics of Acetic Acid and
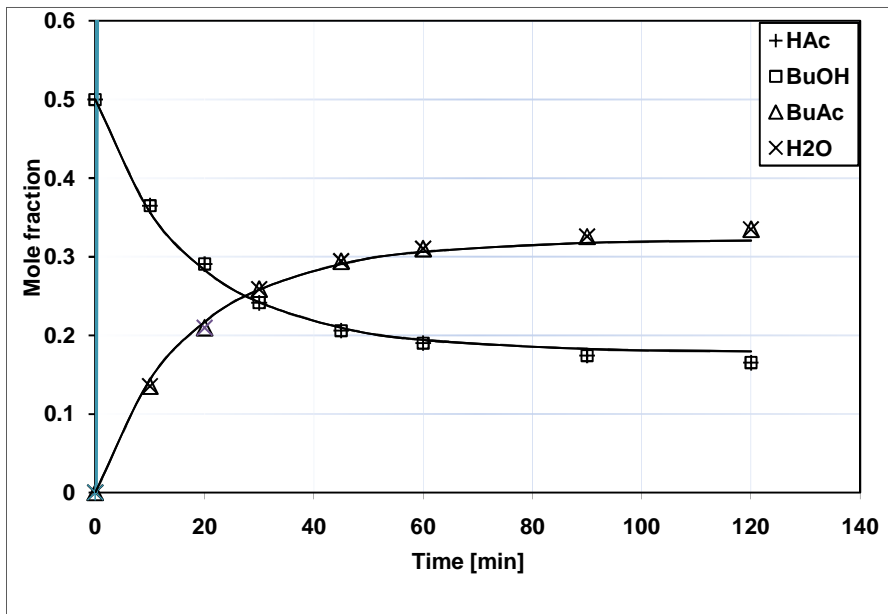n- Butanol Esterification Catalyzed
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**Figure (7) Comparison between experimental data and rate equation results
(catalyst Dowex 50 prepared with HCl, wt:24 gm ,ACH:BuOH=1:1, T=90 C),
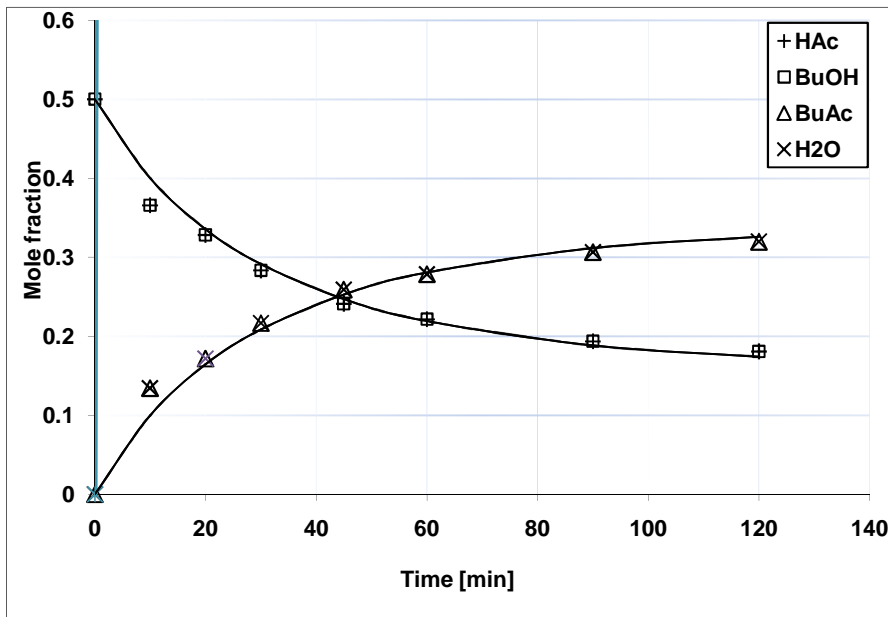solid line represents rate equation results.**

**Figure (8) Comparsion between experimental data and rate equation results
(catalyst Dowex 50 prepared with HCl, wt:24 gm, ACH:BuOH=1:1, T=80 C),
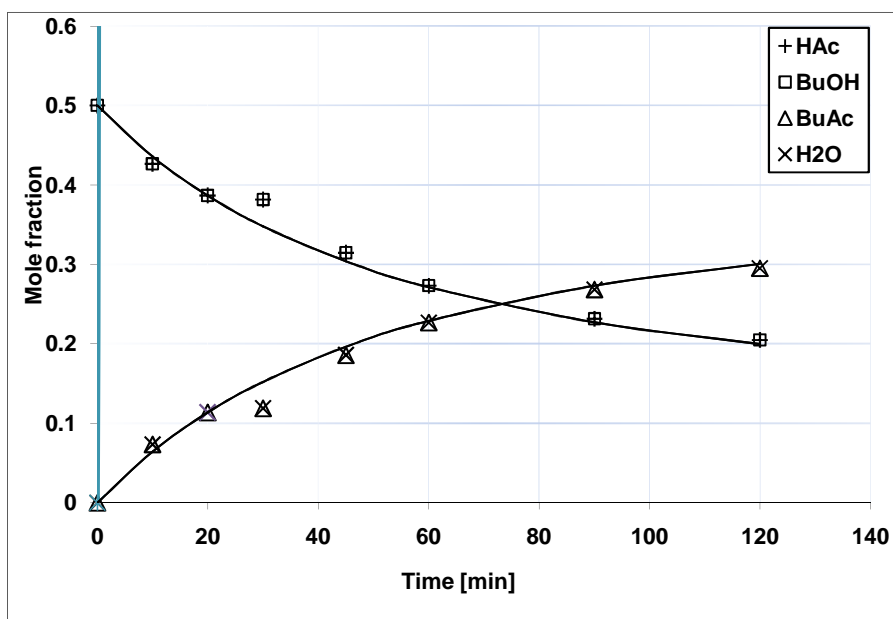Solid line represents rate equation results.**

Figure (9) Comparsion between experimental with rate equation results (catalyst Dowex 50 prepared with HCL, wt:24 gm, ACH:BuOH=1:1, T=70 C), solid line represents rate equation results.