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A Review on Kinetics Esterification of Ethylene Glycol with Acetic acid by using Cation exchange resin catalyst

Manisha S. Gonate, Kandarp.H.Trivedi, SnehaJadhav, Jyoti Bharadwaj.
Department of Chemical Engineering.
Shivajirao.S.Jondhale College of Engineering. Dombivli (E).
Mumbai :- 421204, Maharashtra, India

ABSTRACT :-
The esterification of ethylene glycol with acetic acid was investigated in a batch reactor in presence of a strongly acidic cation exchange resin, seralite SRC-120, as catalyst in the temperature range of 333 to 363 K.Further, two different kinetic models, empirical and kinetic model based on Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach, were developed to correlate the experimental concentration versus time data.
The kinetic parameters of the developed models were then estimated at different temperatures using non-linear regression technique based on modified Levenberg-Marquardt algorithm. The calculated results based on the estimated kinetic and equilibrium constants at different temperatures were then compared with the experimental values and LHHW-based model was found to fit the experimental data reasonably better compared to empirical kinetic model. The estimated rate constants at different temperatures of LHHW-based model were then used to estimate the activation energy and frequency factor of the rate constants

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I.   Introduction :-

The growing international energy crisis coupled with rising oil prices and increasing awareness of the environment and pollution has intensified the research on renewable fuels derived from biomass. The bio-oil produced by the process of biomass pyrolysis is nowadays an emerging technology for the production of renewable fuels and value-added chemicals. The bio-oil was first separated into aqueous and non-aqueous fractions by the addition of water. The aqueous fraction of bio-oils containing sugars, anhydrosugars, acetic acid, hydroxyacetone, furfural, and small amounts of guaiacols is a potential source of alkanes (ranging from C1 to C6) and polyols (ethylene glycol, 1,2-propanediol, 1,4-butanediol etc.).

The esterification process is widely used in industry to produce esters for a wide range of applications such as plasticizers, solvent, perfumery, flavor chemicals, precursors for pharmaceuticals, agrochemicals, and other fine chemicals.[3–4] In recent times, several esterification reactions with different alcohols and carboxylic acids have been reported in open literature using different types of solid acid catalysts such as zeolites (HB, HY, ZSM-5) and cation exchange resin (Amberlyst 15, Amberlyst 36, Amberlite IRA-120).[5–11]

The study of esterification of ethylene glycol with acetic acid is however limited in open literature.[18] Schmid studied the reaction using acidic cation-exchange resin, Amberlyst 36, as catalyst, and pseudo-homogeneous kinetic model based on activity was then developed using the measured thermodynamic properties of ethylene glycol–acetic acid reactive system.

It has been wide applications in plasticizers, solvents, perfumery also used as flavoring agents and preservative in the food industry chemicals and as precursors to a gamut of pharmaceuticals, agrochemicals, and other fine chemicals. Ethylene glycol mono and di-acetate are major product of esterification of ethylene glycol with acetic acid and they have widely used as an engine coolant and antifreeze. Due to its low freezing point, it has also been used as a deicing fluid for windshields and jet engines. The antifreeze capabilities of ethylene glycol derivatives have made it's an important component of vitrification mixtures for low-temperature preservation of biological tissues and organs. Minor uses of ethylene glycol include the manufacture of capacitors and as a chemical intermediate in the manufacture of 1, 4-dioxane.

Experimental:-
Chemicals used:-
Ethylene glycol & acetic acid of 99% purity. The strongly acidic cation ion exchange catalyst that is seralite(SARC – 120). Mesh number 20-50, pH range is 0-14 was procured from laboratories.

Industrial Chemical process available:-
Divided into 4 sections:-
1)   Isomerisation :-In chemistry isomerisation is the process by which one molecule is transformed into another molecule which has exactly the same atoms, but the atoms are rearranged. In some molecules and under some conditions, isomerisation occurs spontaneously. Many isomers are equal or roughly equal in bond energy, and so exist in roughly equal amounts, provided that they can 2 interconvert relatively freely, that is the energy barrier between the two isomers is not too high. When the isomerisation occurs intramolecularly it is considered a rearrangement reaction an intramolecular isomerization that involves the breaking or making of bonds is a special case of a molecular rearrangement [2].

2)   Dehydration :-Dehydration is defined as an excessive loss of body fluid. It is literally the removal of water from reaction system which forms during reaction process. In the case of ethylene glycol and acetic acid reaction system the dehydration play vital role because during reaction excess water has been losses [3].

3)   Etherification :-Etherification of glycol is defined acid catalyzed reaction with formation of mono-, di- and trialkyl glycol ethers. Since etherification reactions are carried out in the liquid phase, reaction becomes slightly slow without catalyst. Etherification of ethylene and propylene glycols with isobutylene was carried out in the presence of cation exchange resin catalysts. In the case of ethylene glycol, the mixture of mono- and di-ethers of corresponding glycol is obtained. The mono-ether of ethylene glycol has good miscibility with water and is used for coating solvents and as a solvent for paints.

4)   Esterfication(Widely   used   ):- Esterification is the chemical process for making esters, which are compounds of the chemical structure R-COOR', where R and R' are either alkyl or aryl groups. A mineral acid catalyst is usually needed to make the reaction occur at a useful rate. Esters can also be formed by various other reactions. These include the reaction of an alcohol with an acid chloride or an anhydride. The chemical structure of the alcohol, the acid, and the acid catalyst used in the esterification reaction all effect its rate. Simple alcohols such as methanol and ethanol react very fast because they are relatively small and contain no carbon atom side chains that would hinder their reaction. These differing rates of reaction were first reported by NikolayMenschutkin in 1879-83. German chemists, during World War II, developed solid acid catalysts or ion exchange resins for use in the manufacture of esters.These solid catalysts work well with acid sensitive esters because they can be separated from the product by filtration and therefore, the catalyst does not spend very much time in contact with the acid unstable product. The esterification process has a broad spectrum of uses from the preparation of highly specialized esters in the chemical laboratory to the production of millions of tons of commercial ester products. These commercial compounds are manufactured by either a batch or a continuous synthetic process. The continuous process for making esters was first patented in 1921 and has been used extensively in the manufacture of large quantities of esters.

Experimental methods & comparison

Esterification of acetic acid with butanol:-

Esterification of acetic acid is well established chemical process, through which methyl, ethyl, butyl and ethylene glycol acetate are formed. Several catalysts are used to synthesis acetate in this process.The acidity and surface area of catalyst were measured with the help FTIR using pyridine as the diagnostic base and BET showed surface areas between 900 and $1000m2 /g$ and pore diameter around 26 °A units. The effect of reaction temperature, mole ratio of the reactant, time and catalyst loading on n-butanol conversion and selectivity of n-butyl acetate was studied. Al-MCM-41 (33 and 25) was found to be more active than the other catalysts owing to its high density of Bronsted acid sites. The low reaction period and low amount of catalyst were required for converting a major amount of the reactants to product with high selectivity. The reaction over as-prepared catalyst showed conversion 68% less than that of calcined sample. Hence the reaction is proposed to occur mainly within the pores of the catalyst. The catalytic activity of the materials was tested for the vapour phase esterification of acetic acid with n-butyl alcohol (NBA), isobutyl alcohol (IBA) and tertiary butyl alcohol (TBA) under autogeneous condition at 100, 150, 175 and 200^0C.NBAconversion was found to be higher than IBA and TBA.The reaction was carried out

under batch and flow conditions. The authors have explained the supported heteropoly acids shown better activity per proton than do conventional catalysts such as sulfuric acid or resins. It was also proved that under flow conditions deactivation of the catalyst was low from 43 to 32% conversion.The formation of n-butyl acetate in the presence of heterogeneous catalysts was also esterified n-butanol with acetic acid. at temperature varying between 100 and 120^{0}C. Three ion-exchange resin catalysts CT-269 monosulfonated, Amberlyst-46 surface-sulfonated and Amberlyst-48 bi-sulfonated are similar matrix 8 but different sulfonation. It is concluded that the esterification occurs mainly on or near the external surface of catalysts particles whereas side reactions occur mainly in the pores. In this study shows that the ion-exchange capacity of A-46 is nearly five times lower than that of CT-269.

Esterification of acrylic acid with 1-butanol has been studied.In a heterogeneous solid liquid reaction system using a variety of solid acids. Cs2.5H0.5PW12O40 exhibited the highest catalytic activity in the unit of catalyst weight among the solid oxide catalysts, while the activity of Cs2.5H0.5PW12O40 was less than those of organic resins such as Nafion and Amberlyst 15.

Esterification of acetic acid with methanol:-

To investigate the similarities and differences between heterogeneous and homogeneous catalyzed esterification, the kinetics of acetic acid esterification with methanol. were investigated using a commercial Nafion/silica nanocomposite catalyst (SAC-13) and H2SO4, respectively. Reactions were carried out in an isothermal well-mixed batch reactor at 600C. It was found that the resin/silica composite is strongly acidic, with highly accessible sites 9 and sufficient robustness to withstand reasonably high temperatures upto 2000C and attrition stress. Reaction on SAC-13 appears to involve single-site catalysis with a probable ratecontrollingEley-Rideal surface reaction, which reaction mechanism involving a nucleophilic attack between adsorbed carboxylic acid and un-adsorbed alcohol as the rate limiting step.It was also found that, with the increase of temperature, adsorption constants decrease, both the forward and backward reaction rate constants increase, and the reaction equilibrium constants for the forward reaction decrease while that for the backward reactions increase. Another esterification isothermal batch experiments carried out between acetic acid with methanol in the presence of hydrogen iodide at temperature of 30-600C. The catalyst concentration was varied between 0.05 and 10.0

wt%.Initial kinetics was measured for the reactions of a series of linear chain carboxylic acids such as acetic, propionic, butyric, hexanoic, and caprylic acid with methanol at 600C. It was shown that reaction 10 rate decreased as the number of carbons in the linear alkyl chain increased for both H2SO4 and SAC-13. It has done work on a set of linear-chain carboxylic acids (acetic acid [HAc], propionic acid [HPr], butyric acid [HBu], hexanoic acid [HHx], caprylic acid. Report the impact of water on liquid-phase sulfuric acid catalyzed esterification of acetic acid with methanol at 60C.

The author and their co-workers were demonstrated the ability of the fibrous polymer-supported sulphonic acid catalyst in the esterification of propanoic acid with methanol and to develop an advanced kinetic model for the esterification. The reaction rate was 11 higher over the fibre catalyst as Smopex-101than over a conventional resin catalyst asAmberlyst15. It has reported that the increase of the temperature as well as the initial molar ratio of propanoic acid and methanol increased the esterification rate. The degree of cross-linking of the fibre catalyst and different fibre dimensions did not affect the reaction rate.

Esterification of acetic acid with ethanol:-

The reactions were conducted at temperature range of 363 to 400 K, with molar ratio of ethanol to acetic acid 1.5. Author has reported that the temperature is critical parameters in this novel EAc synthesis process and the one-pass ethanol conversion was successfully improved from 67 to 85 mol%. It has found maximum yield for ethyl acetate to not more than 67%.Ethanol is converted into ethyl acetate with high selectivity over Cu-ZnO-ZrO2-Al2O3 catalyst, together with low selectivity to methyl ethyl ketone. The ethyl acetate production ability of catalyst is roughly proportional to the Cu surface area of the Cu-ZnO-ZrO2-Al2O3 catalyst. The highest ethanol conversion, the highest ethyl acetate selectivity, and the highest space-time yield of ethyl acetate were achieved at Cu content of 70 mol%.The additive oxides as ZnO, ZrO2, and Al2O3 are necessary for the selective ethyl acetate formation. The esterification of acetic acid with ethanol, catalyzed both homogeneously by the acetic acid, and heterogeneously by Amberlyst 15, has been carried out several temperatures between 303.15 and 353.15K and at various starting reactant compositions. The influence of feed composition and reflux ratio has been analyzed in packed column which is filled by Amberlyst 15. The best results have been obtained using the ASOG method to calculate the activity coefficients. It also

has studied to simplified two mechanisms based on Lanwt%uir– Hinselwood model. The thermal stability and mechanical strength of the resin catalysts were tested by SEM. The order of catalytic activity was found to be: D002<D001<Amberlyst-15< NKC. It also has studied to simplified two mechanisms based on Lanwt%uir– Hinselwood model. The thermal stability and mechanical strength of the resin catalysts were tested by SEM. The order of catalytic activity was found to be: D002<D001<Amberlyst-15< NKC.

Reaction Mechanism

Acetic acid reacts with ethylene glycol in the presence of ion-exchange resin as a catalyst toproduce theester as ethylene glycol mono and di-acetate. Esterification reaction is very slow atwithoutcatalystanditisalsoatypeofreversibleaction.Duetoreversereactionitproduceexcess amount of water during reaction and the water reduces formation of ester as a products. This reverse reaction is following as hydrolysis reaction. The experimental reaction was carried out in generally following two steps, first thereaction between ethylene glycol and acetic acid over acid catalyst and formation of ethylene glycol mono-acetate, second following consecutive step is ethylene glycol mono-acetate to ethylene glycol di-acetate and conversion of product and reactant respectively.

$$C_2H_6O_2 + C_2H_4O_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} C_4H_8O_3 + H_2O \quad\ldots\ldots\ldots\text{I}$$

$$C_4H_8O_3 + C_2H_4O_2 \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} C_6H_{10}O_4 + H_2O \quad\ldots\ldots\ldots\text{II}$$

Scheme 1

$$\frac{dC_{EG}}{dt} = -K_1 C_{EG} C_{AA} + K_{-1} C_{EGMA} C_{H_2O} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{III}$$

$$\frac{dC_{EGDA}}{dt} = K_2 C_{EGMA} C_{AA} - K_{-2} C_{EGDA} C_{H_2O} \quad\ldots\ldots\ldots\ldots\ldots\ldots.\text{IV}$$

Arrhenius equation:

$$K = K_0 e^{\frac{E}{RT}}$$

For equation III:

Rate of forward reaction $= K_1 [C_{EG}] [C_{HAC}]$

Rate of reverse reaction $= K_{-1} [C_{EGMA}] [C_{H_2O}]$

For equation IV:

Rate of forward reaction $= K_2 [C_{EGMA}] [C_{HAC}]$

Rate of reverse reaction $= K_{-2} [C_{EGDA}] [C_{H_2O}]$

II.   Results & Discussion:-

The reaction of ethylene glycol with acetic acid in presence of cation-exchange resin proceeds in two consecutive reversible steps as shown in Scheme 1. In the first step, ethylene glycol reacts with acetic acid to produce EGMA and water. The EGMA formed in the first step reacts further with acetic acid resulting in the formation of EGDA and water. The term selectivity (S) of the two products, EGMA and EGDA, used throughout the article.

1 Effect on conversion of acetic acid
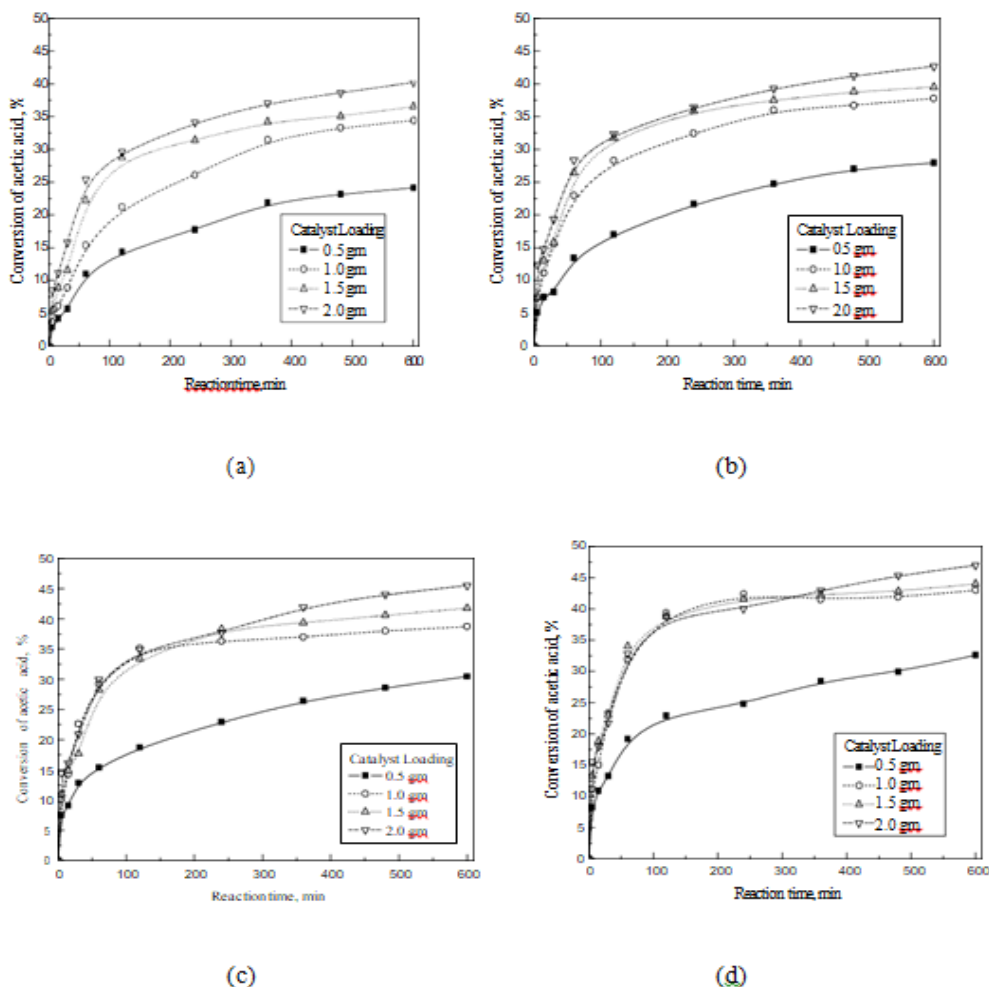

(a)

(b)

(c)

(d)

Fig.1.Plots (a),(b),(c) and (d) show the effect of catalyst loading on conversion of acetic acid at varying reaction time and temperature at 333, 343,353and 363K

Table1 Variation of different parameter at 0.5wt% catalyst loading, 333K reaction temperature and 3.0 molar ratio of AA to EG

Reactiontime	Wt% ofAA	Wt% ofEGDA	Wt% ofEGMA	Wt% ofEG	Wt%Water
0.0000	75.2000	0.0000	0.0000	24.8000	0.0000
5.0000	74.5000	0.2500	0.8571	24.1829	0.2100
15.0000	73.5000	0.7600	1.8639	23.3661	0.5100
30.0000	71.7800	2.1600	2.8507	22.1833	1.0260
60.0000	67.9000	5.6000	4.6752	19.6348	2.1900

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120.0000	64.4000	8.1600	7.0948	17.1052	3.2400
240.0000	61.8700	10.9700	7.4768	15.6842	3.9990
360.0000	58.7600	12.7300	10.3601	13.2179	4.9320
480.0000	57.8000	13.8500	10.4285	12.7015	5.2200
600.0000	57.0500	14.6800	10.5460	12.2790	5.4450

Reactiontime	MolFraction					Conversion%		Selectivity%	
	AA	EGDA	EGMA	Water	EG	AA	EG	EGMA	EGDA
0.00	0.7581	0.0000	0.0000	0.0000	0.2419	0.0000	0.0000	0.0000	0.0000
5.00	0.7510	0.0010	0.0050	0.0071	0.2359	0.9308	2.4885	70.6450	29.3550
15.00	0.7409	0.0031	0.0108	0.0171	0.2279	2.2606	5.7819	63.2550	36.7450
30.00	0.7236	0.0089	0.0166	0.0345	0.2164	4.5478	10.5513	48.0891	51.9109
60.00	0.6845	0.0232	0.0272	0.0736	0.1915	9.7074	20.8275	36.9486	63.0514
120.00	0.6492	0.0338	0.0413	0.1089	0.1669	14.3617	31.0273	37.8994	62.1006
240.00	0.6237	0.0454	0.0435	0.1344	0.1530	17.7260	36.7573	32.3597	67.6403
360.00	0.5923	0.0527	0.0603	0.1657	0.1289	21.8617	46.7020	36.3563	63.6437
480.00	0.5827	0.0574	0.0606	0.1754	0.1239	23.1383	48.7842	34.5772	65.4228
600.00	0.5751	0.0608	0.0613	0.1830	0.1198	24.1356	50.4879	33.5219	66.4781

Table2 Variation of different parameter at 0.5wt% catalyst loading, 343K reaction temperature and 3.0 molar ratio of AA to EG

Reactiontime	Wt% ofAA	Wt% ofEGDA	Wt% ofEGMA	Wt% ofEG	Wt%Water
0.00	75.20	0.00	0.00	24.80	0.00
5.00	73.75	0.65	1.59	23.58	0.44
15.00	72.65	1.36	2.48	22.74	0.77
30.00	70.90	3.03	3.14	21.64	1.29
60.00	65.07	7.50	6.87	17.52	3.04
120.00	62.40	9.77	8.27	15.72	3.84
240.00	58.90	12.76	10.07	13.38	4.89
360.00	56.57	13.98	12.38	11.49	5.59
480.00	54.87	15.49	13.17	10.37	6.10
600.00	54.20	16.52	12.86	10.12	6.30

Reactiontime	MolFraction					Conversion%		Selectivity%	
	AA	EGDA	EGMA	Water	EG	AA	EG	EGMA	EGDA
0.00	0.7581	0.0000	0.0000	0.0000	0.2419	0.0000	0.0000	0.0000	0.0000
5.00	0.7434	0.0027	0.0092	0.0146	0.2300	1.9282	4.9286	63.1549	36.8451
15.00	0.7324	0.0056	0.0144	0.0257	0.2219	3.3909	8.2961	56.1640	43.8360
30.00	0.7147	0.0126	0.0182	0.0433	0.2111	5.7181	12.7282	42.0832	57.9168

60.00	0.6559	0.0311	0.0400	0.1021	0.1709	13.4707	29.3658	39.1471	60.8529
120.00	0.6290	0.0405	0.0481	0.1290	0.1534	17.0213	36.6038	37.2645	62.7355
240.00	0.5938	0.0529	0.0586	0.1643	0.1305	21.6755	46.0673	35.6584	64.3416
360.00	0.5703	0.0579	0.0720	0.1878	0.1120	24.7739	53.6866	38.3230	61.6770
480.00	0.5531	0.0642	0.0766	0.2049	0.1012	27.0346	58.1843	37.3757	62.6243
600.00	0.5464	0.0684	0.0748	0.2117	0.0987	27.9255	59.2122	35.3424	64.6576

Effect on temperature :-

The effect of temperature on conversion of ethylene glycol and selectivity of products was studied in the temperature range of 333–363 K. The effect of temperature on conversion of ethylene glycol is shown in Fig. 2. The conversion of ethylene glycol was found to increase with increase in temperature. The effect of temperature on the selectivity to EGDA is shown in Table 1. It is observed from the table that the selectivity to EGDA is not affected significantly by temperature especially, at high reaction time when the reaction reached close to equilibrium. This is because the standard enthalpy of reaction is relatively small which results in insignificant temperature dependency on the chemical equilibrium. As a result, almost similar equilibrium composition was obtained in the temperature range studied.
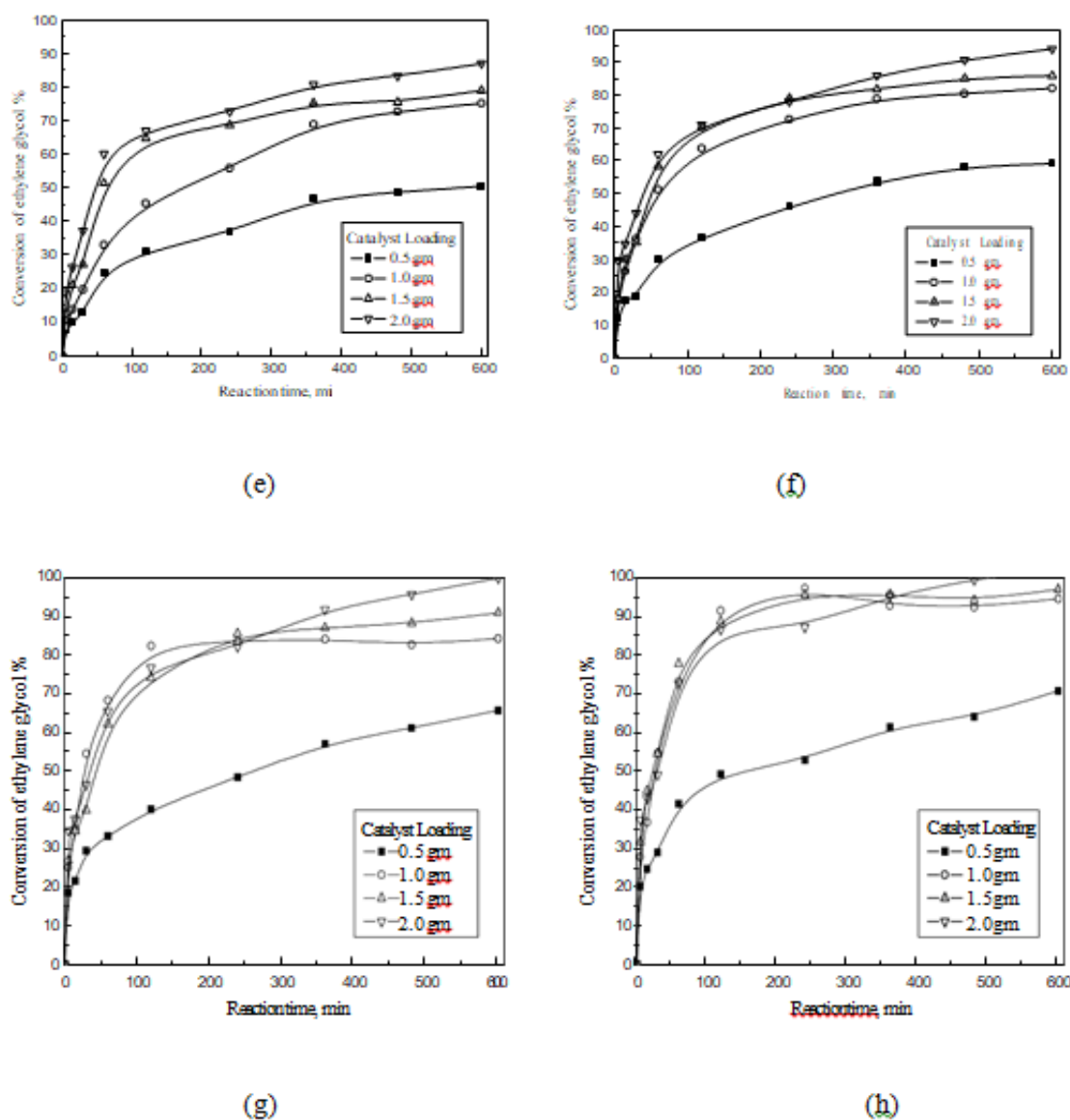
(e)

(f)

(g)

(h)

Fig.2 Plots (e), (f), (g) and (h) show the effect of catalyst loading on conversion of ethylene glycol at varying reaction time and temperature at 333,343, 353K

Effect on catalyst loading:-

The effect of catalyst loading was studied at three different catalyst loadings in the range of 0.5 to 1.5 % (w/v) of catalyst. The conversion of ethylene glycol increases with increase in catalyst loading as shown in Fig. 4. The effect of catalyst loading on selectivity to EGDA is shown in Table 2. The selectivity to EGDA was found to increase with increased reaction time as expected. However, the selectivity to EGDA was found to be almost unaffected by the catalyst loading. From these results, it may be concluded that with increase in catalyst loading, the rate of both esterification and hydrolysis reaction increases equally keeping the selectivity to the products unaffected.
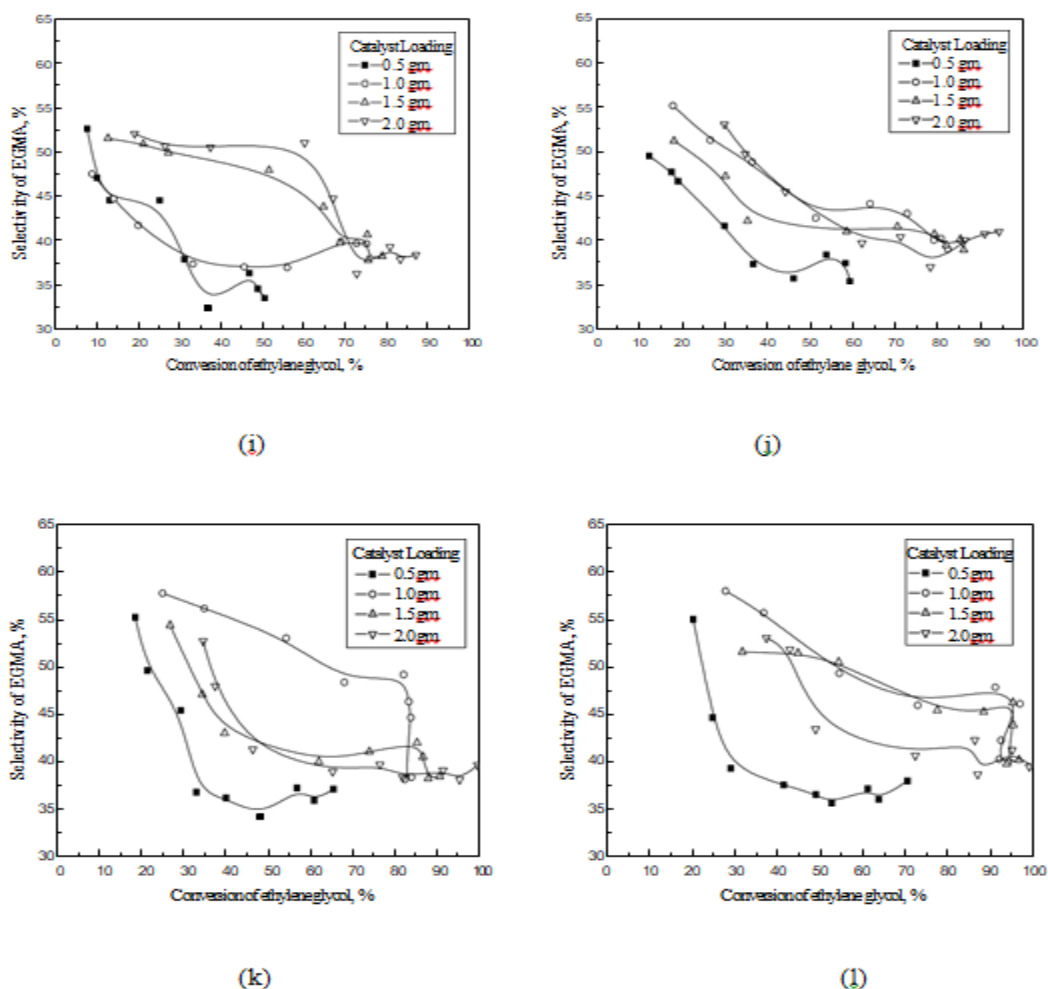
Fig.3 Plots (i), (j), (k) and (l) show the effect of catalyst loading on conversion of ethylene glycol at varying reaction time and temperature at 333,343, 353K

Empherical kinetic model :-

The esterification of ethylene glycol with acetic acid and hydrolysis as reverse reaction are SN2 type reactions (Scheme 1) and hence, the reactions were considered as second order in the developed. empirical model. The rates of formation of five different components involved in the reaction were therefore represented by the following five ordinary differential equations (eqs.1−5).The kinetic models were also formulated following the LHHW approach assuming ethylene glycol, acetic acid, EGMA, and EGDA were adsorbed on surface. Since the reaction was found to be controlled by the kinetics only, the adsorption and desorption resistance was not considered and the model was developed based on surface reaction controlling only. According to this model, the rates of formation of the five components were given by the following five ordinary differential equations (eqs. 6−10).The developed kinetic model involves four rate constants, k_1, k_2, k_{-1}, and k_{-2} and four adsorption equilibrium constants, K_{AA}, K_{EG}, K_{EGMA}, and K_{EGDA}.
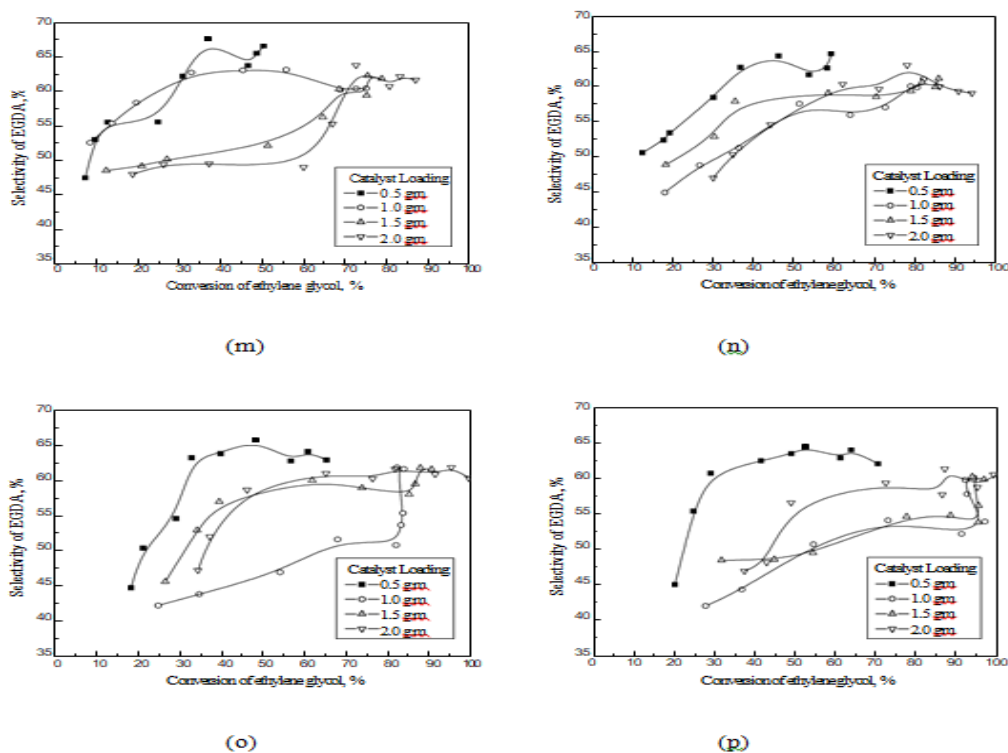
Fig.4 Plots (m), (n), (o) and (p) show the effect of catalyst loading on selectivity of ethylene glycol di-acetate at varying ethylene glycol conversion and temperature at 333, 343,353 and 363 K

III.   Conclusion :-

In the present work, the detailed kinetics of the esterification of ethylene glycol with acetic acid has been investigated in presence of a strongly acidic cation-exchange resin, seralite SRC-120 as catalyst. The acetic acid to ethylene glycol mole ratio was found to have enormous effect on the product selectivity where higher mole ratio favors selective formation of EGDA. The increase in temperature and catalyst loading has been found to enhance the reaction rate without significantly affecting the product selectivity. The two different kinetic models, empirical and kinetic model based on LHHW approach were also developed to correlate the experimental data. The rate constants and equilibrium constants of the developed kinetic models were estimated using the experimental data at different temperatures using non-linear least square techniques based on Levenberg-Marquardt algorithm. The concentration of different components calculated based on estimated parameters were then compared with experimental data and LHHW-based model was found to fit the experimental data better than empirical model. The activation energies and frequency factors of the rate constants of the LHHW-based model were then determined from the intercept and slope of the Arrhenius plot of ln(rate constants) versus 1/T.

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