KINETICS OF CATALYTIC ESTERIFICATION OF BUTANOL WITH ETHANOIC ACID BY SOME NIGERIAN ACTIVATED CLAYS

BY

OLOWOKERE, John

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DECLARATION

I, OLOWOKERE, John with registration number M.ENG/SEET/2008/2080 hereby declare that this thesis titled: "KINETICS OF CATALYTIC ESTERIFICATION OF BUTANOL WITH ETHANOIC ACID BY SOME NIGERIAN ACTIVATED CLAYS" is a record of my own research finding. It has not been presented for any other qualification anywhere. Information from the works of other Scientists (Published or Unpublished) and their contributions here been duly acknowledged.

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CERTIFICATION

This thesis titled: Kinetics of Catalytic Esterification of Butanol with Ethanoic Acid by some Nigerian Activated Clays; by: OLOWOKERE, John (M.ENG/SEET/2008/2080) meets the regulations governing the award of the degree of Masters of Engineering of the Federal University of Technology, Minna and it is approved for its contribution to scientific knowledge and literary presentation.

Dr. J.O. Okafor
Supervisor

10th Feb; 2012
Date

Dr. M.O. Edoga
Head of Department

13 – 02 – 12
Date

Prof. M.S. Abolarin
Dean, School of Engineering and
Engineering Technology

13 – 02 – 12
Date

Prof. (Mrs.) S.N. Zubairu
Dean, Post Graduate School

3/4/12
Date

DEDICATION

This research work is dedicated to Almighty God whose faithfulness has been my stronghold throughout this programme.

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Symbol	Description	Unit
$\hat{C}_v$	Concentration of vacant sites on the surface of catalyst	mol/m^3
$\hat{C}_H$	Equilibrium concentration of ethanoic acid	mol/dm^3
$\hat{C}_m$	Total concentration of the surface of the catalyst	mol/m^3
r_a	Rate of reaction	$mol/dm^3.min$
$\hat{C}_E$	Equilibrium concentration of butylethanoate	mol/dm^3
k_g	Mass tranfer coefficient	Kg/m.s
K	Overall reaction equilibrium constant	—
$\hat{C}$	Concentration of the occupied sites on the catalyst.	mol/m^3
K_W	Equilibrium adsorption constant for water	L/mol.min
C_w	Concentration of water	mol/dm^3
X	Active site of catalyst	—
E_a	Activation energy	KJ/mol
A_0	Pre-exponenetial factor	Kmol/gmin
K_S	Equilibrium adsorption constant of the catalyst surface	L/mol.min
K_E	Equilibrium adsorption constant for butylethanoate	L/mol.min
K_{OH}	Equilibrium adsorption constant for butanol	L/mol.min
K_H	Equilibrium adsorption constant for ethanoic acid	L/mol.min
x	Mole fraction of ethanoic acid	—
x	Mole fraction of butanol	—
x	Mole fraction of butylethanoate	—
x	Mole fraction of water	—
m_{cat}	Mass of catalyst	gram
R	Universal gas constant	J/mol.K
T	Temperature	K
$\hat{C}_{OH}$	Equilibrium concentration of butanol	mol/dm^3
$\hat{C}_w$	Equilibrium concentration of water	mol/dm^3

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

Esterification reaction is widely employed in synthetic organic process industry. The reaction is carried out between a carboxylic acid and an alcohol, with or without the presence of a catalyst, under some specific conditions to yield a product known as ester. Since the reaction occurs at equilibrium, and is reversible in nature, the reaction becomes very slow without a catalyst (Vishnu, 2010). Even though esterification reactions can also be catalysed by acids in homogenous systems, catalyst recovery is uneconomical (Igbokwe *et al*, 2008).

The growing awareness of the unacceptability of conventional liquid catalysts such as sulphuric acid and the resulting legislation give a major impetus to the search for cleaner technologies. Such cleaner technology could be possible by making use of environmentally friendly catalysts involving the use of solid catalysts (Khder *et al*, 2008).

In line with this development, there has been a tremendous upsurge of interest in recent years in the use of different heterogeneous eco- friendly catalysts, such as clay for organic transformations. Such catalyst can help to minimize waste production, and render the synthesis process more attractive from both the environmental and process point of view (Dilip *et al*, 2007).

Natural clays were among the earliest solid acid catalysts used in the oil industry to promote cracking and isomerization reactions. Not long after their introduction in the late 1930s, they were replaced in large part by synthetic amorphous silica—alumina, which gave more consistent results. During the 1960s the amorphous catalysts were superseded by the more active and shape-selective micro-porous crystalline aluminosilicates known as zeolites. However, there has been a renewed interest in the use of clays as catalysts because zeolites are not as suitable for the conversion of relatively large molecules. This interest resulted in the synthesis of highly active clays and in the development of the pillared clays, in which the useful surface has been increased and shape selectivity created by separating the layers with the aid of large cationic clusters (pillars). It is well known that most of the observed catalytic properties of clays are due to their acidic character, which is strongly dependent on the type of clay, exchanged cat ion capacity and the water content (Theng, 1984). According to literature, activated clay catalyst has a surface area of 150 – 225m^2/g, pore volume of 0.4 – 0.52cm^3/g and mean pore radius of 100Å (Smith, 1983).

Most clay are crystalline, that is, they have a definite repeating arrangement of atoms of which they are composed. The majorities are made up of planes of oxygen atoms with silicon and aluminium atoms holding the oxygen together by ionic bonding. The three to four planes of oxygen atoms with intervening silicon and aluminiun ions depending on the clay, makes up a layer. Clay is composed of many layers stacked like a deck of cards. A clay particle is called micelle. A few clays have the oxygen and other atoms less regularly oriented, and are called amorphous materials. (Nku, 2004).

Due to the industrial importance of solid catalysts in esterification reactions, lots of investigations have been reported in literatures concerning its usage. The use of heterogeneous catalyst affords an advantage in catalyst recovery (Igbokwe *et al*, 2008). The most popular solid acids catalyst used to produce esters were ion-exchange organic resins, such as Amberlyst-15, zeolites, and silica-supported heteropoly acids. Nevertheless, they have shown limitations in applicability for catalyzing esterification due to low thermal stability (Amberlyst-15 < 140 °C), mass transfer resistance (zeolites) or loss of active acid sites in the presence of a polar medium (HPA/silica) (Soumaya *et al*, 2009).

Clay catalysts have received considerable attention in different organic syntheses due to their environmental compatibility, low cost, high selectivity, thermal stability and reusability. Acid-activated clays is one of the most widely studied solid acid catalysts for many organic transformations such as alkylation, condensation, dimerisation, isomerisation, ether formation and transesterification reactions (Soumaya *et al*., 2009).

It is interesting to note that for an ester to be formed as a product in a reaction process catalyzed by clay, three steps are involved, namely: adsorption of a molecule onto the surface which is then attached to the active site of the catalyst, the adsorbed molecule react with another on the active site or an incoming one from the bulk stream, and finally desorption of product from the surface which then frees the active site. (Levenspiel, 1981).

Previous studies on kinetics of esterification reaction show surface catalysed chemical reactions involving the interaction of two molecules of the same reactant or two different reactants may proceed either through the Langmuir-Hinshelwood mechanism or Rideal-Eley mechansim. Most of the bimolecular catalytic reactions follow the Langmuir-Hinshelwood mechanism, while reactions such as the hydrogenation of olefins and the conversion of para and ortho hydrogens are known to follow a Rideal-Eley mechanism. In general, the probable mechanisms for esterification reactions according to Schmid *et al*, (2008), follows the pseudo homogeneous model (PH) in esterification systems. In the PH model, adsorption and desorption of all components are negligible. The Langmuir–Hinshelwood–Hougen–Watson (LHHW) model takes into account the adsorption of all components (Teo *et al*, 2004). On the other hand, the Eley–Rideal (ER) model can be applied when the reaction between one adsorbed reactant and one non-adsorbed reactant from the bulk liquid phase is assumed to occur (Kirumakki *et al*, 2006).

Besides these kinetic models, the synthesis of butyl acetate through esterification has been carried out for several years now. Zheng *et al*, (1997) have studied the kinetics of butyl acetate in the presence of cat ion exchange resin. Gangadwala *et al*, (2003) also studied the kinetics of butyl acetate synthesis in the presence of Amberlyst 15 and again Li *et al*, (1997) have studied various zeolites such as HY and HZSM5 in the esterification of butanol with acetic acid. Similarly, some other works which have been done in this field include the esterification of n-propanol, iso-propanol, n-butanol and iso-butanol with acetic acid in the presence of zirconia-based catalysts, which led to the formation of their respective acetates and the results obtained showed that there is a steady increase in the yield of esters, with increase in reaction time; having 100% selectivity on the acetate component. It was equally observed that the percentage of ester formed during esterification reaction depends on the type of catalysts as well as the alcohol used (Joyce *et al*, 2006).

In this work therefore, the experimental data that will be generated will be fitted into the Lagmuir-Hinshelwood-HougenWatson (LHHW) model for the purpose of obtaining the kinetic parameters.

1.2 Aim and objectives

The aim of this work is to study the kinetics of catalytic esterification of butanol with ethanoic acid, in the presence of catalysts obtained from some Nigerian clays. In order to realize the above stated aim, the following objectives must be achieved:

I. To determine the kinetic rate data of the esterirfication reaction between butanol and ethanoic acid in the presence of three activated clays.
II. To determine the order of reactions.
III. To determine the percentage conversion of ethanoic acid while using the activated clays for the esterification reaction.
IV. To compare the catalytic abilities of the three types of activated clays.
V. To obtain the kinetic and adsorption parameter for the best batch esterification process.

1.3 Scope of study

- Collection of clay samples from three selected States in Nigeria, namely: Ohaukon in Ebonyi State, Oyigbo in Rivers State, and Obajana in Kogi State.
- The best clay sample will be characterized to verify the type of clay sample being collected alongside its physio-chemical properties.
- Preparation and thermal/acid activation of the clay samples for usage as catalyst.
- Generation of kinetic rate data will be achieved by varying the process variables such as temperature, catalyst concentration and ethanoic acid to butanol molar ratio. This will be applicable to the three clay samples.
- A global rate equation for the reaction will be developed; by proposing a reaction mechanism in accordance with Langmuir- Hinshwood-Hougen-Watson (LHHW) model.
- Non linear Least square method will be adopted to fit the kinetic rate data; while the kinetic equilibrium parameters will be estimated from the developed LHHW model, through the use of MATLAB software.

1.4 Justification

With the large deposits of clay all over the country, which have so far been unexploited, there is every need to look for avenues through which it can be utilized for the technological and economic well being of the country. The mere fact that in most industries, esterification reactions are generally carried out in the presence of hazardous toxic chemicals as catalyst, such as sulphuric acid and its derivatives or expensive ion exchange resins, hence the need to use cheap and non corrosive heterogeneous based clay catalyst has become imperative, since they can easily be separated from the reaction products by simple filtration and can be quantitatively recovered in their active form. They can also be recycled thereby making the process less expensive and at the same time reduce the contamination of the products. These advantages are not obtainable when using lewis base acid catalysts which usually leaves behind some traces of metallic components of these catalysts.

In addition, since the study of kinetic searches for the factors that influences the rate of chemical reactions, and while measuring this rates, it goes further to propose explanations for the value found. This study then is important for both physical and organic chemist. For chemical Engineers, the kinetics of reaction must be known in order to be able to design equipment to effect these reactions on a technical scale.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Esterification

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. The most common method for preparing esters is to heat a carboxylic acid with an alcohol while removing the water that is formed. A mineral acid catalyst is usually needed to make the reaction occur at a useful rate.

Vishnu, (2010) reported that 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 affect 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 Nikolay Menschutkin 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 (Calvar, 2007).

2.1.1 Preparation

Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product. Esters are common in organic chemistry and biological materials, and often have a characteristic pleasant, fruity odour. This leads to their extensive use in the fragrance and flavor industry. Ester bonds are also found in many polymers.

2.1.2 Esterification of carboxylic acid

The classic synthesis route is the Fischer esterification, which involves treating a carboxylic acid with an alcohol in the presence of a dehydrating agent:

$$RCO_2H + R'OH \rightleftharpoons RCO_2R' + H_2O$$

The equilibrium constant for such reactions is about 5 for typical esters, e.g., ethyl acetate. But the reaction is slow in the absence of a catalyst. Sulfuric acid is a typical catalyst for this reaction. Many other acids are also being used such as polymeric sulfonic acids. Since esterification is highly reversible, the yield of the ester can be improved upon Le Chatelier's principle:

- using the alcohol in large excess (i.e., as a solvent)
- using a dehydrating agent: Sulfuric acid not only catalyzes the reaction but sequesters water (a reaction product). Other drying agents like molecular sieves can also be used.

- removal of water by physical means such as distillation as a low-boiling azeotropes with toluene, in conjunction with a Dean-Stark apparatus (Wikipedia encyclopedia, 2010).

2.1.3 Acetylation

Acetylation also called ethanoylation is described as a reaction that introduces an acetyl functional group into a chemical compound. A reaction involving the replacement of the hydrogen atom of a hydroxyl group with an acetyl group (CH_3CO) yields a specific ester, the acetate. Acetic anhydride is commonly used as an acetylating agent reacting with free hydroxyl groups (Chen *et al*, 1999).

2.1.4 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 was investigated by Liu *et al*, (2006), using a commercial Nafion/silica nanocomposite catalyst (SAC-13) and H_2SO_4, respectively. This same reaction was carried out in an isothermal well-mixed batch reactor at 60°C using resin/silica composite catalyst (Amberlyst – 15) which is known to be strongly acidic, with highly accessible sites and sufficient robustness to withstand reasonably high temperatures up to 200°C and attrition stress. Reaction on SAC-13 appears to involve single-site catalysis with a probable rate controlling Eley-Rideal surface reaction, in which reaction mechanism involving a nucleophilic attack between adsorbed carboxylic acid and un-adsorbed alcohol as the rate limiting step. Adsorption equilibrium constants, dispersion coefficients and kinetic parameters were obtained from the reversible reaction of acetic acid and methanol catalyzed by Amberlyst-15 ion exchange resins (Yu *et al*, 2004). This same experiment was also conducted using a packed bed reactor in the temperature range 313–323K, using a rectangular pulse input. The synthesis of methyl acetate gave rise to the idea of recovering dilute acetic acid from wastewater, and the hydrolysis of methyl acetate. The quasi-homogeneous kinetic model and linear adsorption isotherm are much applicable because of the solvent, methanol or water is present at a large excess concentration. It was also found that with the increase in temperature, adsorption constants decreased, both the forward and backward reaction rate constants increase, and the reaction equilibrium constants for the forward reaction decreased while that for the backward reactions increased. In another isothermal batch esterification experiment carried out by Ronnback et al., (1997) between acetic acid and methanol in the presence of hydrogen iodide at temperatures of 30-60^{0}C; the catalyst concentration was varied between 0.05 to 10.0 wt%. The protolysis equilibria of the acids and the influence of the activity coefficients on the equilibria was explained.

Yet in another work, the impact of carboxylic acid chain length on the kinetics of liquid-phase acid-catalyzed esterification over sulfuric acid and a commercial Nafion/silica composite solid acid catalyst SAC-13 was reported. Initial kinetics were measured for the reactions of a series of linear chain carboxylic acids such as acetic, propionic, butyric, hexanoic, and caprylic acid with methanol at 60°c. It was shown that reaction rate decreased as the number of carbons in the linear alkyl chain increased for both H_2SO_4 and SAC-13. In order to diminish the effect of water on the catalysis, initial reaction kinetics were measured using a low concentration of sulfuric acid and different initial water concentrations. The decrease in initial reaction kinetics with increasing concentration of water indicated that catalysis is impaired as esterification proceeds as water is continuously produced from the condensation of carboxylic acids and alcohols. The negative impact of water on catalysis was found to be essentially independent of temperature or molar ratio of methanol to- acetic acid under the experimental conditions used.

The simultaneous water removal during reaction should not only inhibit the reverse hydrolysis reaction, but also preserve high activity of the catalytic protons throughout the reaction (Liu *et al*, 2006).

Esterification kinetics of propanoic acid with methanol in the presence of a fibrous polymer-supported sulphuric acid catalyst as well as a conventional resin catalyst was reported. Kinetic experiments were carried out in an isothermal batch reactor at 55, 60 and 63^0C with different initial molar proportion of propanoic acid and methanol in the ratio 1:1, 2:3 and 3:2, using both catalyst respectively. It was found that the reaction rate was higher with the fibre catalyst than with the Amberlyst 15, achieving a second-order rate constant of 1.82×10^{-3} $dm^3/(mol^2$ g min) at 60°C, with the initial molar ratio of 1:1, and rate constant of 7.03×10^{-4} $dm^3/(mol^2$ g. min) for the conventional resin catalyst under comparable conditions. It was reported that increase in temperature as well as the initial molar ratio of propanoic acid and methanol enhances the esterification rate. The degree of cross-linking of the fibre catalyst and different fibre dimensions did not affect the reaction rate (Lilja *et al*, 2002).

2.1.5 Esterification Of Acetic Acid With Ethanol

Most of the commercial processes for ethyl acetate production are via liquid-phase esterification (Wu et al., 2004). The reactions were conducted at temperature range of 363 to 400K, with molar ratio of ethanol to acetic acid of 3:2. Several authors have reported that temperature is a critical parameter in this reaction. However ethyl acetate synthesis process and the one-pass ethanol conversion was successfully improved from 67 to 85 mol%, as against the usual maximum yield of 67%. The equilibrium constant is almost constant and is independent of the reaction temperature while the ethanol concentration in the products flow decreased from 14 to 6.5 wt%. The reduction of ethanol concentration is advantageous for further purification processes. Ethanol is converted into ethyl acetate with high selectivity over Cu-ZnO-ZrO_2-Al_2O_3 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-ZrO_2-Al_2O_3 catalyst. The highest ethanol conversion, ethyl acetate selectivity, and the space-time yield of ethyl acetate were achieved at Cu content of 70 mol%. The additive oxides such as ZnO, ZrO_2, and Al_2O_3 are necessary for the selectivity of ethyl acetate formation (Inui *et al*, 2002).

The kinetics of esterification of maleic acid with ethanol over cheap and easily available catalysts, ion-exchange resins and clay supported heteropoly acids as reported by Yadav and Thathagar (2002) achieved the same order of catalytic activity as Amberlyst-36, Amberlyst-15, Indion-170, Amberlyst-18, Amberlite IRA SL 400, Filtrol-24.20% and DTP/K-10. In the same work, a pseudo-homogeneous kinetic model was developed and the activation energy was found to be 14.2 kcal.

The esterification of acetic acid with ethanol, catalyzed homogeneously by acetic acid, and heterogeneously by Amberlyst 15, has been carried out at several temperatures between 303.15 and 353.15K and at various starting reactant compositions. The influence of feed composition and reflux ratio was equally analyzed in packed column filled with Amberlyst 15. (Calvar *et al*, 2007).

According to Yang *et al*, (2004), the effect of catalyst type, catalyst loading, and temperature on the reaction kinetics between lactic acid and ethanol over five different cat ion-exchange resins were evaluated. For the purpose of further studies, the authors tried to analyze which component has the strongest adsorption strength on the resin surface. The thermal stability and mechanical strength of the resin catalysts were tested by SEM. The order of their catalytic activity was found to be: D002<D001<Amberlyst-15< NKC<002. Activation energies were found to be 51.58 KJ/mol and 52.26 KJ/mol, which suggested that this reaction was kinetically controlled. Pervaporation-aided esterification of acetic acid with ethanol was also reported at 343K over zeolite T membranes. Almost complete conversion was reached within 8hrs when initial molar ratio of alcohol to acetic acid is 1.5: 2 (Tanaka *et al*, 2001).

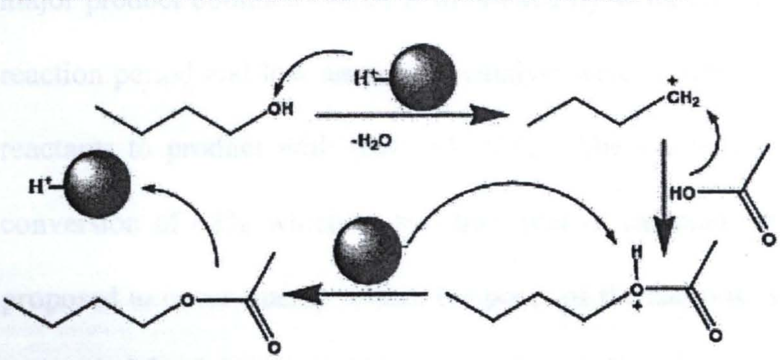
2.1.6 Esterification of acetic acid with 2-propanol.

The kinetics of the esterification of acetic acid with the secondary alcohol, 2-propanol, catalyzed by the cation exchange resins, Dowex 50Wx8-400, Amberlite IR-120, and Amberlyst 15 has been studied by Ali *et al*, (2006), at temperatures of 303, 323, and 343 K using an acid to alcohol molar ratios of 0.5: 1, 0.5:2 and 0.5:3; and catalyst loadings of 20, 40, and 60 g/L. The equilibrium constant was experimentally determined, and the reaction was found to be mildly exothermic. External and internal diffusion limitations were absent under the implemented experimental conditions. Systems catalyzed by gel-type resins (Dowex 50Wx8-400 and Amberlite IR-120) exhibit some similarities in their reaction kinetics. Increase in reaction temperature, acid to alcohol ratio, and catalyst loading is found to enhance reaction kinetics for the three catalysts. According to them, the pseudohomogeneous (PH), Eley Rideal (ER), Langmuir Hinshelwood (LH), modified Langmuir Hinshelwood (ML), and Pöpken (PP) models were found to predict reaction kinetics with mean relative errors of less than 5.4%. However, the ML model was found to be better for predicting reaction kinetics in the systems catalyzed by gel-type resins, while the PP model was better for the system catalyzed by the macroreticular catalyst, Amberlyst 15. The activation energies for the forward reactions are 57.0, 59.0, and 64.0 kJ/mole, for the systems catalyzed by Dowex 50Wx8-400, Amberlite IR-120, and Amberlyst 15, respectively. For these three catalysts, the adsorption equilibrium constants of the components present in the system increase in the same order like that of the solubility parameters of the component. Nonideality in the system is successfully accounted for by the UNIFAC model.

2.1.7 Catalytic activity of butanol and ethanoic acid

The esterification of acetic acid with alcohol such as *n*-butanol is an electrophilic substitution reaction which is relatively a slow reaction and needs activation either by higher temperature or by a catalyst to achieve higher conversion. The reaction following Eley–Rideal mechanism as shown below takes place between *n*-butanol and proton chemisorbed on the active sites (Bronsted acid sites) of the catalyst surface, producing a stable carbocation. Then, the carbocation attacks the nucleophilic center of acetic acid to form an unstable intermediate. Removal of a proton from the intermediate gives the final product, i.e. *n*-butyl acetate along with the regeneration of the catalyst. The acid catalyst facilitates the formation of the carbocation and helps to remove OH¯ from the alcohol (Wikipedia encyclopedia, 2010).

The mechanism involved in the reaction is as follows:



properties of catalyst, alcohols and the stearic properties of alcohols were suggested to play important roles in the esterification.

Other esterification reaction were carried out between propionic acid with *n*-butanol over Amberlyst 15, Amberlyst 35, Amberlyst 39, and HZSM-5 catalysts between the temperatures range of 353 to 383 K in a stirred batch reactor (Liu *et al*, 2001). The results obtained showed that Amberlyst resins such as Amberlysts 15wet, 35wet, and 39wet are more effective catalysts than HZSM-5 for this reaction. The activation energy of the forward reaction was found to be 14.1 kcal/mol. A propionic acid molecule is adsorbed on the acid site of the resin and protonated first, and then reacted with an *n*-butanol molecule in the bulk liquid to form *n*-butyl propionate and water. The heat of reaction determined from the experimental data is quite small, indicating that this reaction is essentially isothermal. However, the esterification of acetic acid with 1-butanol under the temperature range of 353.15 to 393.15K gave the final products as 1-butyl acetate and water (Grob and Hasse, 2005).

Heteropolyacids supported on activated carbon have shown to be an efficient solid catalyst for the esterification of acrylic acid by butanol in liquid phase (DuPont *et al*, 1995). The reaction was carried out under batch and flow conditions. Their work showed that the supported heteropolyacids has better activity per proton than the conventional catalysts such as sulfuric acid or resins. It was also proved that under different flow conditions, deactivation of the Catalyst reduces its efficiency from 43 to 32% conversion. Also the formation of *n*-butyl acetate in the presence of heterogeneous catalysts as carried out by Blagova *et al,* (1995) within the range of 100 to 1200C was achieved. In a similar vain, three ion-exchange resin catalysts, CT-269 mono-sulfonated, Amberlyst-46 surface-sulfonated and Amberlyst-48 bi-sulfonate are known to have similar matrix but different sulfonation. It was observed that the esterification occurs mainly on or near the external surface of catalysts particles whereas side reactions occur mainly in the pores. This study showed that the ion-exchange capacity of A-46 is nearly five times lower than that of CT-269. A detailed study of the esterification of propanoic acid by butanol or 2-ethylhexanol over hetero- polyacids catalyst was carried out by DuPont and Lefebvre, (1996) under homogeneous reaction phase. It was also shown that the reaction rate is proportional to the concentration of protons, and the activity loss increases with the surface area of the carbon support.

Two heteropolyacids such as 12-tungstophosphoric and 12-tungstosilicic acids were also used as catalyst for the esterification reaction between propanoic acid and butanol. It was totally selective for the formation of the ester and water, and the experiment can be run until a conversion of 100% is reached by elimination of water by azeotropic distillation.

2.1.9 Esterification Of Acetic Acid With Other Alcohol

The kinetic behavior of the heterogeneous esterification of acetic acid with amyl alcohol over an acidic cation-exchange resin and Dowex 50Wx8-100 was reported. This work was conducted in a fixed-bed reactor at temperatures ranging from 323 to 393 K and at molar ratios of feed (amyl alcohol to acetic acid) were varied from 1 to 10. It report has shown that the equilibrium conversion of acetic acid increases with increasing reaction temperature. The kinetic data were correlated with the quasi-homogeneous, Langmuir-Hinshelwood, Eley-Rideal, and modified Langmuir-Hinshelwood models. The modified Langmuir-Hinshelwood model yielded the best representation for the kinetic behavior of the reaction over wide ranges of temperature and feed composition. The formation of a gaseous phase, when the reactor operated at 393 K, is also of great advantage for the forward reaction esterification. The rate constant of the most

2.1.8 Esterification of Acetic Acid with Butanol

Esterification of acetic acid is a well established chemical process, through which methyl, ethyl, propyl and butyl acetate can be formed. Several catalysts are used to synthesize acetate in this process. Mesoporous Al-MCM-41 molecular sieves in the Si/Al ratios 33:25, 52:50, 72:75 and 114:100 (Rabindran *et al,* 2005) were synthesized under hydrothermal condition. The acidity and surface area of catalyst were measured with the help of fourier-transform infrared (FTIR) spectroscopy using pyridine as the diagnostic base and BET showed surface areas between 900 and 1000m^2/g and pore diameter around 26 Å units. Rabindran *et al,* (2005) studied the effect of reaction temperature, mole ratio of the reactant, time and catalyst loading on *n*-butanol conversion and selectivity of *n*-butylacetate was studied. Al-MCM-41 with a Si/AI ratio of 33: 25 was found to be more active than the other catalysts owing to its high density of Bronsted acid sites.

The reaction was also studied over H-Mordenite, H-beta, H-ZSM-5 and HY zeolites, and the results are compared to know which of them has the best outcome. *n*-Butyl acetate was the major product obtained which is facilitated by weak and moderate 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 the untreated catalyst showed a conversion of 68% which is less than that of calcined catalyst 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^{0}C. NBA conversion was found to be higher than that of IBA and TBA. The hydrophobic active modified catalyst was obtained at 328K, which clearly exceeds the corresponding rate constant value obtained with a traditional polyvinylbenzene supported catalyst (Wu *et al*, 2000).

However, the Kinetics of heterogeneous catalysed esterification of acetic acid with isoamyl alcohol was also studied over cation-exchange resin catalyst, Purolite CT-175, in a stirred batch reactor to produced isoamyl acetate. The equilibrium conversion of acetic acid was found to increase slightly with an increase in temperature from 333 to 363K, and also it increased appreciably with an excess of isoamyl alcohol in the reacting system. The work was geared towards understanding the chemistry of the reaction and obtaining a suitable rate expression, and checking its validity under different experimental conditions as molar feed ratios of isoamyl alcohol to acetic acid is 1:1 to 10:1. LHHW model gave a better representation of the kinetic behaviour for all practical purposes on the reaction kinetics studied under the given conditions. According to the LHHW mechanism, acetic acid adsorbed on one catalytic centre reacts with isoamyl alcohol adsorbed on another catalytic centre to give isoamyl acetate and water; each adsorbed on one centre (Teo *et al*, 2004). Corma *et al*, (1989) tries to establish the relationship between the characteristics of HY zeolite and its catalytic activity in the esterification of carboxylic esters. A more precise understanding of the factors governing the catalytic properties of these inorganic materials has been obtained, and some progress has been made in the design of more adequate zeolites for general organic syntheses.The best materials are therefore obtained by dealuminating the zeolite to a framework Si/Al ratio of at least 5:1. These dealuminated materials have an average activity per acid site very similar to that found for sulfuric acid. Additionally these heterogeneous catalysts can overcome equilibrium limitations due to the hydrophobicity of surfaces, where the concentration of water must be quite small. Zeolite catalysts have been found to be valuable, especially for the direct esterification of phenols.

Yeramian *et al*, (1968) proposed the vapor-phase reactions catalyzed by ion exchange resins with isopropyl alcohol with acetic acid. The esterification reactions have been done at three different temperatures 110°C, 116°C and 120°C. In this case, it was found that the experimental data are explained fairly well by a Hinshelwood- Langmuir model. The influence of both reactants on the reaction was observed to be of paramount importance and no general order of reaction with respect to them can be deduced, It was also observed that both esterification and dehydration reactions proceed through the same rate mechanism. Also the esterification of acetic acid with styrene in the presence of cation exchange resins as catalysts within the temperature range of 20-60°C was studied. The reaction was accompanied by dimerization of styrene. The selectivity with respect to the ester was greatly influenced by the catalyst, solvent and other operating conditions. Monodisperse K2661 was found to be the best catalyst among the catalyst used (Chakrabarti and Sharma 1991).

Tzong et al., (2001), also determined the kinetic data on the esterification of propionic acid with *n*-butanol catalyzed by Amberlyst 15, Amberlyst 35, Amberlyst 39, and HZSM-5 pellets and at the temperatures of 353 to 383K in a stirred batch reactor. The data indicated that the Amberlyst series resins were all effective to carry out this esterification. The activation energy of the forward reaction was found to be 14.1 kcal/mol and, kinetic model developed conformed to Rideal-Eley theory. Also, the activity-based equilibrium constant increases slightly with an increase in temperature.

Gangadwala *et al*,(2003) , reported the esterification of acetic acid with butanol, acetic acid with glycerol and acetic acid with isobutanol in the presence of amberlyst catalyst respectively. Pseudohomogeneous, Eley-Rideal, Langmuir-Hinshelwood-Hougen-Watson (LHHW), and modified LHHW models were developed and tested from the data generated. The kinetics for the side-reaction etherification was also investigated. The equilibrium constant, which is independent of temperature ranging from 318 to 368 K, was found to be 4. In this same work, the synthesis of triacetine, starting from glycerol and acetic acid, using reactive chromatography on acidic polymeric resins was investigated. The obtained data was compared with the predictions of a mathematical model, in which kinetic and equilibrium parameters were estimated from the batch experiments mentioned above. It is known that reactive chromatography is an attractive method for chemical synthesis because chemical reactions and product separation occur simultaneously in the same unit.

2.1.10 Optimizing the Yield of Ester

Organic esters belong to a very important class of chemicals having applications as intermediates in the synthesis of fine chemicals, drugs, plasticizers, perfumes, food preservatives, cosmetics, pharmaceuticals, as solvents and chiral auxiliaries. In industry, the esterifications are generally carried out in the presence of hazardous, toxic and corrosive sulfuric acid and its derivatives or expensive ion exchange resins.

To optimise the yields of ester formation from equimolar amounts of alcohols and carboxylic acids, 2-15 molar equivalents of the condensing agents such as sulfuric acid, tosylchloride, triofluoroacetic anhydride, polyphosphate ester, dicyclohexyl cabodiimide, graphite etc., are generally employed. Heterogeneous acidic and superacid catalysts have proved to be useful in some reactions because of their activity, selectivity, reusability, non-corrosivity and virtual absence of effluent treatment which is associated with the homogeneous catalysts.(patent 6472555 , 2002).

Table 2.1 Physical and Chemical Properties of three Components Mixture. (Oxford Health and Safety Service Website, 2004)

Property	**Component**		
	Ethanoic acid	Butanol	Butylethanoate
Formular	CH_3COOH	$CH_3CH_2CH_2CH_2OH$	$CH_3COOCH_2CH_2CH_2CH_3$
Physical state	colourless liquid	colourless liquid	clear liquid
Molecular weight (g/mol)	60.05	74.12	102.13
Boiling point (^oC)	118-119	118	126
Melting point (^oC)	16.7	-90	-106
Specific gravity	1.05	0.81- 0.812	0.882
Flash point (^oC)	40	15	24
Stability	Stable	stable	Less stable
Density ($g/cm^{3)}$	1.049	0.81	0.882
Solubility in water	miscible	miscible	slightly soluble

2.2.1 Classification of clay

The following classification has proved to be a workable one. A major subdivision into amorphous and crystalline groups is made even though the amorphous components are relatively rare and of little importance (Mc Graw hill, 1982).

- Expanding structure such as montmorillonite group(montronite,saponite and hectorite).
- Crystalline groups e.g kaolinite group.
- None expanding structure e.g illite group.
- Regular mixed layer types e.g chlorolite group.

2.2.2 Montmorillonite Clay

Montmorillonite was discovered in 1847 in Montmorillon in the Vienne prefecture of France, more than 50 years before the discovery of bentonite in the US. It is found in many locations world wide and known by other names. (li and Zhang,2008). Minerals in this group are sometimes called smectite, and have a variable composition. The name montmorilonite is reserved for hydrated aluminosilicate species with little substitution. Many clay deposit contain large amount of montmorillonite. This type of clay is frequently called bentolite and commercially grade montmorillonite is also refered to as bentonite. This clay type has an essential characteristics. Its expanding structure, that is, the property of adsorbing variable amount of water between individual unit layers. Members of this type of clay shows considerable variation in the ratio of SiO_2 to Al_2O_3. There can be replacement of aluminium by iron and magnesium. The iron rich montmorilonite is called montonite, while the magnenium rich variety is known as saponite. The chemical formular is given as $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$

2.2.3 Uses of Montmorillonite Clay

Montmorillonite is used in the oil drilling industry as a component of drilling mud, making the mud slurry viscous which helps in keeping the drilling bit cool and removing drilled solids. It is also used as a soil additive to hold soil water in drought prone soils, to the construction of earthen dams and levees and to prevent the leakage of fluids. It is also used as a component of foundry sand and as a desiccant to remove moisture from air and gases.

Similar to many other clays, montmorillonite swells with the addition of water. However, some montmorillonites expand considerably more than other clays due to water penetrating the interlayer molecular spaces and concomitant adsorption. The amount of expansion is due largely to the type of exchangeable cation contained in the sample. The presence of sodium as the predominant exchangeable cat ion can result in the clay swelling to several times its original volume. Hence, sodium montmorillonite has come to stay as the major constituent in non-explosive agents for splitting rock in natural stone quarries in order to limit the amount of waste, or for the demolition of concrete structures where the use of explosive charges is unacceptable. This swelling property makes montmorillonite-containing bentonite useful also as an annular seal or plug for water wells and as a protective liner for landfills. Other uses include as an anti-caking agent in animal feed, in paper making to minimize deposit formation and as a retention and drainage aid component. Montmorillonite has also been used in cosmetics. Montmorillonite is known for its adsorbent qualities and has been used successfully in scientific trials to eliminate atrazine from water. (www.interscience wiley.com)

Finally it was found that natural montmorillonite is an efficient catalyst for the exclusive formation of esters from various alcohols in the presence of acetic acid and its activity is comparable with Cu^{2+} -exchanged K10 montmorillonite (patent 6472555,2002).

2.2.4 Kaolinite Clay

Kaolin Clay is the purest kind of clay because it is close to where its originally developed. In its raw state, it breaks apart easily when bent because the particles are not as worn as with earthenware. This group is a more extensively distributed clay mineral in acidic soil; than montmorilonite. Kaolinte has only one silica tetrahedral per sheet of alumina octahedral per layer. Thus, it is 1:1 type clay. Almost no substitution of Al^{3+} for Si^{4+}, Mg^{2+} for Al^{3+} has occurred in kaolinite; so the net negative charge (cation exchange capacity) is low. However, each layer has one plane of oxygen (O_2) replaced by hydroxyl (OH), which results in strong hydrogen(-H-) bonds to oxygen: planes of adjacent layer kaolinite limits have such strong hydrogen bonding that do not allow water to penetrate between the layers and have almost no swelling. These are the types of clay used porcelain pottery works because they do not shrink or swell (Raymond, 1990). The chemical formular of kaolinite clay is given as, $Al_2O_3.2SiO_2.2H_2O$.

2.2.5 Illite Group

Illite was first described for occurrences in the Maquoketa shale in Calhoun County, illnois,U.S.A, in 1937. The name was derived from its type location in Illinois. Illite is also called hydromica or hydromuscovite. However, illite clay is a non expanding clay-sized, micaceous mineral. Illite is a phyllosilicate or layered alumino- silicate. It is constituted by the repetation of tetrahedron- octahedron- tetrahedron (TOT) layers. The interlayer space is mainly occupied by poorly hydrated potassium cations responsible for the absence of swelling. Structurally, illite is quite similar to muscovite with slightly more silicon, magnesium, iron and water and slightly less tetrahedral aluminium and interlayer potassium. there is considerable ion substitution. it occurs as aggregates of small monoclinic grey to white crystal. Nevertheless, the cation exchange capacity (CEC) of illite is smaller than that of smectite but higher that that of kaolinite, typically around 20-30meq/100g (Mitchel, 1993).

2.2.6 Chlorite group

The name chlorite is from the greek word chloros, meaning green, in reference to its colour. This is a group of phyllosilicate minerals which can described by the following four endmember based on their chemistry via substitution of the following four elements in the silicates lattice; Mg, Fe, Ni, and Mn. In addition , zinc litium, and calcium species are known. The great range in composition results in considerable variation in physical, optical and X-ray properties. Similarly, the range of cheemical composition allows chlorite group minerals to exist over a wide range of temperature and pressure conditions. For this reason chlorite mineral are ubiquitous minerals within low and medium temperature metamorphic rocks, some igneous rocks, hydrothermal rocks and deeply buried sediments. Based on texture, chlorite is so soft that it can be scratched by a finger nail. The powder generated by sractching is green. It feels oily when rubbed between the fingers. The plates are flexible, but not elastic like mica. Research shows that chlorite group can be stable peridotite of the earth's mantle above the ocean lithosphere carried down by subduction. Chlorite is found in large boulders scattered on the ground surface. Some members of the chlorite group are; baileychlore, chamosite, clinochlore, cookeite, donbassite e.t.c. (Wikipedia encyclopedia, 2010).

2.3.1 Advantages Of Clay As Catalyst Over Other Forms Of Catalyst.

1. The use of clay as catalyst completely eliminates the use of expensive acetic anhydride as acetylating agent.

2. Acetic acid can be used as acetylating agent in place of the acetic anhydride for the acetylation of various substrates (aliphatic, aromatic, α,β-unsaturated, cyclic and heterocyclic alcohols).

3. Clays can be use as catalysts in place of hazardous and corrosive sulphuric, and expensive resins for the acetylation of various alcohols.

4. An eco-friendly process for the production of esters is developed.

5. The selectivity and yields obtained in this process are excellent.

6. The reactions are simple with shorter reaction time and simple workup procedure.

7. The support of the catalyst is cheap and abundantly available in nature.

8. The present process envisage no disposal problem as the catalyst can be used for several cycles. The catalyst can be subjected to four cycles while displaying consistent activity.

9. The present process is environmentally safe since there is no effluent disposable problem (patent 6472555, 2002).

2.3.2 Adsorption and Absorption Properties of Clay

The two words are similar but their differences are fundamental to understanding how clay minerals function and how clay works. Clays that have the ability to absorb and adsorb are called Living or Active clays, because they are capable of changing and exchanging (www.aboutclay.com 2008). Adsorption is the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. It is different from absorption, in which a substance diffuses into a liquid or solid to a solution. The term sorption encompasses both processes, while desorption is the reverse of process. Adsorbent are used usually in the form of spherical pellets rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10mm. They must have high abrasion resistance, high thermal stability and small pore diameters which result in high exposure capacity for adsorption, the adsorbents must have high distinct pore structure which enables fast transport of targeted molecules (Cussler, 1997). Adsorption also describes the process by which the charged particles of other substances combine with the charged particles on the outer surface of the clay molecule. The positively charged ions are attracted to the stronger negatively charged surfaces of the clay molecule. An exchange reaction occurs in which the clay mineral ions are swapped for the ions of the positively charged substance. The clay molecule is electrically satisfied and binds with the substances capturing them (www. aboutclay.com, 2008).

Absorption on the other hand is a slower and more complex process. All absorbent clays have a charge on their inner layers. This means that charged ions sit between the layers of the clay molecule surrounded by water molecules. The expanded clay attracts foreign substances that are absorbed and fill the spaces between the clay molecule's stacked layers. Absorbent clay will absorb positively charged ions and impurities and ignore negatively charged nutrients.

On a molecular level, Robert (2008), a mineralogist, pointed out that the Bentonite's minute particle size creates a large surface area in proportion to the volume used. "The greater the surface area, the greater its power to pick up positively charged particles of ions." He also stated that one gram of clay has a surface area of 800 square meters. Thus, the greater the surface area, the greater the power to pick up positively charged ions many times its own weight. Swelling clays of the right mineral composition have a great potential for absorption. The pH of Living Clay is 9.7, and thus it acts as an alkalizing agent for the body. The pH scale goes from 0 to 14, with 7 being neutral. Below 7 is acidic and above 7 is alkaline. Due to the homeostatic ability of clays, it helps to balance the body's pH level, naturally. Bentonite clay baths are increasingly popular for detoxifying, cleansing the skin and balancing the bodies pH levels (www.aboutclay.com 2008).

2.3.3 The Acidic Properties of Clays

Previous studies have shown that the presence of water influences the acidic properties of clays. For cat ion-exchanged clays, Bronsted acidity is mainly due to the dissociation of adsorbed water. This dissociation is induced by the polarizing power of the cation (e.g., $Al^{3+,}$ Fe^{3+}), which depends on the size and the charge of the ion. When the water content of a clay is reduced to less than approximately 5% by weight, the acidity increases, because polarization by the cat ion is less dissipated. Removing all of the water from the clay, by calcinations at a temperature above 200°C, results in a clear reduction in Bronsted acidity. The clay assumes a much more pronounced Lewis acid character, which is due to the transformation of Bronsted acidity into Lewis acidity (Theng, 1982).

Isomorphous substitution which is second source of charge on clay particle, is the substitution of one ion for another of similar size and often with lower positive valence.in clay structures, certain ions fits into some mineral lattice sites because of their convenient size and charge. Only during clay formation from soluble mineral ion and other ions of similar size and charge, if they are present ,occupy some of those sites. Dominantly, clays have Si^{4+} in tetrahedral sites and AI^{3+} in octahedral sites. Other ions present in large amounts during crystallization can replace some of the Al^{3+} and Si^{4+} cat ions. Substitution that are common are the Si^{4+} replaced by AI^{3+}, and even more extensive replacement of Al^{3+} by one or more of these Fe^{3+}, Fe^{2+},Mg^{2+} Zn^{2+}·Notice that, most substitution are ions with lower charge (less positive) than the ones being replaced. Since the total negative charge from the ions (the oxygen) remains unchanged, the lower positive charge because of substitution result in an excess negative charge at the location in the structure.

A different kind of acidity is due to H^+ located at exchange positions. The positive charge compensates for the negative charge of the layers induced by isomorphous substitution with lower-valence cat ions. The effect of calcining H^+ (exchanged) clays depends on the type of silicate layer. In the case of octahedral substituted clays (montmorillonite type), the protons will migrate into vacancies in the octahedral sheet, where they associate with lattice oxygens (Wright et al., 1972; Davidtz, 1976). In general, these protons are not accessible to catalysis, because the pore diameter of the hexagonal hole in the tetrahedral sheet is only 0.26nm (Barrer, 1978). After calcination, the acidic sites left will be situated at the edges. It can then be deduced that, the acidic properties are strongly dependent on the type of clay, the exchanged cat ion, and the H_2O content. (Theng ,1984).

The charge in clays comes from ionizable hydrogen ions and from isomophous substitution. Ionizable hydrogen ions are hydrogen from hydroxyl ion on clay ionize surfaces. The –AI-OH or -Si- OH portion of the clay ionizes the H^+ and leaves the un-neutralized negative charge on the oxygen -AL-O or –Si-O. The extension of ionized hydrogen depends on solution pH, where more ionization occurs in more alkaline solutions. Owing their Bronsted and Lewis acidities, clays, both in their natural and ion-exchanged forms, function as efficient catalysts for various organic transformations (Nku, 2004).

2.3.4 Purification of Natural Clays for use as Catalyst

Natural clays often contain quite large amounts of impurities, which should be removed to prevent interference with the catalytic function. As the variation in amount and type of impurities is as large as the variation in clay types, it is not possible to give here a specific purification recipe. Therefore, we limit ourselves to some general methods for clay purification. (Van Olphen, 1977).

Each purification method involves separation of coarse mineral impurities from the clay. This is best achieved by suspending the sample in water and allowing the large particles to settle. The clay particles can then be siphoned off (van Olphen, 1977). If the sample contains a relatively large amount of organic material, the dry material can be brought in contact with concentrated hydrogen peroxide. Several methods exist for the removal of inorganic impurities, for instance, carbonates and free ferric oxide can be removed by treatment with sodium acetate buffer solution and sodium dithionite/sodium citrate (Tzou, 1983).

2.3.5 Treatment and Activation of Clay

Some of the methods of treating clays and activating them for use as catalyst will be discussed as follows:

2.3.6 Cation Exchange Treatment

The first step in the activation procedure, which is required for both natural and synthetic clays, is to convert the clay into the desired ion form. In the case of metal ions, this can be done with relative ease by ion exchange using a concentrated solution of a suitable salt. The excess salt can be removed by repeated washings, employing a centrifuge, followed by dialysis. As an alternative, one can use ion-exchange resins in the suitable ion form. In contrast, it is not as easy to prepare the H^+ form of a clay via ion exchange with an acid or a resin in the H^+ form. The acid attacks the clay structure and part of the aluminum in the structure is transferred to ion-exchange sites. This effect occurs even under relatively mild conditions. For example, van Olphen (1977) found that the conversion of Wyoming bentonite (montmorillonite) with 0.01 N HCI at room temperature led to the occupation of 60% of the exchange sites by Al. The best way to overcome this acid leaching problem is to prepare the $NH4^+$ form via ion exchange, followed by a heat treatment at 550°C (Wright *et al.*, 1972). The $NH4^+$ ion will decompose, leaving an H^+ ion on the clay. By performing the heat treatment in air all of the residual organic material will be burnt off, which results in a ready-to-use acidic catalyst.

2.3.7 Acid Treatment

Modified clays exhibit attractive properties as solid acids. These modified clay minerals have attracted considerable attention as acid catalysts for petroleum refining and other acid-catalyzed reactions. Hydroxyl groups on the surface of the layer aluminosilicates are very important with respect to the use of these solids in catalysis or adsorption (Theng, 1984).

However, according toTzou,(1983), treatment of clays with acid has been reported to replace exchangeable cat ions with H ions and leaching A1 and other cations out of both tetrahedral and octahedral sites, but leaving the SiO_4 groups largely intact. Acid treatment produces an increase in surface area and acidity. The nature, strength and density of acidic sites on activated samples can be investigated by IR spectroscopy and differential scanning colorimetric using pyridine and ammonia as probe molecules.. The effect of temperature and concentration of the acid used for the preparation of the catalyst also have significant influence on the catalytic activity.

2.3.8 Thermal treatment

Calcinations of clay is known to increase the whiteness, hardness, improves the electrical properties and alters the shape and size of clay particles. It usually carried out a temperature of at 700°C. montmorillonite clay in particular can be calcined to produce arcillite, a porous calcined clay sold as a soil conditioner for playing fields and other soil products such as for use as bonsai soil as an alternative to akadama.(Wikipedia encyclopedia, 2010).

2.3.9 Catalyst regeneration

Clay can be separated from the reaction mixture by filtration, washed with hexane, dried at 80 °C for 24 h, and reused to study its activity for the esterification reaction which can be carried out in both conventional and semi-continuous reactors (Soumaya *et al*,2009).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials and Reagents

3.1.1: Materials

The clay samples used for production of clay catalyst were collected from three selected States in Nigeria, namely: Ohaukon, in Ebonyi State, Oyigbo, in Rivers State and Obajana, in Kogi State.

Table 3.1 and 3.2 shows the list of reagents and equipment used for the experiment.

Table 3.1 : Reagents used in Performing the Experiments

Reagents	Grade/Manufacturer
Sulphuric acid	BDH Chemical Ltd Poole England- General purpose reagent
Butanol	BDH Chemical Ltd Poole England
Ethanoic acid	BDH Chemical Ltd Poole England
Distilled water	Biochemistry Lab, FUT, Minna, Niger State
Sodium hydroxide	BDH Chemical Ltd Poole England
Phenolphthalein	BDH Chemical Ltd Poole England

Table 3.2 : Equipment used in Performing the Experiments.

Equipment	Specification/model	Manufacturer
Water bath	B$T	A SEARLE Company, England
pH meter	CRISON-MicropH 2000	Spain
Furnace	EL 195	FISHER UK
Gas- Liquid Chromatography	HP 6890	England
Oven	ISOTEM 175	FISHER UK
X-ray Diffractometer machine	Philips PW-1050/25	Germany
Magnetic heating stirrer	78HW-1	B.Bran Scientific and Instrument Company, England
Digital weighing balance	Brainwieght B300	OHAUS SCALE CORP.USA
X-ray fluorescence machine	CRX 2000	India

Other apparatus used for the experiment include: measuring cylinder, condenser, 250cm^3 three necked glass reactor, filter paper, funnel, burette, Sieves, mortar, throng, pipette, beakers, conical flasks, volumetric flasks, test tubes, filter cloth, filter paper, thermometer, stirring rod, spatula and stop watch.

3.2 Methods

3.2.1 Sample collection, purification and preparation

Activated clay catalysts were developed from samples of clay obtained from three selected States in Nigeria, namely: Ohaukon, Ebonyi State, Oyigbo, Rivers State and Obajana, Kogi State. The crude clay samples were crushed and purified by soaking in distilled water for 24hrs in order to allow organic and large particles to settle down. The clay particles which are usually < 2μm are then skimmed off and dried in an oven. The three clay samples were ground and sieved into different particle sizes, in the range of 1.96 – 75μm.

3.2.2 Thermal activation

All the three clay samples were thermally activated in a furnace at 673K, 973K and 1,273K for two hours respectively and used for the esterification reaction.

3.2.3 Chemical Activation

The three different samples of clay were chemically activated by adding 15g of clay to 150ml of sulphuric acid solution of different concentrations (1M, 2M and 3M), followed by heating in a water bath for 4hrs at 100°C with constant stirring. At the end of the reaction time, the samples were cooled to room temperature, collected over a filter paper and washed with double distilled water until it is free of excess acid having a pH of 2.5 – 4. The activated clays were dried in an oven at 110°C for 2hr and then calcined at 250°C for 2hrs. It was finally ground to a particle size of 1.96 -75μm range; ready for characterization and usage as catalyst for the esterification reaction (Achyut *et al*, 2010).

3.2.4 Kinetic Studies

Ethanoic acid and butanol (BDH grades) were used without further purification. A batch reactor consisting of a three-necked flat bottom flask of 250 cm^3 capacity, fitted with a reflux condenser and a sampling device was used, while heating and stirring of the mixture was achieved using a hot plate coupled with a magnetic stirrer. All the runs were carried out at high temperatures, catalyst loadings and mole ratios. Non linear least square method will be adopted to fit the kinetic data. The model parameters will also be estimated from the kinetic model.

3.3.2Film Resistance Controls

When the gas film resistance is much greater than the other resistances, then the rate of reaction is limited by the movement of reactant to the surface of the catalyst as given by the mass transfer coefficient, k_g.

3.3.3 Surface Phenomenon Controls

Due to the great industrial importance of catalytic reactions, considerable effort has been spent in developing theories from which kinetic equations can rationally be developed. The most useful for our purposes, supposes that the reaction takes place on an active site on the surface of the catalyst. Thus three steps are viewed to occur successively at the surface as listed below:

- A molecule is adsorbed onto the surface and is attached to an active site.
- It then reacts either with another molecule on an adjacent site (dual-site mechanism), with one coming from the main gas stream (single-site mechanism), or it simply decomposes while on the site (single site mechanism).
- Products are desorbed from the surface, which then frees the site.

In addition, all species of the molecules, free reactants, and free products as well as site-attached reactants, intermediates, and products taking part in these three processes are assumed to be in equilibrium. (levenspiel, 1981)

Rate expression derived from various postulated mechanisms are all of the form shown below:

$$rate\ of\ reaction = \frac{\text{(kinetic term)(driving force or displacement from equilibrium)}}{\text{(resistance term)}}$$

3.4 Langmuir-Hinshelwood-Hougen-Watson (LHHW) heterogeneous model

The kinetic model will be developed by considering the following assumptions from LHHW model:

- The adsorption sites are uniformly energetic.
- Catalyst surface consists of uniform active sites.
- The site activity is dependent on temperature and a molecule on one site does not influence what attaches onto a nearby site.
- The surface reaction is the rate-controlling step (Levenspiel , 1981).

The chemical reaction for the esterification of ethanoic acid with butanol is given as:

$$CH_3COOH + CH_3CH_2CH_2CH_2OH \rightleftharpoons CH_3COOCH_2CH_2CH_2CH_3 + H_2O \qquad 1$$

Where, ethanoic acid is denoted as H, butanol as OH, butylethanoate as E and Water as W.

A possible step by step mechanism for adsorption of reactants and desorption of products on the surface of the catalyst is represented as follows:

$$CH_3COOH + \text{X} \rightleftharpoons CH_3COOH\ldots\text{X} \quad \text{(Adsorption)} \qquad 2$$

$$CH_3CH_2CH_2CH_2OH + \text{X} \rightleftharpoons CH_3CH_2CH_2CH_2OH\ldots\text{X} \quad \text{(Adsorption)} \qquad 3$$

$CH_3COOH...X + CH_3CH_2CH_2CH_2OH...X \rightleftharpoons CH_3COOCH_2CH_2CH_2CH_3...X + H_2O...X$

(Surface reaction) 4

$CH_3COOCH_2CH_2CH_2CH_3..X + H_2O..X \rightleftharpoons CH_3COOCH_2CH_2CH_2CH_3 + H_2O + 2X$

(Desorption reaction) 5

3.4.1 Adsorption of Reactants on the Surface of the Catalyst

For ethanoic acid

$$r_a = k_a C_H(\hat{C}_m - \hat{C}) - k_a'\hat{C}_H \quad 6$$

Where $(\hat{C}_m - \hat{C}) = \hat{C}_V$, stated as follows:

$\hat{C}_m$ = Total concentration of the surface of the catalyst.

$\hat{C}$ = Concentration of the occupied sites on the catalyst.

$\hat{C}_V$ = Concentration of the vacant sites on the catalyst.

C_H = Concentration of the sites occupied by ethanoic acid molecules

$$r_a = k_a C_H \hat{C}_V - k_a'\hat{C}_H \quad 7$$

Let $k_a' = \frac{k_a}{K_H}$ 8

Substitute 8 into equation 7

$$r_a = k_a C_H \hat{C}_V - \frac{k_a}{K_H}\hat{C}_H$$

$$r_a = k_a(C_H \hat{C}_V - \frac{1}{K_H}\hat{C}_H)$$

At equilibrium $r_a = 0$

$$k_a\left(C_H\hat{C}_V - \frac{1}{K_H}\hat{C}_H\right) = 0$$

Divide through by k_a

$$C_H\hat{C}_V - \frac{1}{K_H}\hat{C}_H = 0$$

$$(\hat{C}_H)_{\mathrm{eq}} = K_H C_H \hat{C}_V \qquad 9$$

Therefore the expression for net rate of adsorption for ethanoic acid on the surface of a catalyst is given by equation (9)

Similarly the net rate of adsorption for butanol on the surface of a catalyst will be express as:

$$(\hat{C}_{OH})_{\mathrm{eq}} = K_{OH} C_{OH} \hat{C}_V \qquad 10$$

3.4.2 Surface Reaction

The mechanism which is assumed for the surface reaction process will depend on the nature of reaction as shown below:

$$CH_3COOH + CH_3CH_2CH_2CH_2OH \rightleftharpoons CH_3COOCH_2CH_2CH_2CH_3 + H_2O$$

Note that the reaction at the surface is between adsorbed molecule of both CH_3COOH and $CH_3CH_2CH_2CH_2OH$ on adjacent active sites.

The rate of the forward reaction at the surface is:

$$r_s = k_s \hat{C}_H \frac{\hat{C}_{OH}}{\hat{C}_m} \qquad 11$$

The reverse rate is propotional to the pairs of centres formed by the adsorbed product of butylethanoate and water ($CH_3COOCH_2CH_2CH_2CH_3$ and H_2O) molecules at adjacent sides to each other.

$$r_s' = k_s' \hat{C}_E \frac{\hat{C}_W}{\hat{C}_m} \qquad 12$$

Combining equation 11 and 12 gives the net surface rate by the mechanism of the surface reaction as shown below:

$$r_s = k_s \hat{C}_H \frac{\hat{C}_{OH}}{\hat{C}_m} - k_s' \hat{C}_E \frac{\hat{C}_W}{\hat{C}_m} \qquad 13$$

Where $k_s' = \frac{k_s}{K_S}$ in the above expression

$$r_s = k_s \hat{C}_H \frac{\hat{C}_{OH}}{\hat{C}_m} - \frac{k_s}{K_S} \hat{C}_E \frac{\hat{C}_W}{\hat{C}_m}$$

The net surface reaction rate for the forward and backward reaction is given as:

$$\mathrm{r_s} = \frac{k_S}{\hat{C}_m} \left(\hat{C}_H \, \hat{C}_{OH} - \frac{1}{K_S} \hat{C}_E \, \hat{C}_W\right) \qquad 14$$

If the surface reaction is intrinsically fast with respect to the others, then the process would occur at equilibrium. Then $\mathrm{r_s} = 0$

equation 14 becomes:

$$K_S = \left(\hat{C}_E \hat{C}_W / \hat{C}_H \hat{C}_{OH}\right)_{eq} \qquad 15$$

3.4.3 Desorption of Product

As earlier shown, the mechanism for the desorption of ester and water as products from the surface of the catalyst may be represented as:

$$CH_3COOCH_2CH_2CH_2CH_3 ..X \rightleftharpoons CH_3COOCH_2CH_2CH_2CH_3 + X$$

$$H_2O..X \rightleftharpoons H_2O + X$$

For butyl ethanoate

$$r_d = k'_d \hat{C}_E - k_d C_E \left(\hat{C}_m - \hat{C}\right) \qquad 16$$

Where $\left(\hat{C}_m - \hat{C}\right) = \hat{C}_V$

$$r_d = k'_d \hat{C}_E - k_d C_E \hat{C}_V \qquad 17$$

Let $k'_d = \frac{k_d}{K_E}$ 18

Substitute 18 into equation (17)

$$r_d = \frac{k_d}{K_E} \hat{C}_E - k_d C_E \hat{C}_V$$

$$r_d = k_d(\frac{1}{K_E}\hat{C}_E - C_E\hat{C}_V)$$

At equilibrium $r_d = 0$

$$k_d(\frac{1}{K_E}\hat{C}_E - C_E\hat{C}_V) = 0$$

Divide through by k_d

$$\frac{1}{K_E}\hat{C}_E = C_E\hat{C}_V$$

$$(\hat{C}_E)_{\mathrm{eq}} = K_E C_E \hat{C}_V \qquad 19$$

Similarly, the equilibrium concentration of water (H_2O) will be:

$$(\hat{C}_W)_{\mathrm{eq}} = K_W C_W \hat{C}_V \qquad 20$$

3.4.4 Surface Reaction as the Controlling Step

The concentration of $\hat{C}_H$, $\hat{C}_{OH}$, $\hat{C}_{E,}$ and $\hat{C}_W$ at equilibrium for adsorption and desorption steps are listed in equation 9, 10, 19 and 20 respectively.

Substituting the equilibrium concentrations in equation 9,10,19 and 20 into eqution 14, we will have

$$\mathrm{r_s} = \frac{k_S}{\hat{C}_m}\left[(K_H C_H \hat{C}_V)(K_{OH} C_{OH} \hat{C}_V) - \frac{1}{K_s}(K_E C_E \hat{C}_V)(K_W C_W \hat{C}_V)\right] \qquad 21$$

But, $\hat{C}_m = \hat{C}_H + \hat{C}_{OH} + \hat{C}_E + \hat{C}_W + \hat{C}_V$ 22

Where, $\hat{C}_m$ is the total concentration of the catalyst.

$$\text{Therefore, } \hat{C}_V = \frac{\hat{C}_m}{1 + K_H C_H + K_{OH} C_{OH} + K_E C_E + K_w C_w} \qquad 23$$

Substituting for $\hat{C}_V$ in equation 21,we have

$$r_s = \frac{k_s \hat{C}_m \left[K_H K_{OH} C_H C_{OH} - (\frac{K_E K_W}{K_S}) C_E C_W \right]}{[1 + K_H C_H + K_{OH} C_{OH} + K C_E + K_W C_W]^2} \qquad 24$$

The overall equilibrium constant K for the reaction as shown in equation 15 will be represented as:

$$K_{overall} = (C_E C_W / C_H C_{OH}) \qquad 25$$

Substituting for each of this parameter in equation 25 , which are obtained from their equilibrium concentrations (equation 9,10,19 and 20), we will have

$$K = \frac{\hat{C}_E}{K_E \hat{C}_V} \times \frac{\hat{C}_W}{K_W \hat{C}_V} \times \frac{K_H \hat{C}_V}{\hat{C}_H} \times \frac{K_{OH} \hat{C}_V}{\hat{C}_{OH}}$$

Rearranging the above equation we will have

$$K = K_H K_{OH} / K_E K_W \left(\hat{C}_E \hat{C}_W / \hat{C}_H \hat{C}_{OH} \right)_{eq} \qquad 26$$

Recall that from equation 15, $K_S = \left(\frac{\hat{C}_E \hat{C}_W}{\hat{C}_H \hat{C}_{OH}} \right)_{eq}$

Replace $\left(\frac{\hat{C}_E\hat{C}_W}{\hat{C}_H\hat{C}_{OH}}\right)_{eq}$ by k_s in equation 26, yields

$$K = (K_H K_{OH}/K_E K_W).K_s \qquad 27$$

Rearranging equation 26 gives

$$\frac{K_E K_W}{K_s} = \frac{K_H K_{OH}}{K}$$

Then substitute for $\frac{K_E K_W}{K_s}$ on the right hand side of equation 24, we will have

$$r_s = \frac{k_s\hat{C}_m\left[K_H K_{OH} C_H C_{OH} - (\frac{K_H K_{OH}}{K}) C_E C_W\right]}{[1+K_H C_H+K_{OH}C_{OH}+K_E C_E+K_W C_W]^2} \qquad 28$$

Therefore, the final proposed global rate equation in accordance to Langmuir Hinshwood Houston Watson (LHHW) model, for the esterification reaction between ethanoic acid and butanol in the presence of clay catalyst will be given as:

$$r_s = \frac{k_s\hat{C}_m K_H K_{OH}\left[C_H C_{OH} - (\frac{1}{K}) C_E C_W\right]}{[1+K_H C_H+K_{OH}C_{OH}+K_E C_E+K_W C_W]^2} \qquad 29$$

Concentrations (C) can also be expressed as mole fraction (x), and $\hat{C}_m$ as m_{cat} (mass of catalyst) as shown in equation 30, which represent the final form of the LHHW model for this process.

$$r_s = \frac{m_{cat}k_s K_H K_{OH}\left[x_H x_{OH} - (\frac{1}{K}) x_E x_W\right]}{[1+K_H x_H+K_{OH}x_{OH}+K_E x_E+K_W x_W]^2} \qquad 30$$

From the LHHW model as shown in equation 30, $\mathrm{m_{cat}}$ is the mass of catalyst, x_i is mole fraction of the components or species , K_i is the equilibrium constant for each components , K is the overall reaction equilibrium constant and K_s is equilibrium rate constant for the surface reaction.

The steps used in resolving the final model equation through the use of non linear least square method that led to obtaining the resultant equations solved by MATLAB are itemized below:

- Linearize the model equation to take the form $y = mx + C$ 31
- Introduce an error term R and square the expression so that the sum of errors is minimum.
- Obtain the partial derivatives of the linearized model equation with respect to the various equilibrium adsorption contants, $K_{H,}\ K_{OH}\ , K_{E,}\ K_W\ and\ K_{s.}$
- The five equations that were obtained from the resultant model equation after resolving using the least square method was then solved using MATLAB software.

Also the kinetic constant parameter such as activation energy and pre-exponential factor will be obtained from Arrhenius equation as shown below:

$$K = A_0\, e^{\frac{-E}{RT}} \qquad 32$$

Where K is rate contaant, A_0 is exponential factor and E is activation energy.

CHAPTER FOUR

4.0 RESULTS

4.1 Experimental Results

This chapter presents the characterization results of Ohaukon montmorillonite clay and the experimental results obtained by varying the variation of temperature, catalyst concentration and mole ratio during the esterification reaction between butanol and ethanoic acid, catalyzed by three Nigerian clays; as well as the estimated kinetic parameters.

Table 4.1 shows the elemental percentage composition of both raw and acid activated Ohaukon montmorillonite clay as presented by X-ray fluorescence machine.

Table 4.1 X-Ray Fluorescence Compositional Analysis

	Elemental Composition, %						
Clay Samples	AI	Si	Mg	Ca	Ti	Sr	Fe
Raw Ohaukon montmorillonite	14.6	41.03	2.99	6.03	1.41	0.128	31.57
Acid activated Ohaukon mont.	8.4	72.58	1.10	0.583	2.77	.029	11.8

4.2 Effect of Temperature Variation

Preliminary reaction runs were carried out at 328K, 338K and 348K to determine the effect of temperature at 0% catalyst concentration and 3% catalyst concentration respectively, in-order to deduce the values of activation energy for reactions with catalyst and without catalyst loading.

Figure 4.3 shows the effect of temperature variation (328K, 338K, and 348K) at 0% catalyst concentration for the esterification reaction.

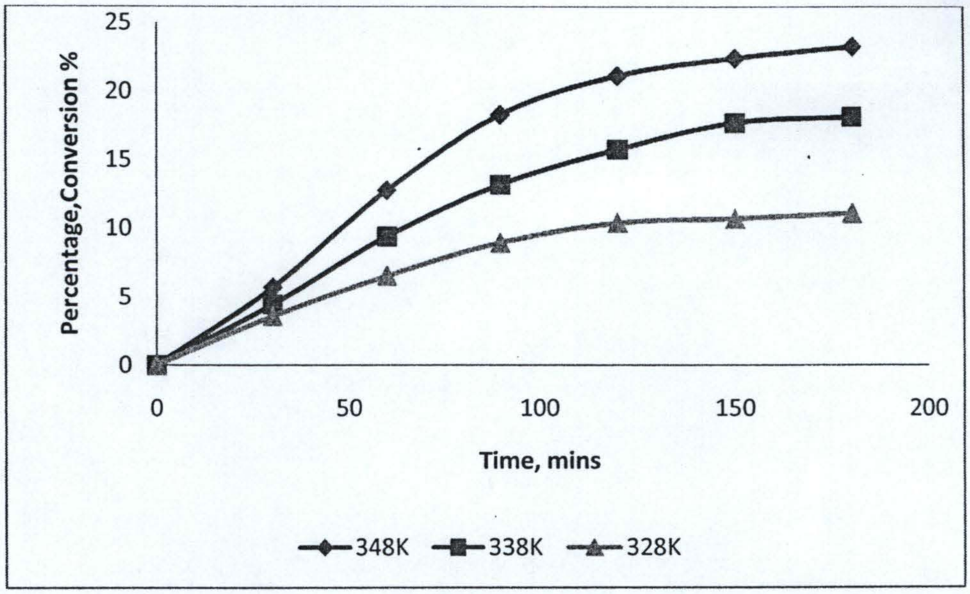


Fig.4.3Effect of temperature at 0% catalyst concentration

Figure 4.4 shows the plot of values of $1/x_H$ against time for the determination of the rate constants (K) as the gradients of each plot for 0% catalyst concentration ranging from 328K – 348K depicting a second order kinetic.

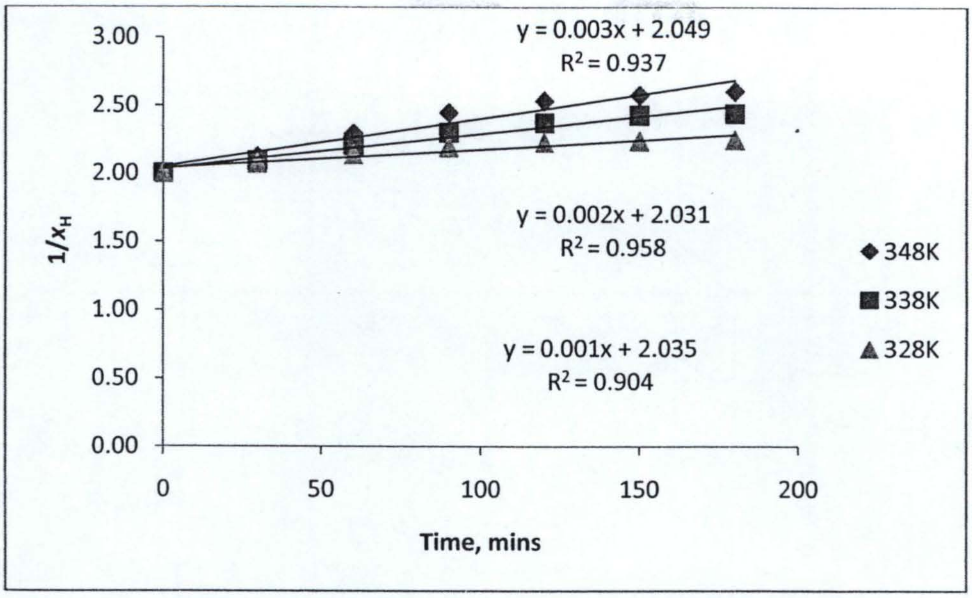


Fig4.4: Plot of $1/x_H$ against time

Table 4.2 shows the kinetic rate constant at different temperatures for 0% catalyst concentration.

Table 4.2 : Kinetic rate constant at different temperatures for 0% catalyst concentration

Temperature (^oK)	**K (min^{-1})**	**$T^{-1}(k^{-1})$**	**InK (min^{-1})**
328	1.0×10^{-3}	3.05×10^{-3}	-6.90779
338	$2.0.0\times10^{-3}$	2.96×10^{-3}	-6.21461
348	3.0×10^{-3}	2.87×10^{-3}	-5.80914

Figure 4.5 is the plot of InK against the reciprocal of the temperatures which described the Arrhenius equation for the deduction of activation energy and exponential factor.

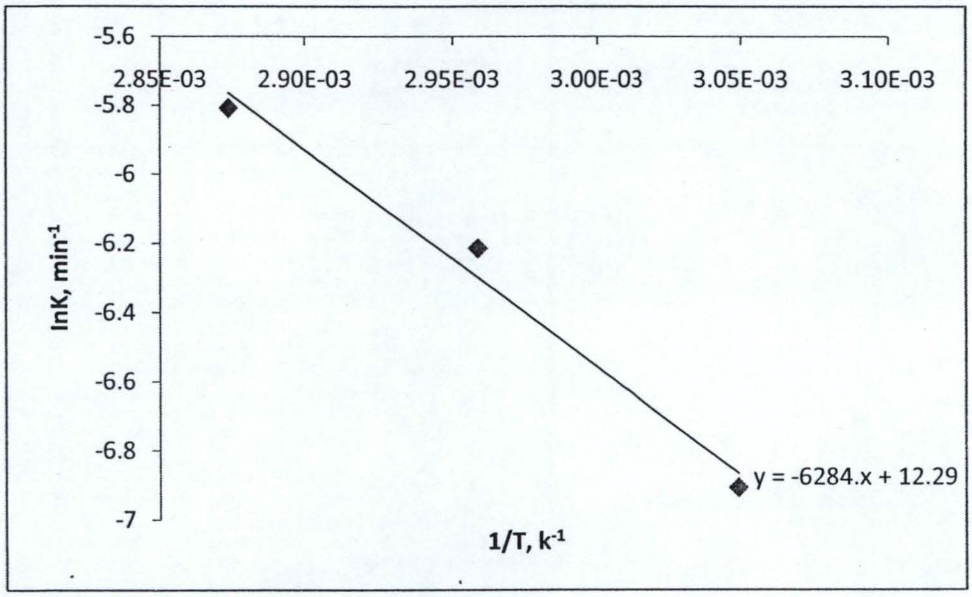


Fig.4.5: Plot of InK versus 1/T

Figure 4.6 shows the effect of temperature variation (328K, 338K, and 348K) at 3% catalyst concentration for the esterification reaction.

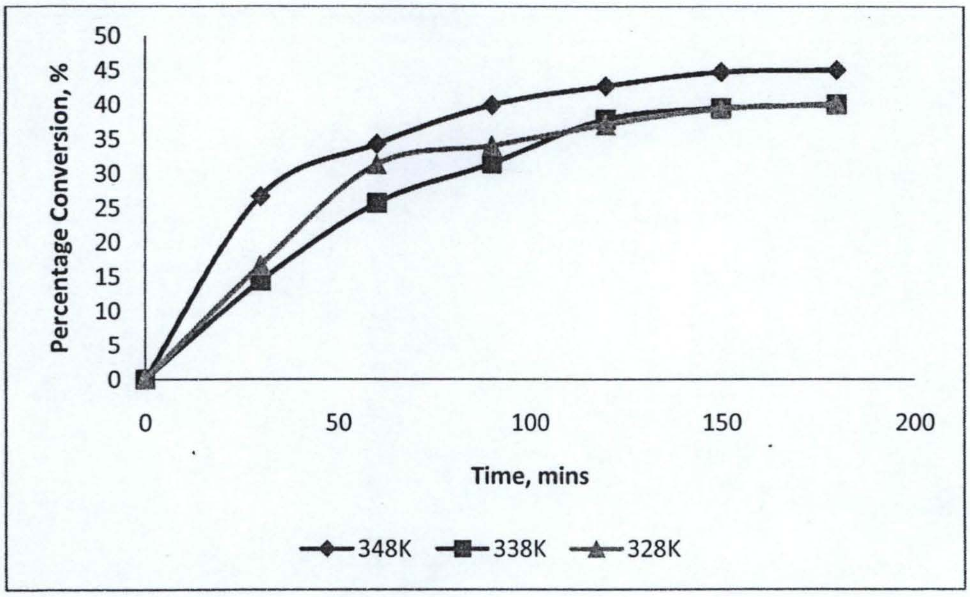


Fig4.6: Effect of temperature at 3% catalyst.

Figure 4.7 shows the plot of values of $1/x_H$ against time for the determination of the rate constants (K) as the gradients of each plot for 3% catalyst concentration ranging from 328k - 348k depicting a second order kinetic.

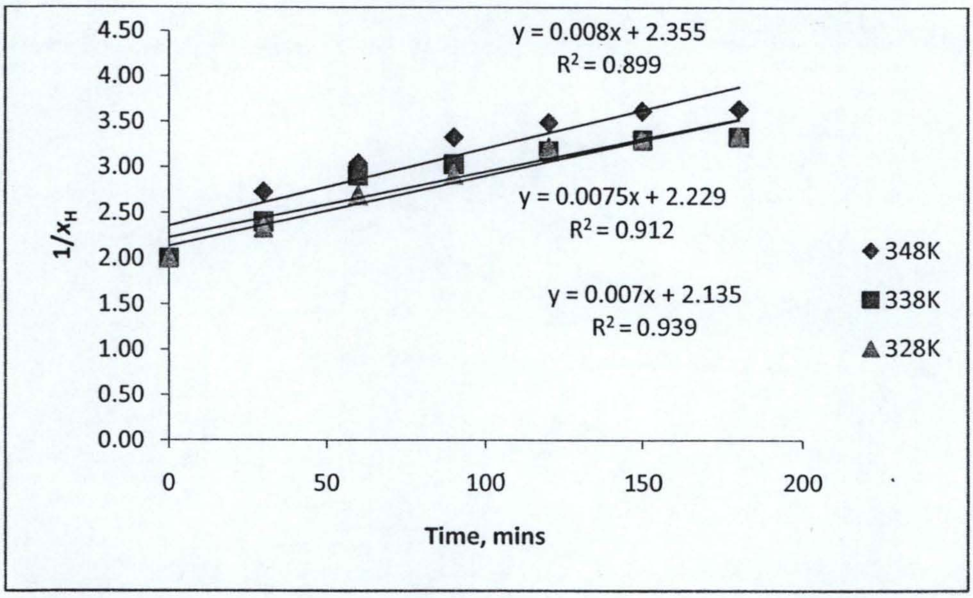


Fig. 4.7: Plot of values of $1/x_H$ against time

Table 4.3 shows the kinetic rate constant at different temperatures for 3% catalyst concentration.

Table 4.3 : Kinetic rate constant at different temperatures for 3% catalyst concentration

Temperature (^oK)	K (min^{-1})	$T^{-1}(k^{-1})$	InK (min^{-1})
328	7.0×10^{-3}	3.05×10^{-3}	-4.96185
338	$7.5.0\times10^{-3}$	2.96×10^{-3}	-4.89285
348	8.0×10^{-3}	2.87×10^{-3}	-4.82831

Figure 4.8 is the plot of InK against the reciprocal of the temperatures which described the Arrhenius equation for the deduction of activation energy and exponential factor.

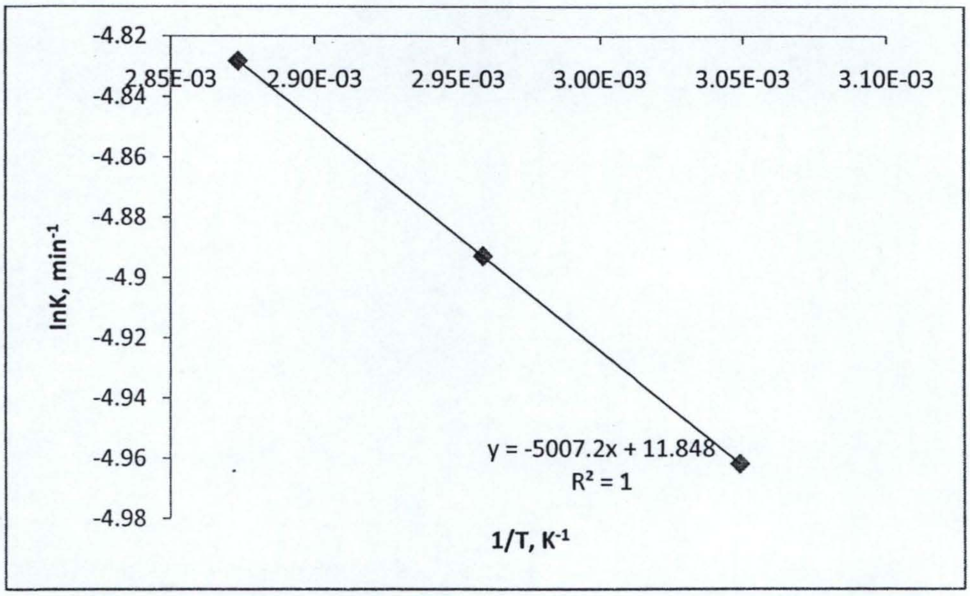


Fig.4.8: Plot of InK versus 1/T

4.3 Effect of Variation of Catalyst Concentration

Figure 4.9 to 4.11 shows the effect of variation of catalyst concentration on the percentage conversion of ethanoic acid for thermally activated Ohaukon, Obajana and Oyigbo clay at 348K.

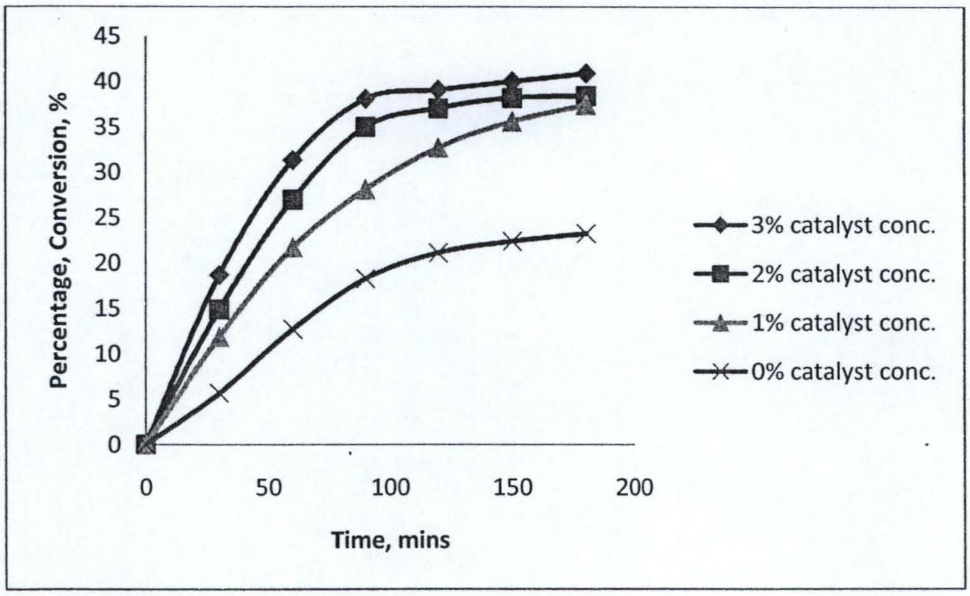


Fig. 4.9: Effect of catalyst concentration on % conversion of ethanoic acid using thermally activated Ohaukon clay at 348K.

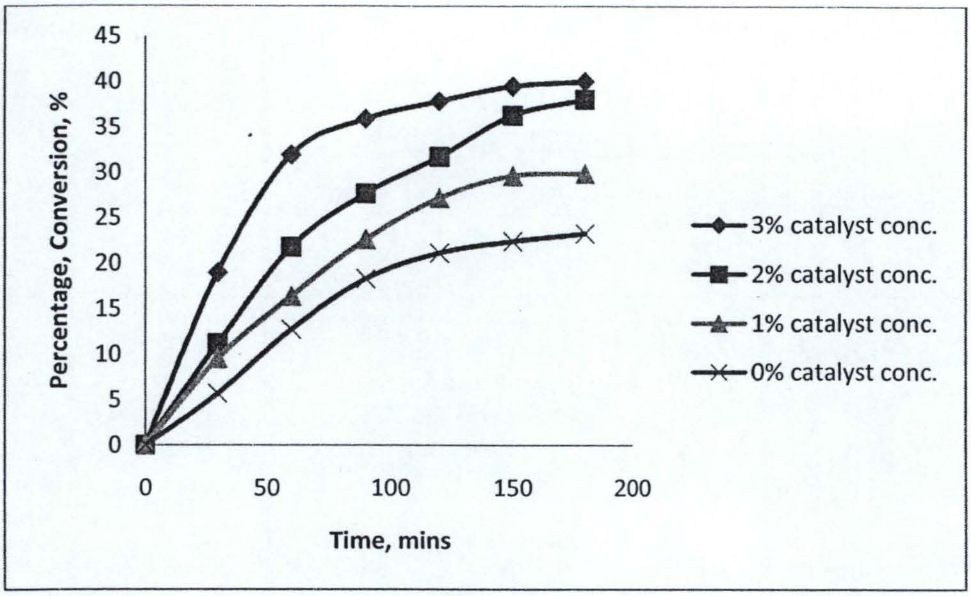


Fig. 4.10: Effect of catalyst concentration on % conversion of ethanoic acid using thermally activated Obajana clay at 348K.

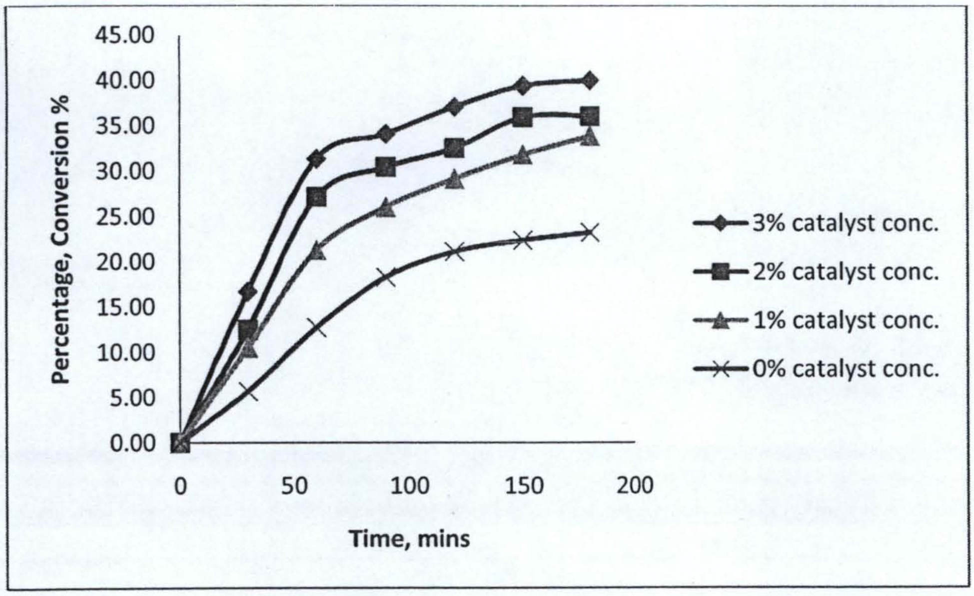


Fig.4.11: Effect of catalyst concentration on % conversion of ethanoic acid using thermally activated Oyigbo clay at 348K.

Figure 4.12 to 4.14 shows the effect of variation of catalyst concentration on the percentage conversion of ethanoic acid for acid activated Ohaukon, Obajana and Oyigbo clay at 348K.

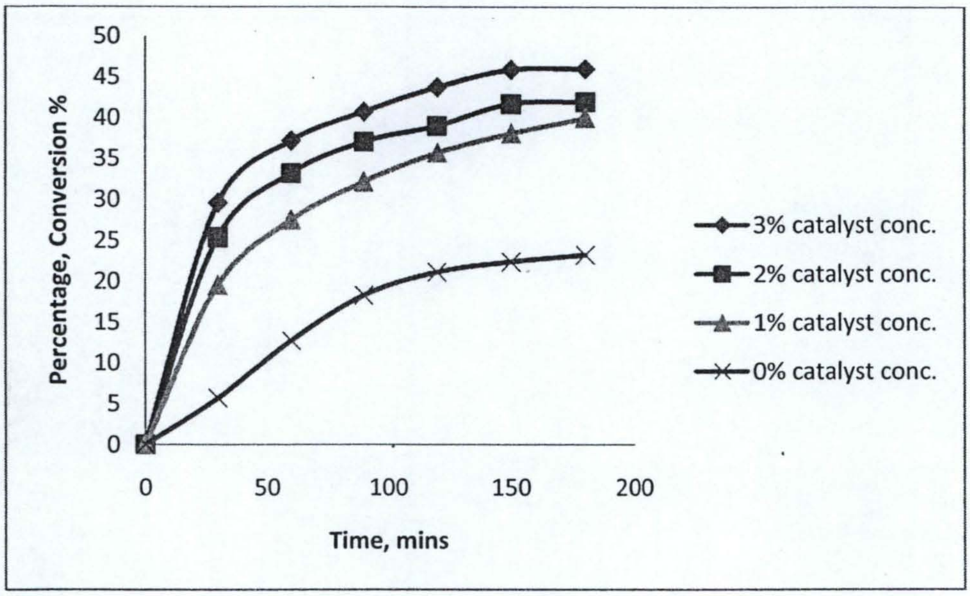


Fig.4.12: Effect of catalyst concentration on % conversion of ethanoic acid using acid activated Ohaukon clay at 348K.

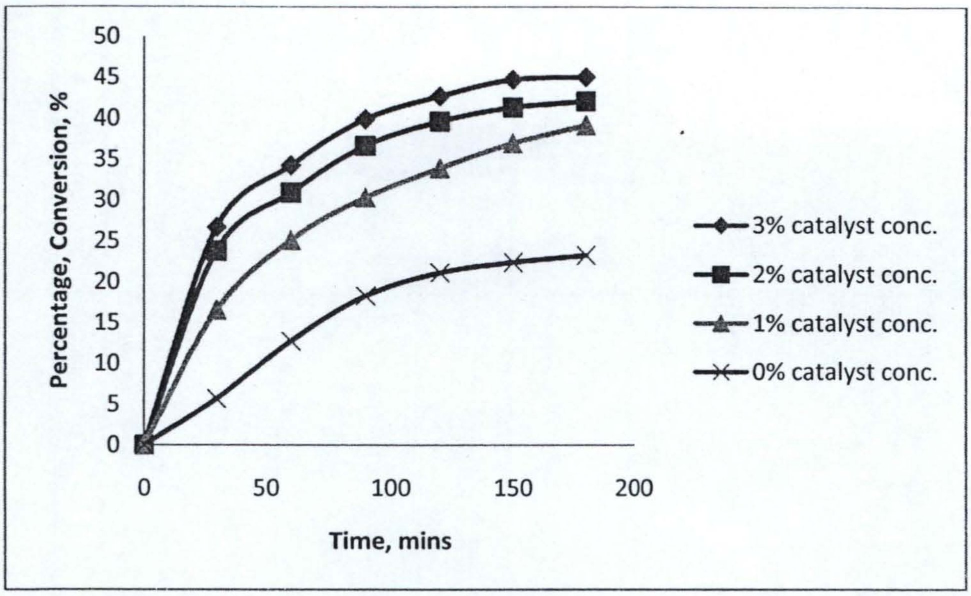


Fig.4.13: Effect of catalyst concentration on % conversion of ethanoic acid using acid activated Obajana clay at 348K.

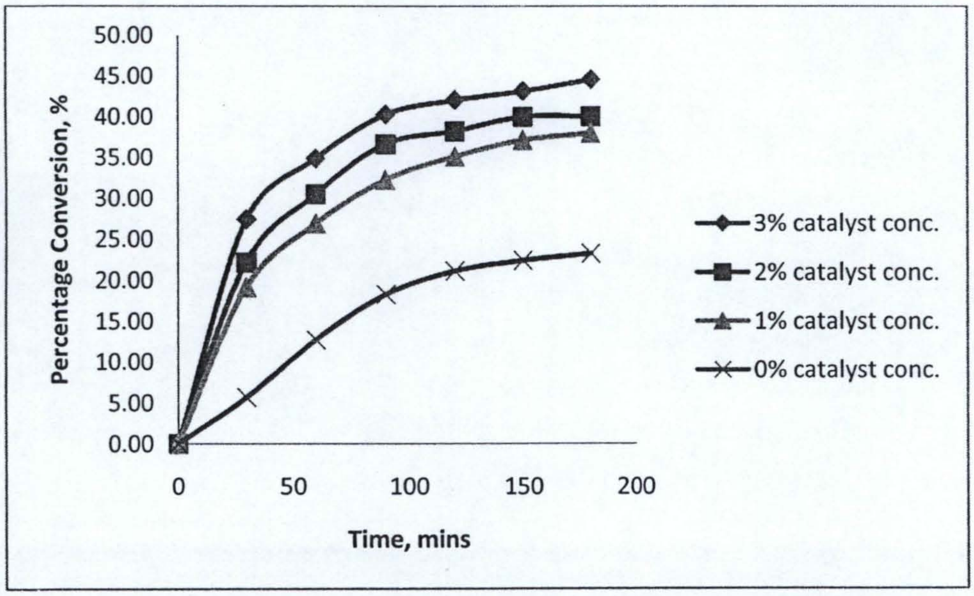


Fig.4.14: Effect of catalyst concentration on % conversion of ethanoic acid using acid activated Oyigbo clay at 348K.

4.4 Effect of Mole Ratio Variation

Figure 4.15 to 4.17 shows the effect of variation of mole ratio on the percentage conversion of ethanoic acid for thermally activated Ohaukon, Obajana and Oyigbo clay at 348K and 3% catalyst concentration.

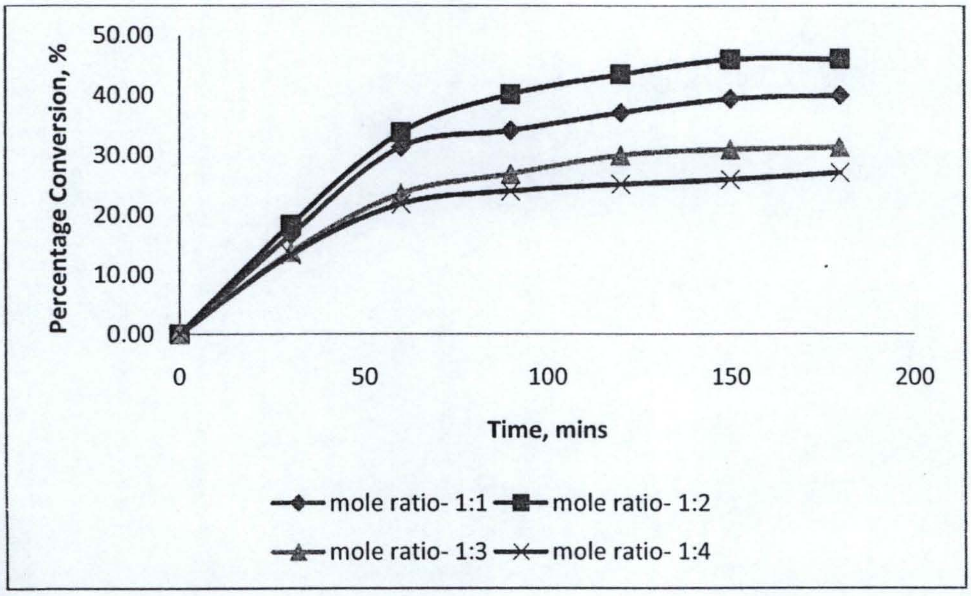


Fig.4.15: Effect of mole ratio on % conversion of ethanoic acid using thermally activated Ohaukon clay at 348K and 3% catalyst concentration.

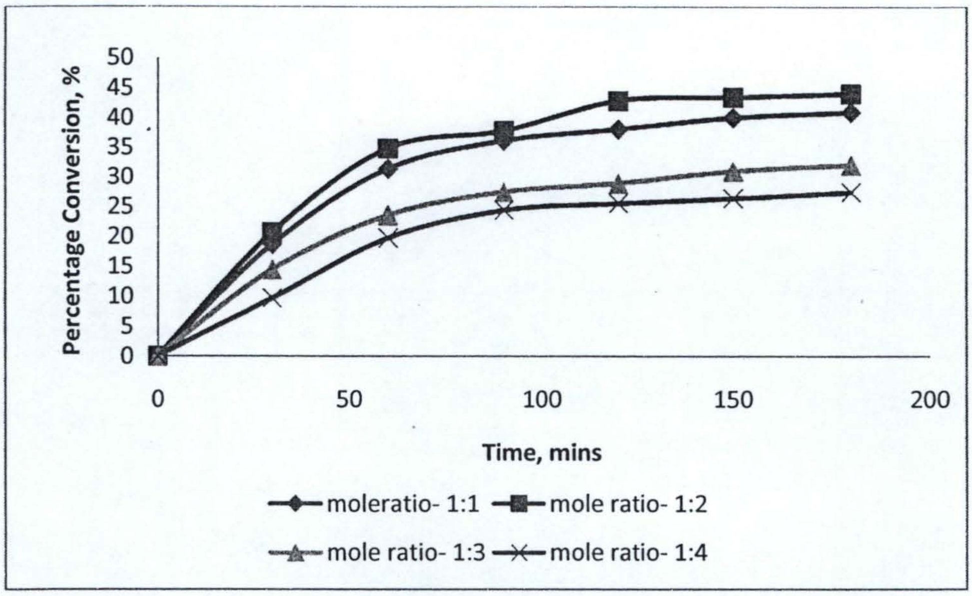


Fig.4.16: Effect of mole ratio on % conversion of ethanoic acid using thermally activated Obajana clay at 348K and 3% catalyst concentration.

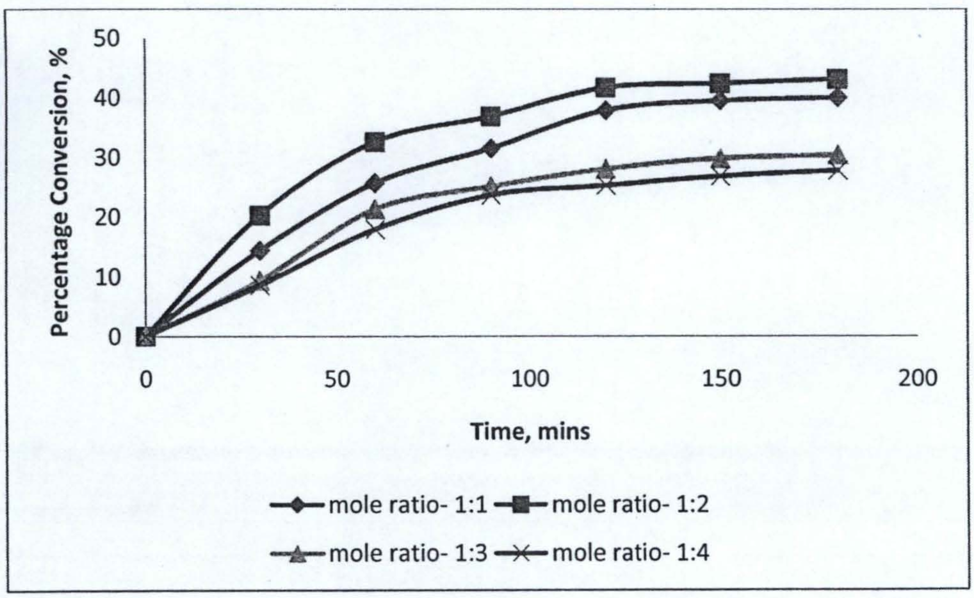


Fig.4.17: Effect of mole ratio on % conversion of ethanoic acid using thermally activated Oyigbo clay at 348K and 3% catalyst concentration.

Figure 4.18 to 4.20 shows the effect of variation of mole ratio on the percentage conversion of ethanoic acid for acid activated Ohaukon, Obajana and Oyigbo clay at 348K and 3% catalyst concentration.

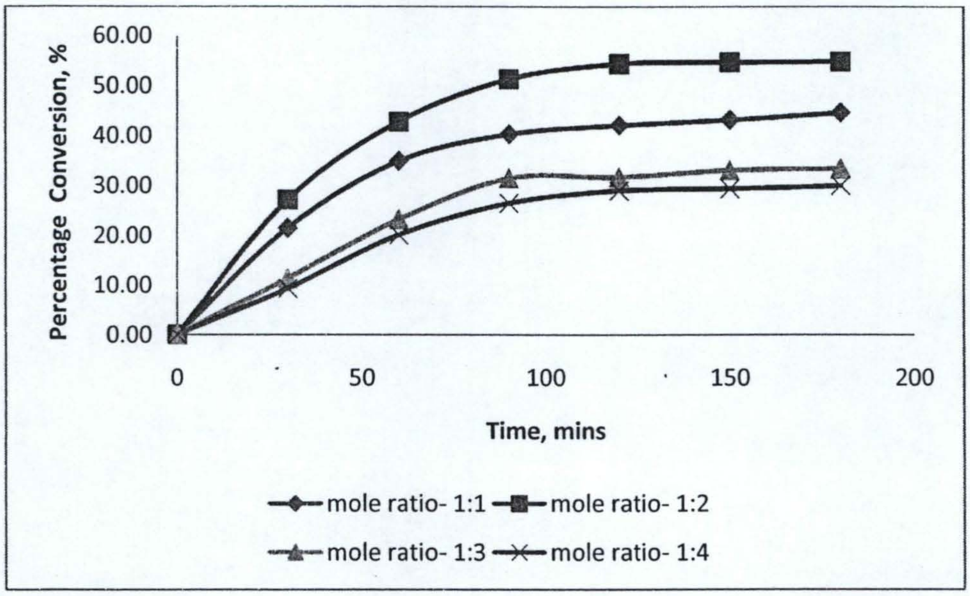


Fig.4.18: Effect of mole ratio on % conversion of ethanoic acid using acid activated Ohaukon clay at 348K and 3% catalyst concentration.

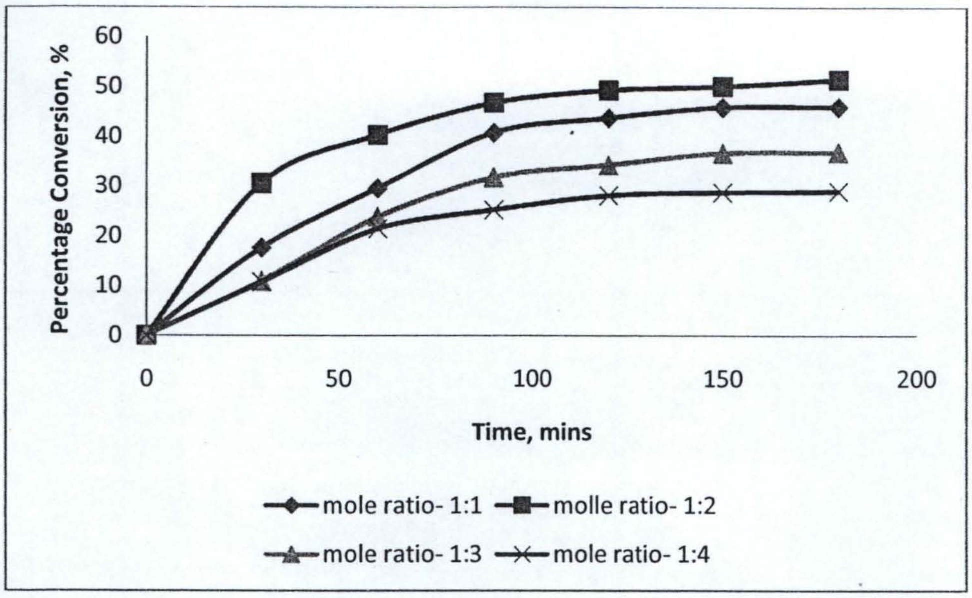


Fig.4.19: Effect of mole ratio on % conversion of ethanoic acid using acid activated Obajana clay at 348K and 3% catalyst concentration.

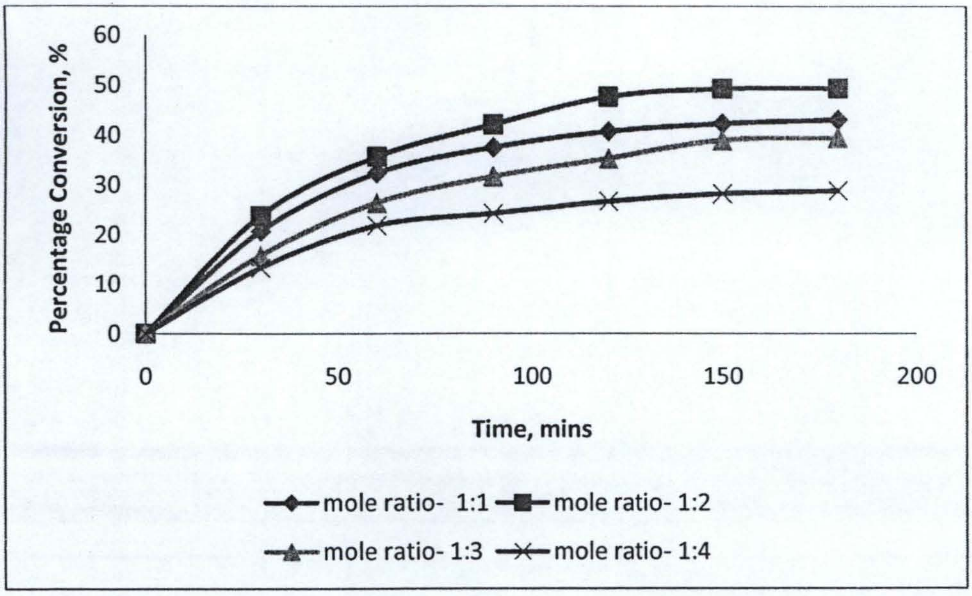


Fig.4.20: Effect of mole ratio on % conversion of ethanoic acid using acid activated Oyigbo clay at 348K and 3% catalyst concentration.

Using the rate expression below for LHHW model as shown in equation 30,

$$r_s = \frac{\mathrm{m_{cat}}\mathrm{k_s} k_H K_{OH}\left[x_H x_{OH} - (\frac{1}{K}) x_E x_W\right]}{[1+\mathrm{k_H}X_\mathrm{H}+\mathrm{k_{OH}}X_\mathrm{OH}+\mathrm{k_E}X_\mathrm{E}+\mathrm{k_W}X_\mathrm{W}]^2}$$

The kinetic model parameters were estimated using the non linear least square method with the help of MATLAB software. The kinetic data with the highest ethanoic acid conversion from the esterification reaction at 348K using 3 % catalyst concentration (acid activated Ohaukon clay) and at an ethanoic acid to butanol ratio of 1:2 was used. These parameters are shown on Table 4.4:

Table 4.4: Summary of the Kinetic and Adsortion Parameters from LHHW Model. .

Kinetic Parameter	Unit	Value
Activation energy for 0% catalyst loading (E_0)	KJ/mol	52.25
Activation energy for 3% catalyst loading (E)	KJ/mol	41.63
Pre-exponential factor for 0% catalyst loading (A_0)	Kmol/g.min	217.51
Pre-exponential factor for 3% catalyst loading (A_0)	K mol/g.min	139.78
Overall Equilibrium constant (K_E)	——	4.19
Adsorption constant for ethanoic acid K_H	L/mol.min	3.3138
Adsorption constant for butanol K_{OH}	L/mol.min	0.5059
Adsorption constant for butylethanoate K_E	L/mol.min	1.9743
Adsorption constant for water acid K_W	L/mol.min	0.1559
Adsorption constant for catalyst surface K_s	L/mol.min	0.3119

CHAPTER FIVE

5.0 DISCUSSION, CONCLUSION AND RECOMMENDATION

5.1 Discussion of Results

5.1.1 Effect of Acid Treatment as shown on the X-Ray Fluorescence Result of Ohaukon Clay.

Comparing the elemental analysis on Table 4.1 of the crude and acid activated monmorillonite Ohaukon clay, it is apparent that the acid-activation process on the clay sample has brought about a significant change on the percentage of its chemical composition. Table 4.1 also indicates that the composition of metal components decreased as a result of the acid treatment. This shows that acid activation of the clay has dissolved the metal components to form acid cation. According to Meesuk and Vorasith, (2006), it implies that the acid activation has enhanced the zeolitic properties of the clay since the ratio of Si-Al was increased after acid activation treatment. Furthermore, when montmorillonite clay undergoes acid activation process, the acid dissolves the octahedral sheets and acid cations moves to the interlayer of the clay and replaces the metal components such as Fe^{2+},Ca^{2+} and Mg^{2+}.

5.1.2 Effect of Acid Treatment as shown on the X-Ray Diffractogram Result of Ohaukon Clay

Figure 4.1 shows clearly the diffractogram features of crude montmorillonite clay which usually peaks at the left hand side of the diffractogram. The left most peaks on the diffractogram decreases when montmorillonite clays are treated with acid. These peaks represent the presence of bentonite in the clay sample. Bentonite, in fact is a mineral with high content of smectite, and montmorillonite is the most widespread smectite in nature.These attributes are synonymous with Ohaukon montmorillonite clay. While the result from Figure 4.2 shows that the acid activation process has led to large reduction of the montmorillonite peaks. This is due to the acid attack on some of the octahedral layers of Ohaukon clay to form acid cations. This is in conformity with the report of Djoufac *et al*,(2004).

5.1.3 Effect of the reaction temperature

Reactions were carried out at 328, 338 and 348K to determine the effect of temperature on conversion using three clay catalyst samples at 0% and 3 % loading. It was seen that higher temperatures gave greater conversions for the three clay catalysts. The maximum conversions were obtained at 348K. Thus an increase in temperature generally favours the forward reaction. This is due to increase in kinetic collision between the molecules, as also confirmed by Igbokwe *et al*,(2008). Furthermore, literature has it that in esterification reaction, significant yield of ester is produced for every 10^0C rise in temperature (Wikipedia encyclopedia, 2010).

5.1.4 Effect of catalyst concentration

The effect of variation in catalyst concentrations of 1 %, 2 % and 3 % on the reaction kinetics at 348K was shown in Figure 4.9 to Figure 4.11 for all the three thermally activated clay catalysts; and in Figure 4.12 to figure 4.14 for all the three acid activated clay catalysts, respectively. It was observed that the degree of conversion increases with increase in catalyst concentration. This is due to the fact that increase in catalyst concentration will lower the activation energy for enough reacting molecules to ascend and overcome the energy barrier leading to more product formation (Wikipedia encyclopedia 2010). This decrease in value of activation energy can be seen on Table 4.4. The values are around the neighborhood of Yeong *et al*,(2005) results.

5.1.5 Effect of increase in mole ratio

Based on the variation of alcohol to ethanoic acid mole ratio ranging from 1:1 to 4:1, the conversion was seen to decrease as the mole ratio of alcohol to acid increases beyond 2:1 (as shown on Figure 4.15 to Figure 4.20). This is due to the fact that increase of the alcohol molecules on the active sites of the catalyst hinders the adsorption of the acid and consequently slows the reaction as dual site mechanism as noted also by Igbokwe *et al*,(2008). This shows that the adsorption of ethanoic acid (condensing agent) on the surface of the catalyst in this reaction is necessary and was hindered in the presence of excess alcohol. Thus, the adsorption of the acid is hindered by the competitive adsorption of alcohol, a behaviour which can be explained using both the Langmuir – Hinshelwood and Eley – Rideal kinetic models.

5.1.6 Effect of the clay catalyst type

Figure 4.18 show that the acid activated Ohaukon clay catalyst gave the highest ethanoic acid conversion of 54.74% than Obajana and Oyigbo clay catalyst. This was due to the differences in composition of the three clays. In addition, Ohaukon clay is characterized by high porosity owing to its imperfect crystal formation, having a high moisture content which results in dehydration when activated, leading to subsequent creation of more active sites for the adsorption of the reacting species (Igbokwe *et al*,2004).

5.1.7 Reaction rate data

Using the integral method of analysis of rate data, the appropriate function of concentration corresponding to the rate law, which is linear with time, was determined. Rate data were obtained at 343K for different mole ratios of acid to alcohol (1:2, 1:3, and 1:4, respectively) and different clay catalyst concentrations (1%, 2 % and 3 %, respectively). Figure 4.4 and Figure 4.7 show linear relationships for plots of $1/x_H$ versus t, depicting second order reactions for esterification for all the three clays at the different mole ratios of the acid to alcohol. This is in agreement with Igbokwe *et al*,(2008).

5.1.8 Reaction mechanism and kinetic modelling

Using the Lagmuir-Hinshelwood-HougenWatson (LHHW) model, the surface reaction is considered the rate limiting step. Assuming that adsorption occurs on vacant sites and adsorbed molecules are immobile, vacant sites can accommodate one adsorbed species; heat of adsorption is constant for all sites. This means that there was no heat interaction between adjacent sites and these are also uniform. Using the rate expression for LHHW model as shown in equation (30), the model parameters were estimated using the non linear least squares method. These parameters are shown in Table 4.4. Discussing the results on table 4.4, it was observed that the activation energy of the reaction reduced from 52.25KJ/mol for 0% catalyst to 41.63KJ/mol for 3% catalyst indicating the viability of the activated clay samples as catalyst. Judging from the equilibrium adsorption constants of ethanoic acid, butanol butylethanoate and water as shown onTable 4.4 (3.3138L/mol.min, 0.5059L/mol.min, 1.9743L/mol.min and 0.1559L/mol.min), it was deduced that ethanoic acid has the highest value indicating that its conversion rate exceeds that of the other three components; while the overall equilibrium constant was found to be 4.19 whose value is dependent on temperature change.

5.2 Conclusions

In this work, the kinetics of the esterification of butanol with ethanoic acid using 3 montmorillonite-based thermally activated and acid treated clay catalysts obtained from three selected States in Nigeria was studied. The viability of these clays was investigated in order to know the best suited clay catalyst for this reaction. Ohaukon emerged as the best of all three montmorillonite clay catalysts, both for thermally activated and acid treated form. The effect of varying reaction conditions such as temperature, catalyst concentration and reactants mole ratio shows that the best set of results were obtained at a temperature of 348K, catalyst concentration of 3% and ethanoic acid to butanol ratio of 1:2, having 54.74% conversion of ethanoic acid. A kinetic model in accordance to Lagmuir-Hinshelwood-HougenWatson (LHHW) was developed for the purpose of correlating the experimental data in order to obtain the kinetic parameters of the model. This model is based on the reaction between adsorbed butanol with adsorbed ethanoic acid on the surface of the catalyst to form butylethanoate as product. The catalytic activity of the clay catalyst has proven to be worthwhile since the activation energy of the reaction reduced from 52.25KJ/mol for 0% catalyst to 41.63KJ/mol for 3% catalyst.

5.3 Recommendations

Since organic esters belong to a very important class of chemicals having applications as intermediates in the synthesis of an array of products such as fine chemical, drugs, plasticizers, perfumes food preservatives, cosmetics e.t.c, the need to suggest ways on how research findings can be improve in the field of catalysis has become imperative through the following recommendation:

- Esterification reactions should be carried out using a mixture of two or more types of Nigerian local clay in order to determine their combined viability.
- Inorder to complement research in this field of catalysis using Nigerian montmorillonite clay catalyst, esterification of different types of alcohol with ethanoic acid should be investigated using montmorillonite clays from other geo-political zones.
- Due to the efficacy of Ohaukon clay as catalyst in this research work, further research studies such as the production of zeolite from Ohaukon clay should be ventured into and used for various suitable reactions involving catalysis.
- The viability of local kaolinite clays as catalyst from other clay deposits in Nigeria should be investigated by means of esterification reaction.
- Finally, for the purpose of harnessing our local resources in Nigeria, the aspect of regeneration and recycling of used clay- based catalyst should be encouraged.

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APPENDIX

Calculation of the amount of ethanoic acid to butanol used for ratio 1:1

concentration= $\frac{Density \times weight\ \% \times 10}{molarmass}$

density=1.049 g/dm^3

weight % = 99.7

molarmass = 60.05g/mol

solution

concentration= $\frac{1.049 \times 99.7 \times 10}{60.05}$ =17.4164mol/dm^3(M)

since mole = concentration × volume

mole = 17.4164 mol/dm^3 × 0.02871 dm^3 =0.5mol

Calculation of the Amount of Butanol used

concentration= $\frac{Density \times weight\ \% \times 10}{molarmass}$

density=0.81 g/dm^3

weight % = 99.5

molarmass = 74.12g/mol

Experimental Results

Where : AA=Ethanoic acid, OH=Butanol, Ester= Butylethanoate

The values of AA, OH, ESTER, and WATER are given in mole fractions, assuming that this four components mixture is an ideal mixture.

Effect of Temperature Variation

Table.4.5: Effect of Temperature Variation on Percentage Conversion of Ethanoic Acid at 0% Catalyst Concentration, and at 328K, 338K and 348K.

328K

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4822	0.4211	0.0580	0.0387	3.56
60	0.4675	0.3945	0.0828	0.0552	6.5
90	0.4555	0.3742	0.1022	0.0681	8.9
120	0.4483	0.3676	0.1105	0.0736	10.34
150	0.4467	0.2954	0.1547	0.1032	10.66
180	0.4448	0.2923	0.1577	0.1052	11.04

338K

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4779	0.4171	0.0630	0.0420	4.42
60	0.4532	0.3853	0.0969	0.0646	9.36
90	0.4343	0.3626	0.1219	0.0812	13.14
120	0.4214	0.3564	0.1333	0.0889	15.72
150	0.4116	0.2845	0.1823	0.1216	17.68
180	0.4095	0.2832	0.1844	0.1229	18.1

348K

TIME					CONVERSION
(mins)	AA	OH	ESTER	WATER	(%)
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4717	0.4305	0.0587	0.0391	5.66
60	0.4364	0.4028	0.0965	0.0643	12.72
90	0.4087	0.3812	0.1261	0.0840	18.26
120	0.3945	0.3755	0.1380	0.0920	21.1
150	0.3881	0.3013	0.1864	0.1242	22.38
180	0.3839	0.3009	0.1891	0.1261	23.22

Table4.6: Effect of Temperature Variation on Percentage Conversion of Ethanoic Acid at 3% Catalyst Concentration, and at 328K, 338K and 348K.

328K

TIME **(mins)**	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION** **(%)**
0	0.5000	0.5	0.0000	0.0000	0.00
30	0.4167	0.4604	0.0922	0.0307	16.66
60	0.3434	0.4301	0.1699	0.0566	31.32
90	0.3297	0.4107	0.1947	0.0649	34.06
120	0.3147	0.4102	0.2063	0.0688	37.06
150	0.3030	0.3248	0.2792	0.0931	39.40
180	0.3001	0.3167	0.2860	0.0972	39.98

338K

TIME **(mins)**	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION** **(%)**
0	0.5	0.5	0.0000	0.0000	0
30	0.4283	0.4697	0.0765	0.0255	14.34
60	0.3716	0.4379	0.1429	0.0476	25.68
90	0.3427	0.4174	0.1799	0.0600	31.46
120	0.3108	0.3793	0.2324	0.0775	37.84
150	0.3026	0.3327	0.2735	0.0912	39.48
180	0.2999	0.3132	0.2916	0.0953	40.02

348K

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5000	0.5	0.0000	0.0000	0
30	0.3667	0.4655	0.1259	0.0420	26.66
60	0.3287	0.4341	0.1779	0.0593	34.26
90	0.3005	0.4147	0.2136	0.0712	39.9
120	0.2866	0.4139	0.2246	0.0749	42.68
150	0.2764	0.3318	0.2939	0.0980	44.72
180	0.2749	0.3169	0.3062	0.1021	45.02

Effect of Catalyst Concentration Variation

Table.4.7: Effect of Variation of Catalyst Concentration on Percentage Conversion of Ethanoic Acid using Thermally Activated Ohaukon Clay at 348K.

1%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5	0.5	0	0	0
30	0.4405	0.4479	0.0781	0.0335	11.9
60	0.3915	0.4331	0.1228	0.0526	21.7
90	0.3594	0.4137	0.1588	0.0681	28.12
120	0.3364	0.4064	0.1800	0.0772	32.72
150	0.3218	0.3285	0.2448	0.1049	35.64
180	0.3129	0.3256	0.2531	0.1085	37.42

2%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4256	0.4599	0.0802	0.0344	14.88
60	0.3651	0.4422	0.1349	0.0578	26.98
90	0.3249	0.4273	0.1735	0.0743	35.02
120	0.3146	0.4105	0.1924	0.0825	37.08
150	0.3089	0.3258	0.2557	0.1096	38.22
180	0.3079	0.3024	0.2728	0.1169	38.42

3%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5	0.5	0.0000	0.0000	0
30	0.4065	0.4623	0.0984	0.0328	18.7
60	0.3433	0.4311	0.1692	0.0564	31.34
90	0.3095	0.4137	0.2076	0.0692	38.1
120	0.3045	0.4119	0.2127	0.0709	39.1
150	0.2999	0.3305	0.2772	0.0924	40.02
180	0.2954	0.3154	0.2919	0.0973	40.92

Table.4.8: Effect of variation of catalyst concentration on percentage conversion of ethanoic acid using thermally activated Obajana clay at 348K.

		1%			
TIME	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION**
(mins)					**(%)**
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4524	0.4428	0.0734	0.0314	9.52
60	0.4181	0.4171	0.1154	0.0494	16.38
90	0.3871	0.3973	0.1509	0.0647	22.58
120	0.3641	0.3572	0.1951	0.0836	27.18
150	0.3518	0.3126	0.2349	0.1007	29.64
180	0.3507	0.3098	0.2377	0.1019	29.86

2%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5	0.5	0	0	0
30	0.4442	0.4579	0.0685	0.0294	11.16
60	0.3913	0.4282	0.1264	0.0542	21.74
90	0.3617	0.4047	0.1635	0.0701	27.66
120	0.3414	0.3619	0.2077	0.0890	31.72
150	0.3186	0.3201	0.2529	0.1084	36.28
180	0.3099	0.3023	0.2715	0.1163	38.02

3%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5	0.5	0.0000	0.0000	0
30	0.4283	0.4697	0.0765	0.0255	14.34
60	0.3716	0.4379	0.1429	0.0476	25.68
90	0.3427	0.4174	0.1799	0.0600	31.46
120	0.3108	0.3793	0.2324	0.0775	37.84
150	0.3026	0.3327	0.2735	0.0912	39.48
180	0.2999	0.3188	0.2860	0.0953	40.02

Table.4.9: Effect of variation of catalyst concentration on percentage conversion of ethanoic acid using thermally activated Oyigbo clay at 348K.

1%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4475	0.440	0.0785	0.0336	10.5
60	0.3936	0.4123	0.1359	0.0582	21.28
90	0.3698	0.3901	0.1681	0.0720	26.04
120	0.3543	0.3823	0.1844	0.0790	29.14
150	0.3410	0.3151	0.2407	0.1032	31.8
180	0.3308	0.3102	0.2513	0.1077	33.84

2%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4376	0.4540	0.0759	0.0325	12.48
60	0.3643	0.4210	0.1503	0.0644	27.14
90	0.3479	0.4070	0.1716	0.0735	30.42
120	0.3374	0.3954	0.1870	0.0802	32.52
150	0.3203	0.3215	0.2507	0.1075	35.94
180	0.3197	0.3208	0.2517	0.1079	36.06

3%

TIME **(mins)**	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION** **(%)**
0	0.5000	0.5	0.0000	0.0000	0.00
30	0.4167	0.4604	0.0922	0.0307	16.66
60	0.3434	0.4301	0.1699	0.0566	31.32
90	0.3297	0.4107	0.1947	0.0649	34.06
120	0.3147	0.4102	0.2063	0.0688	37.06
150	0.3030	0.3248	0.2792	0.0931	39.40
180	0.3001	0.3111	0.2916	0.0972	39.98

Table.4.10: Effect of variation of catalyst concentration on percentage conversion of ethanoic acid using acid activated Ohaukon clay at 348K.

			1%		
TIME (mins)	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION (%)**
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4023	0.4496	0.1037	0.0444	19.54
60	0.3625	0.4395	0.1386	0.0594	27.5
90	0.3393	0.4125	0.1737	0.0745	32.14
120	0.3216	0.4088	0.1887	0.0809	35.68
150	0.3096	0.3952	0.2066	0.0886	38.08
180	0.3002	0.3941	0.2140	0.0917	39.96

2%

TIME (mins)	AA	OH	ESTER	WATER	COVERSION ((%)
0	0.5000	0.5000	0.0000	0.0000	0
30	0.3732	0.4599	0.1168	0.0501	25.36
60	0.3342	0.4469	0.1532	0.0657	33.16
90	0.3149	0.4242	0.1826	0.0783	37.02
120	0.3051	0.4206	0.1920	0.0823	38.98
150	0.2915	0.3301	0.2649	0.1135	41.7
180	0.2904	0.3115	0.2787	0.1194	41.92

3%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5	0.5	0	0	0.00
30	0.4121	0.4619	0.0945	0.0315	17.58
60	0.3524	0.4309	0.1625	0.0542	29.52
90	0.2964	0.4124	0.2184	0.0728	40.72
120	0.2815	0.4114	0.2303	0.0768	43.70
150	0.2706	0.3304	0.2993	0.0998	45.88
180	0.2701	0.3139	0.3120	0.1040	45.98

Table.4.11: Effect of variation of catalyst concentration on percentage conversion of ethanoic acid using acid activated Obajana clay at 348K.

1%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4172	0.4432	0.0977	0.0419	16.56
60	0.3746	0.4183	0.1450	0.0621	25.08
90	0.3485	0.3976	0.1777	0.0762	30.3
120	0.3304	0.3458	0.2267	0.0971	33.92
150	0.3151	0.3053	0.2657	0.1139	36.98
180	0.3043	0.2989	0.2778	0.1190	39.14

2%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5	0.5	0	0	0
30	0.3811	0.4521	0.1168	0.0500	23.78
60	0.3454	0.4217	0.1630	0.0699	30.92
90	0.3168	0.4002	0.1981	0.0849	36.64
120	0.3019	0.3567	0.2390	0.1024	39.62
150	0.2934	0.3155	0.2738	0.1173	41.32
180	0.2898	0.3052	0.2835	0.1215	42.04

3%

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.5000	0.5	0.0000	0.0000	0
30	0.3667	0.4655	0.1259	0.0420	26.66
60	0.3287	0.4341	0.1779	0.0593	34.26
90	0.3005	0.4147	0.2136	0.0712	39.9
120	0.2866	0.4139	0.2246	0.0749	42.68
150	0.2764	0.3318	0.2939	0.0980	44.72
180	0.2749	0.3169	0.3062	0.1021	45.02

Table.4.12: Effect of variation of catalyst concentration on percentage conversion of ethanoic acid using acid activated Oyigbo clay at 348K.

			1%		
TIME (mins)	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION (%)**
0	0.5000	0.5000	0.0000	0.0000	0
30	0.4042	0.4487	0.1030	0.0441	19.16
60	0.3656	0.4178	0.1516	0.0650	26.88
90	0.3387	0.3939	0.1872	0.0802	32.26
120	0.3245	0.3877	0.2015	0.0863	35.1
150	0.3143	0.3086	0.2640	0.1131	37.14
180	0.3101	0.3021	0.2715	0.1163	37.98

2%

TIME (mins)	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION (%)**
0	0.5000	0.5000	0.0000	0.0000	0
30	0.3891	0.4599	0.1057	0.0453	22.18
60	0.3475	0.4287	0.1567	0.0671	30.5
90	0.3168	0.4031	0.1961	0.0840	36.64
120	0.3089	0.3998	0.2039	0.0874	38.22
150	0.3001	0.3177	0.2675	0.1147	39.98
180	0.2999	0.3098	0.2732	0.1171	40.02

3%

TIME (mins)	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION (%)**
0	0.5000	0.5	0.0000	0.0000	0.00
30	0.3929	0.4611	0.1095	0.0365	21.42
60	0.3257	0.4305	0.1829	0.0610	34.86
90	0.2986	0.4113	0.2176	0.0725	40.28
120	0.2898	0.4108	0.2246	0.0749	42.04
150	0.2843	0.3298	0.2894	0.0965	43.14
180	0.2772	0.3125	0.3077	0.1026	44.56

Effect of Mole Ratio Variation

Table.4.13: Effect of variation of mole ratio on percentage conversion of ethanoic acid using thermally activated Ohaukon clay at 348K and 3% catalyst concentration.

1:2

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.3330	0.6670	0.0000	0.0000	0.00
30	0.2718	0.6404	0.0790	0.0088	18.38
60	0.2207	0.6312	0.1333	0.0148	33.72
90	0.1994	0.6228	0.1600	0.0178	40.12
120	0.1882	0.5913	0.1985	0.0221	43.48
150	0.1799	0.5806	0.2156	0.0240	45.98
180	0.1797	0.5708	0.2246	0.0250	46.04

1:3

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.25	0.75	0	0	0
30	0.2157	0.7418	0.0347	0.0078	13.72
60	0.1912	0.7225	0.0694	0.0169	23.52
90	0.1829	0.6834	0.0999	0.0338	26.84
120	0.1751	0.6677	0.1098	0.0474	29.96
150	0.1726	0.6549	0.1198	0.0527	30.96
180	0.1718	0.6511	0.1208	0.0563	31.28

1:4

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.2000	0.8000	0.0000	0.0000	0.00
30	0.1734	0.7801	0.0279	0.0186	13.30
60	0.1564	0.7700	0.0442	0.0294	21.80
90	0.1521	0.7514	0.0579	0.0386	23.95
120	0.1498	0.7325	0.0706	0.0471	25.10
150	0.1482	0.7256	0.0757	0.0505	25.90
180	0.1459	0.7243	0.0779	0.0519	27.05

Table.4.14: Effect of variation of mole ratio on percentage conversion of ethanoic acid using thermally activated Obajana clay at 348K and 3% catalyst concentration.

1:2

TIME (mins)	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION (%)**
0	0.333	0.667	0	0	0.00
30	0.2641	0.6435	0.0832	0.0092	20.69
60	0.2171	0.6343	0.1337	0.0149	34.80
90	0.2072	0.6251	0.1509	0.0168	37.78
120	0.1903	0.5930	0.1950	0.0217	42.85
150	0.1883	0.5839	0.2050	0.0228	43.45
180	0.1864	0.5742	0.2155	0.0239	44.02

1:3

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.25	0.75	0	0	0
30	0.2138	0.7312	0.0419	0.0131	14.48
60	0.1911	0.7245	0.0629	0.0215	23.56
90	0.1813	0.6986	0.0843	0.0358	27.48
120	0.1776	0.6712	0.104	0.0472	28.96
150	0.1725	0.6679	0.1063	0.0533	31
180	0.1699	0.6588	0.1141	0.0572	32.04

1:4

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.2000	0.8000	0.0000	0.0000	0.00
30	0.1806	0.7821	0.0224	0.0149	9.70
60	0.1605	0.7758	0.0382	0.0255	19.75
90	0.1512	0.7543	0.0567	0.0378	24.40
120	0.1489	0.7379	0.0679	0.0453	25.55
150	0.1472	0.7345	0.0710	0.0473	26.40
180	0.1451	0.7211	0.0803	0.0535	27.45

Table.4.15: Effect of variation of mole ratio on percentage conversion of ethanoic acid using thermally activated Oyigbo clay at 348K and 3% catalyst concentration.

1:2

TIME (mins)	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION (%)**
0	0.3330	0.667	0.0000	0.0000	0.00
30	0.2655	0.6456	0.0800	0.0089	20.27
60	0.2245	0.6355	0.1260	0.0140	32.58
90	0.2102	0.6263	0.1472	0.0164	36.88
120	0.1941	0.596	0.1889	0.0210	41.71
150	0.1916	0.5863	0.1999	0.0222	42.46
180	0.1893	0.5766	0.2107	0.0234	43.15

1:3

TIME (mins)	**AA**	**0H**	**ESTER**	**WATER**	**CONVERSION (%)**
0	0.25	0.75	0	0	0
30	0.2267	0.7421	0.0256	0.0056	9.32
60	0.1967	0.7398	0.054	0.0095	21.32
90	0.1873	0.7123	0.0797	0.0207	25.08
120	0.1799	0.6998	0.0926	0.0277	28.04
150	0.1755	0.6825	0.1046	0.0374	29.8
180	0.1741	0.6779	0.1076	0.0404	30.36

1:4

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.2000	0.8000	0.0000	0.0000	0.00
30	0.1829	0.7921	0.0150	0.0100	8.55
60	0.1642	0.7898	0.0276	0.0184	17.90
90	0.1527	0.7623	0.0510	0.0340	23.65
120	0.1495	0.7498	0.0604	0.0403	25.25
150	0.1464	0.7328	0.0725	0.0483	26.80
180	0.1445	0.7282	0.0764	0.0509	27.75

Table.4.16: Effect of variation of mole ratio on percentage conversion of ethanoic acid using acid activated Ohaukon clay at 348K and 3% catalyst concentration.

		1:2			
TIME (mins)	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION (%)**
0	0.3330	0.6670	0.0000	0.0000	0.00
30	0.2428	0.6415	0.1041	0.0116	27.09
60	0.1906	0.6324	0.1593	0.0177	42.76
90	0.1624	0.6237	0.1925	0.0214	51.23
120	0.1521	0.5918	0.2305	0.0256	54.32
150	0.1511	0.5814	0.2408	0.0268	54.62
180	0.1507	0.5719	0.2497	0.0277	54.74

TIME		**1:3**			**CONVERSION**
(mins)	**AA**	**OH**	**ESTER**	**WATER**	**(%)**
0	0.25	0.75	0	0	0
30	0.2216	0.7323	0.0312	0.0149	11.36
60	0.1921	0.7181	0.0665	0.0233	23.16
90	0.1714	0.6809	0.1033	0.0444	31.44
120	0.1708	0.6575	0.1144	0.0573	31.68
150	0.1673	0.6424	0.1267	0.0636	33.08
180	0.1665	0.6335	0.1332	0.0668	33.4

1:4

TIME	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION**
(mins)					**(%)**
0	0.2000	0.8000	0.0000	0.0000	0.00
30	0.1814	0.7806	0.0228	0.0152	9.30
60	0.1599	0.7711	0.0414	0.0276	20.05
90	0.1471	0.7524	0.0603	0.0402	26.45
120	0.1421	0.7334	0.0747	0.0498	28.95
150	0.1413	0.7288	0.0779	0.0520	29.35
180	0.1401	0.7269	0.0798	0.0532	29.95

Table.4.17: Effect of variation of mole ratio on percentage conversion of ethanoic acid using acid activated Obajana clay at 348K and 3% catalyst concentration.

		1:2			
TIME (mins)	**AA**	**OH**	**ESTER**	**WATER**	**CONVERSION (%)**
0	0.3330	0.6670	0.0000	0.0000	0.00
30	0.2315	0.6429	0.1130	0.0126	30.48
60	0.1988	0.6335	0.1509	0.0168	40.30
90	0.1774	0.6244	0.1784	0.0198	46.73
120	0.1689	0.5921	0.2151	0.0239	49.28
150	0.1663	0.5829	0.2257	0.0251	50.06
180	0.1618	0.5728	0.2389	0.0265	51.41

1:3

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.25	0.75	0	0	0
30	0.2226	0.7308	0.0351	0.0115	10.96
60	0.1906	0.7225	0.0703	0.0166	23.76
90	0.1707	0.6945	0.1047	0.0301	31.72
120	0.1644	0.6727	0.1172	0.0457	34.24
150	0.1583	0.6683	0.1253	0.0481	36.68
180	0.1579	0.6599	0.1288	0.0534	36.84

1:4

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.2000	0.8000	0.0000	0.0000	0
30	0.1786	0.7815	0.0239	0.0160	10.7
60	0.1572	0.7732	0.0418	0.0278	21.4
90	0.1497	0.7533	0.0582	0.0388	25.15
120	0.1439	0.7345	0.0730	0.0486	28.05
150	0.1426	0.7301	0.0764	0.0509	28.7
180	0.1421	0.7298	0.0769	0.0512	28.95

Table.4.18: Effect of variation of mole ratio on percentage conversion of ethanoic acid using acid activated Oyigbo clay at 348K and 3% catalyst concentration.

1:2

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.3330	0.667	0.0000	0.0000	0.00
30	0.2537	0.6449	0.0913	0.0101	23.81
60	0.2143	0.6352	0.1355	0.0151	35.65
90	0.1929	0.6267	0.1624	0.0180	42.07
120	0.1745	0.5934	0.2089	0.0232	47.60
150	0.1692	0.5846	0.2216	0.0246	49.19
180	0.1688	0.5758	0.2299	0.0255	49.31

1:3

TIME	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.25	0.75	0	0	0
30	0.2105	0.7401	0.0427	0.0067	15.8
60	0.1839	0.7311	0.072	0.013	26.44
90	0.1708	0.7089	0.0965	0.0238	31.68
120	0.1617	0.6877	0.1139	0.0367	35.32
150	0.1526	0.6789	0.1271	0.0414	38.96
180	0.1515	0.6642	0.136	0.0483	39.4

1:4

TIME (mins)	AA	OH	ESTER	WATER	CONVERSION (%)
0	0.2000	0.8000	0.0000	0.0000	0
30	0.1734	0.7899	0.0220	0.0147	13.3
60	0.1563	0.7[illegible]76	0.0397	0.0264	21.85
90	0.1514	0.7569	0.0550	0.0367	24.3
120	0.1466	0.7411	0.0674	0.0449	26.7
150	0.1435	0.7397	0.0701	0.0467	28.25
180	0.1423	0.7255	0.0793	0.0529	28.85