# ADSORPTION CHARACTERISTICS OF BUTANE GAS OVER ACTIVATED CLAY CATALYSTS

*BY*

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A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING, SCHOOL OF ENGINEERING AND ENGINEERING TECHNOLOGY,
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NOVEMBER 2005

# CERTIFICATION

This is to certify that I have supervised, read and approved this project report which I have found adequate both in scope and quality for the partial fulfilment of the requirement for the award of Bachelor of Engineering in Chemical Engineering.

……………………………… 01/12/2008

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# DECLARATION

I hereby declare that this is my work and that it has not been submitted before, anywhere for the purpose of awarding a degree in any institution, to the best of my knowledge.

.............................................  NOV. 2025

MR. AYENI DANIEL O.  Date

# DEDICATION

This piece of work is dedicated safely to Almighty God, the author and fresher of our faith, the supreme being. For his mercy and blessings. For giving me knowledge and wisdom.

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I owe a debt of thanks to many precious people whose invaluable experience, assistance and advice helped bring this project together;

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## NOMENCLATURE

P = operating pressure

$P_e$ = equilibrium pressure

T = Temperature

A, B, C and C = Antione coefficients

K = Adsorption equilibrium

R = gas constant

C 1 = concentration of the adsorbate gas

V = volume of adsorbate gas

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# ABSTRACT

The adsorption characteristic of butane gas over an activated clay catalyst was understudied. The characteristic that was determined is the relative strength of adsorption to the surface area and effect of particle size. This was done using a laboratory fluidized bed reactor for two different weights of clay sample; 100g and 150g all of 300um particle size, at the temperature range of $62^0$C to 75°C and for each sample weight and at a constant pressure of 1.5 bar for different flow rate range of 1000-4000 $m^3/s$. the result obtained showed that for the 100g clay sample, the concentration increased from 0.063648971 to 0.069219093 and then dropping to 0.039645804 and finally rising to 0.045640108 $Kmol/m^3$.

For the 150g-clay sample, the reverse is the case in the pattern as the concentration is found to have decreased from 0.058941595 to 0.05085681 and the rising to 0.05613111 and finally decreasing to 0.037128824. The results obtained were used to plot some adsorption isotherms, which displays the behaviour of the adsorbate gas over the activated clay catalyst.

# CHAPTER ONE

## 1.0 INTRODUCTION

Adsorption is a separation process in which certain components of a fluid phase are transferred to the surface of a solid absorbent. Usually, the small particle of adsorption are held in a fixed led, the fluid is passed continuously through the beds until the solid is nearly saturated and the desired separation can no longer be achieved.

The flow is then switched to a second bed until the saturated adsorbent can be replaced or regenerated (activated). For this process, the performance depend on solid – fluid equilibrium and on main –transfer rate. (1) ①

Adsorption involves the transfer of a constituent of a fluid to the surface of a solid phase. To complete the separation, the absorbed constituent must then be removed from the solid. The fluid phase can be a gas or a liquid. If several constituents are absorbed to varying extents, it is often possible to separate them into relatively pure component (2).

Adsorption is the selective collection and concentration onto solid surfaces, of particular types of molecules contained in a liquid in a liquid or gas. Solid adsorbents area usually proves granular particles used in fixed bed (up to 5mm dia) and in fluidized bed (down to about 0.05mm dia). The interior pure, often with diameters of 0.01m or less and with total volume approaching 50% of the whole particle, give rise to interior surfaces totalling 102 – 104m$^2$/g. the adsorptive capacity of such particle increase with the solute content of the gas in contact with them, but may reach 20% or more of the mass of the solid (3).

Though used as a physical process over a long period, it is only over the last three decade that adsorption has developed to a stage where it is now a major industrial separation process. Adsorption can be equally effective in removing trace components from the liquid phase and may be used either to recorver the component or simply to adsorped Butene gas from activated day catalyst (4).

Thus, adsorption is a separation process in which the molecules of a fluid phase ie gas or liquid are transferred to a solid surface. Therefore the composition of the system is heterogeneous consisting of two or more fluid phases including the solid adsorbent. Molecules that have been adsorbent onto solid surface are referred to as adsorbents, and the surface to which them are adsorbent are referred to as the substrate or adsorbent. adsorbet ②

Adsorbent takes place in the boundary between the phases called the interface. Most adsorbents are ingulyprorous material and adsorption occurs on the walls of the pores. In many cases the components are held strongly enough to permit complete removal of a component with very adsorption of other components. The adsorptive separation is achieved by one of three mechanisms.

- Steric
- Knetic
- Equilibrium affect.

The steric effect is achieved from the molecular sieving property of Zeohtes Kinatie separation achieved by virtue of the differences. A large majority of process operate through the equilibrium adsorption of the mixture and hence are called equilibrium separation processes.

Based on the boundary between the adsorbate molecule and the solid surface, adsorption can be categorized as. ③

- Chemical/Adsorption (or chemisorptions) where forced of chemical or valence nature between adsorbate and adsorbent are involved.
- Vander waals Adsorption (or physical adsorption) involving weak van der waals and columbic forces of attraction responsible for the adsorption process. The atom and molecules in the interior of a solid are completely. Surrounded; thus, their attractive forces are satisfied on all sides.
- Van der waals (or physical adsorption) is encountered in gas separation process. Therefore chemical adsorption will be the major emphasis of this research work.

There are varieties of adsorbents. The most common are.

✓ Activated clay
✓ Silical
✓ Aluminia
✓ Zeolites
✓ Film diffusion
✓ Activated carbon ④
✓ Pore diffusion
✓ Adhesion in the solute molecules to the carbon surface.

Film diffusion is the penetration of the solute molecule, the adsorbate, through the particles surface film.

Pore diffusion involves the migration of solute molecules through the carbon pore to an adsorption site. Adhesion occur when the solute molecule adheres to the pore surface.

An example of adsorptions is purification where impurities are filtered from liquids or gases by surface area solid such as activated charcoal, other example include the segregation of surfactant molecules to the surface of liquid, the bonding of reaction molecules to the solid surface of a heterogeneous catalyst and the migration of ions to the surface of a cheaper election (5).

## 1.1 OBJECTIVE OF THE PROJECT WORK.

In line with the nations economic objective of self- reliance, this work preparation of activated day from inexpensive and abundant local raw materials (cow bone and dry wood) and used same in purification and adsorption of butane gas. Activated clay is used in the following way: its usefulness are highlighted below;

i Motivate local industries to embarked on the production of activated clay which will in effect help to conserve foreign exchange need for the importation of material and to bridge the gap between demand and supply of activate clay, thereby checking the presence of ost crises.

ii Demonstrate the relationship between chemical activation and adsorption capacity of the adsorbents under different variables such as concentration pressure, temperature, PH and particle size.

iii Evaluate the efficient activating agents that can be used to produce activated clay and it determine of the best adsorption.

## 1.2 PROJECT MOTIVATION.

(1) In developing countries like Nigeria, where the economy is weak and the proper technology and facilitates to adapt high – tech method of Adsoption gases, it has become necessary to find on alternative method which is viable effective; achievable and sustainable with in present economic and technical realities of the country. Physical – chemical adsorption method using different adsorbents appeared to be very promising and this is what this piece of work intent to investigate.

(2) The demand for activated clay increasing partly due to it use in industries in the adsorption of gases and in research laboratories as catalyst support. Yet activated clay is not ready available locally and the quantity consumed in Nigeria is relatively large.

# CHAPTER TWO

## 2.0 BRIEF HISTORY OF ADSORPTION

The use of solids for removing substances from either gaseous or liquid solutions has been widely used since biblical times. The process known as ADSORPTION, involves nothing more than the preferential partitioning of substances from gaseous or liquid phase on to the surface of solid substrate. From the early days of using bone char for decolourization of sugar solutions and other foods, to the later implementation of activated carbon for removing nerve gases from the battle field, to today's thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation.

Adsorption phenomena are operative in most natural, physical, biological and chemical systems and adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and waste waters.

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed. Adsorption is thus different from adsorption, a process in which material transferred from one phase to another (e.g. liquid) interpretates the second phase to form a "solution". The term sorption is a general expression encompassing both processes.

Physical adsorption is caused mainly by Van der Waals forces and electrostatic forces between adosbate molecules and the atoms which compose the adsorbent surface. Thus adsorbents are characterised first by surface properties such as surface area and polarity. A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area numbers of small sized pres between adsorption surfaces. The size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsortivity of adsorbents. Especially materials such as Zeolite and carbon molecular sieves, activated clay can be specifically engineered with precise pore size distribution and hence tuned for a particular separations.

Surface polarity corresponds to affinity with polar substances such as water or alcohols. Polar adsorbents are thus called "*hydrophilic*" and aluminosilicates such as Zeolite, porous alumina, silica gel or silica –alumina are examples of adsorbent of this type on the other hand, non polar adsorbents are generally "*hydrophilic*" carbonaceous adsorbents, polymer adsorbents and silicate are typical non polar adsorbents. These adsorbents have more affinity with oil or hydrocarbon than water.

The adsorbent is the separating agent used to express the difference between molecules in a mixture.

Adsorption and adsorbents: An important properties of surface is that known as Adsorption; This is used to describe the existence of a higher concentration of any particular substance at the surface of a liquid or solid than is present in the bulk of the medium.

Adsorption of Gases: - Increase of pressure and decrease of temperature increase the extent of the Adsorption of a gas by a solid;

It is necessary to distinguish between "Adsorption" and "absorption" as applied to solids, while the former refers to an excess concentration at the surface, the latter implies a more or less uniform penetration of the solid by a given substance. It is probable that Adsorption occurs at all surfaces, but for the purpose of studying the phenomena of Adsorption it is convenient to employ porous substances which have a large effective area for a given mass. It should be clearly understood that although the large surface is of importance in determining the adsorbing properties of a given material, the extent and firmness of Adsorption are dependent to a great extent on the nature of the adsorbent and the substance adsorbed.

## 2.1 ADSORPTION ISOTHERMS

A plot obtained between the amount of substance adsorbed per unit mass of the adsorbent and the equilibrium or concentration at constant temperature is known as Adsorption Isotherms. Adsorption isotherms provides information on the amount of hydrocarbon adsorbed in porous material of a given pressure and temperature.

The Freudlich Adsorption Isotherms shows the variation of the amount of gas adsorbed per unit mass of the adsorbent with pressure at constant temperature, Freudlich suggested an empirical equation, which is known as Freudlich Adsorption Isotherms the equation is

$$\frac{x}{m} = kp^{1/n} \qquad \text{(a)}$$

where x = is mass of gas adsorbed

m = mass of adsorbent

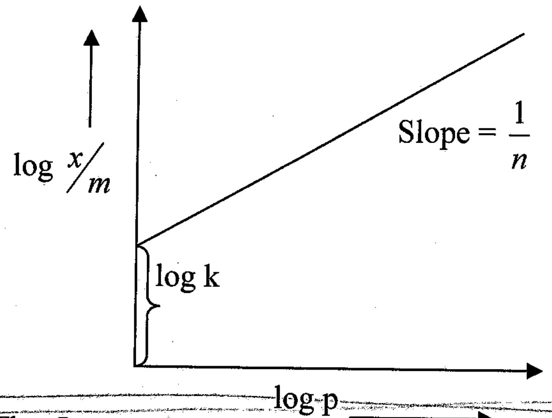
p = equilibrium pressure

k and n = are constants which depend on the nature of absolute and adsorbent and on the temperature

This equation is applicable only at low temperature in order to test equation (a) take the logarithm of both sides, when it will take the form

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log p \qquad \text{(b)}$$

According to equation (b) ,a plot of log $\frac{x}{m}$ against log p should be a straight line with slope equal to $\frac{1}{n}$ and intercepts log k.



The Langmuir Adsorption Isotherm – Since chemical forces off very rapidly with distance, it is probable that chemisorption does not extend beyond a single layer of gas molecule on the surface of solid.

When a state of equilibrium is attained, the rate at which the gas molecule is strikes the surface and are held there i.e. the rate of adsorption will be equal to the rate of evaporation under the given conditions. According to the kinetic theory of gases, at constant temperature gas molecule strike a surface at a rate proportional to the pressure (P) of the gas.

If at any instant a fraction 1-θ of the surface will be bare. Since only a single layer of molecules is to be adsorbed, it follows that only those molecules is to be adsorbed, it follows that only those molecules striking the bare parts of the surface can be retained i.e. adsorbed, hence

Rate of adsorption of gas molecule z

$Kp(1-\theta)$ (i)

Where k is a proportionality constant the rate at which gas molecule evaporate from the surface will be proportional to the extent θ to which it is covered with these molecule, consequently,

Rate of evaporation of gas molecule = $k'\theta$ ..... (ii)

At equilibrium the rates of Adsorption and evaporation (or desorption) as given by equation (i) and (ii) will be equal, so that

$$Kp(1-\theta) = K^1\theta \qquad \text{(iii)}$$

$$\theta = \frac{Kp}{Kp + K^1} \qquad \text{(iv)}$$

If the surface can become covered with a uniform layer of gas, one molecule in thickness, the amount of gas adsorbed per unit mass of adsorbents is directly proportional to the fraction θ of the surface covered, i.e. $a = k''\theta$. inserting the value of θ given by equation (iv) and dividing through numerator and denominator by k', the result is

$$a = \frac{\left(KK^{11}/K^{1}\right)P}{\left(K/K^{1}\right)P+1} \qquad \text{(v)}$$

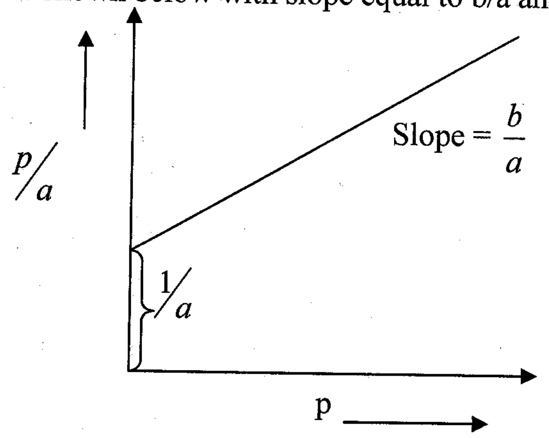
$$\Rightarrow \frac{K_iP}{K_2P+1} \qquad \text{(vi)}$$

Where $K_1 = kk'/k'$ and $K_2 = k/k'$

It is seen that equation (vi) relates the extent of adsorption to the pressure of the gas, at constant temperature, it is consequently known as the Longmuir Adsorption Isotherm. In order to test this isotherm by means of experimental data, equation (vi) is rearranged so as to give

$$\frac{p}{d} = \frac{1}{k_1} + \frac{k_2}{k_1}P$$

Hence, if p/a is plotted against the pressure P, a straight line should be obtained this is shown below with slope equal to b/a and intercept equal to 1/a



The role of catalyst on the surfaces i.e. (activated clay)

The term is applied generally to cases in which the rate f chemical reaction is accelerated by the presence of a substance which is itself unchanged chemically in the process. The substance causing the acceleration is called a catalyst. Many types of catalysed reactions, both homogenous and heterogenous, are known , but in spite of their many differences there are certain characteristics common to then all; these will be considered briefly.

i. The catalyst is unchanged chemically at end of the reaction; the total amount of the catalyst is the same at the end as the beginning of the reaction; hence, it must be unchanged chemically, although it frequently undergoes a change in physical form.

*ii.* A small quantity of catalyst is often sufficient to bring about a considerable amount of reaction.

*iii.* The catalyst does not affect the position of equilibrium in a reversible reaction.

*iv.* The catalyst does not imitate the reaction, it merely accelearytes a reaction that is already occurring, although perhaps extremely slowly.

A catalyst cause a given reaction totake place in such stages that the slowest has an activation energy considerably les than for the unanalyzed reaction.

A theoretical deduction

Consider a reaction involving a substance A and a substance B to give AB viz

$A + B \rightarrow AB$

If the free energy Δf for this reaction is negative under the experimental conditions, the process will be possible theoretically, but it may be very slow; suppose a catalyst C is added which accelerates the formation of AB; the reactin may occur in the following relative rapid stages,

$A + C \rightarrow AC$

$AC + B \rightarrow AB + C$

## 2.2 CLAY IN PERSPECTIVE

Clay may be defined as a natural, earthly fine grained material that develops plasticity when mixed with a limited amount of water. The term is also used to designate the smallest particles in sedimentary rocks and soils e.t.c. The maximum size of particles in the clay size grade is commonly considered to be two microns (0.002millimetre) caly are composed essentially of silica, alumina, and water and appreciable quantities of 1mm alkalis and alkaline earth are frequently present. Until recently there were no analytical techniques by which to determine the precise nature of the components of these elements in clays and soils. X –ray diffraction techniques developed in the 1920s followed a few years later by improved microscope and thermal procedures, established that clay are composed of a few groups of crystalline minerals that have coe to be called the clay minerals. Small amounts of such minerals as quartz, feldspar, mica and iron oxides may also be present. The clay mineral components provides the essential characteristics and properties of clay, however, clay minerals occur in flake shaped, lath shaped, and needle shaped units. The individual units are measured in Armstrong $A^0 = 10^{-4}$ microns) but then occur in clays in booklike particles, aggregates of flakes or bundles of laths and needles that are of the order of microns in diameter –kaolin type clay, for example, is essentially on aggregation of book shaped units of sheets of the clay mineral kaolinite.

Clay minerals occur in nature in sedimentary rock of all age and in continued and marine sediments accumulating at the present time. They are formed as a result of weathering processes and a a consequence are found as the essential components of most soils. Clay minerals are also formed as result of hydrothermal activity and are associated with volcanic activity and some metallic ore deposits.

Clay have a wide variety of physical characteristics such as plasticity, refractioness, colour and colloidal properties that make them suitable for a wide variety of industrial purposes. They are used for example in the ceramic industries for the manufacture of white ware, porcelain, refractories and other clay products, some types pf clay are extensively used for filling and coating paper as fillers extenders and reinforcing agents in plastics, paint, adhesive and rubber manufacturing their colloidal properties in water system make them suitable for use as drilling muds, which is of great importance tpo the oil industry.

## 2.3 IMPORTANT OF CLAY

The important properties of the clay minerals that made it suitable for Adsorption. Is ion exchange: Clay minerals are able to adsorp certain positively and negatively charged particles (cations and anions) and retain them around the outside of the structural unit in an exchangeable state. The exchange reaction differs from simple sorption because it is stoicheometric (involving equal amounts) and generally does not affect the silica – alumina structure. The range of the cation and anion exchange capacities of the clay minerals is given in table.

Exchange capacities vary with particle size, perfection of crystallinity and nature of the adsorbed ion, hence, a range of values exists for a given mineral rather their a single specific capacity cation exchange capacity results fro broken bonds around the edges of the structural units, which give rise to unsatisfied charges. Substitutions withinthe lattice structure (fro example, trivalent aluminium for quadrivalent silica) and possibly the hydrogen of exposed hydrolysis also provide cation exchange capacity.

**TABLE 2.0**

Exchange Capacities of Clay Minerals (mill equivalent per 100g)

| **Cation exchange capacity** | **Anion exchange capacity (approximate)** |
|---|---|
| Kaolinite 3 – 15 | Smealite 23 |
| Halloysite($2H_2O$) 5-10 | Nonalonite 20 |
| Halloysite($4H_2O$) 40-50 | Saponite 21 |
| Smeetite 80 -150 | Vermieulite 4 |
| Illite 10 – 40 | Kaolinite 13.3 |
| Vermiculites 100 -150 | |
| Chlorite 10-40 | |
| Seprolite-anapulgite 3-15 | |
| Palygorske | |

Anion –exchange capacity may be due to (1) the replacement of hydroxyl ions at the edges of the lattice structure (2) adsorption because of the geometry of the anion in relation to the geometry of the clay mineral structural units (the adsorption of phosphate at the edges of silica tetrahedrons) for example, and (3) possibly because of unbalanced charges within the lattice, such as that which result from an excess of aluminium in octahedral positions.

The rate of ion exchange varies with clay mineral type and the nature and concentration of the ions in general the reaction for kaolinite is most rapid, being almost instantaneous. It is slower for sneatite and for Uttapulgite and requires even longer time, perhaps hours or days, to reach completion for illites under a given set of conditions the various cations are not equally replaceable and do not have the same replating power. Power. Calcium for example will replace sodium more easiy than sodium will replace calcium.

The ion exchange properties of the clay are extremely important because these properties determine their physical characteristics and economic use. The availability abd retention of fertilizer in soils, plasticity and other clay properties depend to a great extent on ion exchange in general and on the identity of the exchange cation.

## 2.4 ACTIVATED CLAY

Activated clay is an amorphous form of clay which has been specially treated that it posses a very large surface area. This large surface area obtained by developing the internal pore structure of the clay, provides the clay with the ability to adsorb gases and the vapours from gases or dissolved and dispersed vapours from gases or dissolved and dispersed substances, from liquids.

Activated clay has an extremely large surface area per unit weight, the activation of clay and its manufacture produces many pores within the particles, and it the vast areas of the walls with these pores that account for most of the total surface of the molecule. In water, activated clay has preference for large organic molecules and for substances that are non – polar in nature. The forces of attraction between the clay and the adsorbed molecules are greater with a molecules size close to that of the pore size. The best adsorption occurs when the pores are just large enough to admit the molecules.

Activated clay has high adsorptive power for the impurities that odour, colour and can finely powered for high porosity to offer a great number of adsorption sites. Its action in adsorbing the impurities is physical,

## 2.5 ADSORPTION

### 2.5.1 HISTORICAL PERSPECTIVE

The use of solids for removing substances from either gaseous or liquid solutions has been widely used since biblical times. This process, known as adsorption, involves nothing more than the preferential partitioning of substances from the gaseous or liquid phase on the surface of a solid substrate. From the early days of using bone char for decolourization of sugar solutions and other foods, to the later implementation of activated carbon for removing nerve gases from the battle field, to today's thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation(17)

Adsorption is a process that uses special solids (called adsorbents) to remove substances from either gaseous or liquid mixtures. The term "adsorption" was first cined in the late 19th century but the process itself was not widely used until the 1940s and 50s, it is usually important to adsorb the component in a fluid that is richer that from which it was originally adsorbed. This accomplishes enrichment or purification in a cyclic manner (18)

✓ Adsorption phenomena are operative in most natural physical, biological and chemical systems and adsorption operations employing solids such as activated cla, and synthetic resins are used widely in industrial applications for adsorption of gases. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent and the material concentration or adsorbed at the surface of that phase is the adsorb ate (17)

## 2.6 WHEN IS ADSORPTION USED

- ✓ If materials being removed are mostly metals.
- ✓ If compounds are not compliant for bio degradation
- ✓ If the molecule contains branced chains, has a large molecular weight, low polarity; unsaturated organics better than single bonded.
- ✓ If concentration of organics < 500mg/l (0.5% - 0.005 %) and if concentration of an organics < 100mg/l ( 0.1 % - ).001%)
- ✓ If concentration of solids < 50ppm, concentration of oil < 10ppm
- ✓ If boiling temperature is between 20 – 175$^0$C

## 2.7 USES OF ADSORPTION

Adsorption is effective for purification, for example taking a contaminant ranging from 1ppb to 100oppm out of a stream of liquid.

Addition, adsorption is good for bulk separations, for example taking 1 to 10% out of a liquid.

Adsorption is also used for recovery of certain constituents ( solvent from air), preventing pollution, purifying materials that will react and soon.

## 2.8 EFFECTS OF PROCESS VARIABLES ON ACTIVATED CLAY

### 2.8.1 EFFECTS OF TEMPERATURE.

The equilibrium capacity of molecular sieves decreases with increasing temperature. Commercial absorbers work adabatuicpoually and the release of heat of adsorption results in a temperature rise. Because of this thermal effect, the working capacity of dynamic absorber is reduced. However, this effect is less pronounced with molecular sieves then with other absorbers (3)

### 2.8.2 EFFECT OF PRESSURE

The adsorption capacity increases with an increase in partial pressure to the point at which the micropore is completely filled with adsorbates. For a given mole fraction (concentration for liquid) of gas the partial pressure is proportional to total pressure. Hence, the increase in total pressure not only increase the adsorption capacities of all species not excluded, but also promotes competition for the available adsorption site among the adsorbtaes(3).

### 2.8.3 EFFECT OF ADSORB ATE

The driving force which causes the adsorb ate to migrate to the adsorbent surface is a function of concentration gradient. The driving force may be expresses as the adsorb ate in the fluid phase in the cavities of the molecular sieves. Thus adsorption from systems containing a high concentration of adsorb ate Is more rapid than from very dilute systems. The actual mass transfer Zone in a concentration stream tends to be longer than in dilute stream, but the overall unit rate of transfer is more rapid

From a purely theoretical point of view, the rate at which molecules may be adsorbed, other factors being equal, will depend on the rate at which they contact the surface of adsorbent particles and the speed with which they diffuse into particles after contact. One or the other of these factors may be controlling in any given situation. One way to speed the mass transfer, in either case, is to reduce the size of adsorbent particles and accept a higher pressure drop[(3)

### 2.8.4 EFFECT OF SURFACE AREA

A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. The size of the microspores determines the accessibility of adsorb ate molecules determines the accessibility of adsorb ate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsorptive of adsobents. Especially materials engineered with precise pore size distribution and hence tuned for a particular separation (7)

### 2.8.5 EFFECT OF PARTICLE SIZE

From a purely theoretical point of view, the rate at which molecules may be adsorbed, other factors being equal, will depend on the rate at which then contact the surface of adsorbent particles and the speed with which they diffuse into particle after contact. One or the other of these factors may be controlling in any given situation, one way to speed the mass transfer, in either case, is to reduce the size of adsorbent particle and accept a higher pressure drop (3).

### 2.9 DEFINITION OF BUTANE

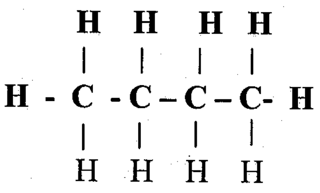
Butane is alkaline with four carbon atoms, one having a straight cahin and the other a " branched" chain

n – butane, $CH_3CH_2CH_2CH_3$

melting point – 138.3$^0$C

Boiling point : - 0.50$^0$C

Structural, n – butane has a straight chain structure



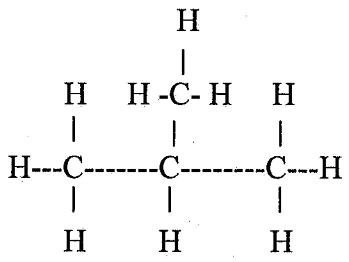
$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

Isobutane, $CH_3CH(CH_3)CH_3$

Melting point: -159.6$^0$C

Boiling point: -11.7$^0$C

Structurally isobutene has a branched chain structure



$$\begin{array}{ccccccc} & & & H & & & \\ & & & | & & & \\ & H & & H-C-H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

This two compounds isomers of one another have the same molecular formulas $C_4H_{10}$, but they have different atom arrangements. Thus, we call them more specifically structural isomers. The strength chain isomer is called n-butane, where n stand for normal term always applied to the straight –chain isomer of any hydrocarbon. The branched – chain isomer is iso butane

# CHAPTER THREE

## 3.0 EXPERIMENT AND EXPERIMENT PROCEDURE

### 3.1 RAW MATERIAL

Clay

Butane gas

### 3.2 CHEMICALS AND REAGENTS

Orthophosphonic Acid ( $H_3PO_4$)

Tetraoxosulphate (iv) Acid ($H_2SO_4$)

Trioxonitrate (v) Acid ( $HNO_3$)

Hydrochloric Acid ( Hcl)

Potassium Hydroxide (KOH)

Calcium Chloride ($CaCl_2$)

Magnesium chloride ($Mgcl_2$)

Zinc chloride ($Zncl_2$)

Petroleum Ether

### 3.2 EQUIPMENTS USED

Manifold gauge

Thermometer

PH meter ( modle/serial No 7020/4397 ), Electron instrument Limited, survey England.

Muffle Furnace (model FSE250 – 010 – F/7B – 1171 –D )

Gallen kamp product, England

Hot plate ( model kat No: NPL – 600 – 0100/oc – 4405 – G)

Gallenkamp 3 co.Ltd, England.

Mass balance (model 9471), 310g capacity, ottair USA

UV spectrophotometer ( model UV 2100 shinadzu product / GDU – 200)

Refractometer ( model N.A 80249 ) bellinghant Stanley limited (BS) England.

Electric shoker (setacco Di prova – laboratory test sieve BS 410) controls milano Italy.

Red Devil (Presuure equipment)

### 3.3 SOURCE OF MATERIALS AND EQUIPMENT

The raw clay used is gotten from Kutigi town in Niger state. The butane gas is obtained from the gas company in Nigeria here. Ther chemicals used are gotten from both the chemical engineering Department, chemistry Department and science laboratory Technology Department of the Federal university of Technology, Minna, Niger state.

### a. CLAY CATALYST PRE –TREATMENT

The catalyst was prepared from obtained locally. It was powered and sieved to a particle size of 300microns and later calined between 550 – $600^0$C. The catalyst was acidified using 0.1% w/w dilute sulphuric acid. 0.15kg of the sample was placed in a beaker where distilled water was added to make paste slurry. 150ml of dilute acid was added to sok the paste for 60 minutes at a controlled temperature range of 80 – 100°C. This was later dried at 393K for about 12 hours. The stated procedure was carried out since catalyst surface is where the conversion in a catalytic reaction takes place.

The surface of the catalyst is non – uniform or heterogeneous and, certain spots or locations on the catalyst that catually participate in the reaction are reffered to as, active centres or sites. As regards activity and selectivity, active centres have a certain activity associated with them. Catalyst activity refers to the rate at which the catalyst causes a reaction to proceed toward equilibrium while selectivity is for a certain product or reaction, normally some intermediate product

## 3.5 CLAY CASAINATION

Clay casaination was carried out in a specially entrusted burning chamber, (furnace) which limited air in supply. Each sample was first dries for several hours, the samples were then introduced into the furnace for charring at different temperature of 450°C, 550°C, 600°C, 650°C, for the different sample of the clay and was then allowed to remain in the furnace for 2 hrs after alternating the required temperature before the removal. The chaired product was allowed to cool down to room temperature ground to a workable size with a mortal and pestle, and screened to obtain samples of three different particle size ranges.

## 3.6 CHEMICAL ACTIVATION

The activation of samples were carried out in a muffle furnace using orthosporic Acid ($H_3 PO_4$),Potassium hydroxide (KOH), and Zinc chloride ($Zncl_2$) separately as activating reagents. A carefully wailed sample was put in a beaker containing 500cm$^3$ of 0.5m solution or activating reagent. The content of the beaker is thoroughly mixed and heated until it forms a paste. The paste is then transferred to a crucible, the crucible is placed in a furnace, and the furnace is heated at 500°C for two or more. After allowing the activated sample to cool down to room temperature.

## b. EXPERIMENTAL PROCEDURE

The experiments were carried out in a lagged fluidized bed reactor at high pressure equipped with a cyclone thermometer, and a pressure gauge. The effective volume of the rector is 1 litre (1100mL). a thermal sensor, an external heating element together with a thermostat provided temperature control in the reactor with a accuracy of ± 1°C. the gas sample was collected through a delivery tube into petroleum ether for adsorption. This was analysed using a gas chromatograph with the liquid – injection method were used percentage conversion and composition of other product were obtain.

The experiment were carried out in a fluidized – bed operation in a 0.085m diameter reactor with a total height of 0.195m. The distributor plate has holes with diameter of

0.002 and is 0.005m thick. The gas – phase feed into the reactor is through a manifold gauge connected to the butane cylinder source and volumetric meter where the pressure was obtained. Two types of experiments were performed during te study. The first series of experiments were performed at low gas flow rate of 2500ml/hr while the second series were performed at high gas flow rate of 7000ml/hr. both types of experiments were undertaken at temperature range of $62^0$C – $75^0$C and at a constant pressure of $1.5 \times 10^5 N/m^2$

The dimension of the reactor is as given above. The test section of the reactor is made of Pyrex transparent glass in order to roually observe the motion of the particles in the bed. In the present experiment, the pressure of supplied gas (butane or air) is measured by a manifold gauge from which the minimum fluidizing velocity was calculated. The solid particles adopted in this experiment are clay (aluminosilicates).

The physical properties of these particles are given below in the table. The size of the particles listed in this table is evaluated by the mesh screen analysis, prior to each run; the particles is evaluated by the mesh screen analysis prior to each run, the particles bed is pre fluidized to ensure uniformity of packing. The pressure drop across the bed is measured before and after fluidization.

In a fluiding state, the experiment of the bed is also measure and a relationship between pressure drop and flow rate of gas is examine for several height raying from 10mm to 100mm.

Experimental conditions

| Solid material | Particle size(μm) | Paticle Density (kg/$m^3$) | Fluidizing fluid (medium) |
|---|---|---|---|
| Clay | 300 | 1110 | Air |

Catalyst pre- treatment

The catalyst was prepared from clay obtained locally i.e. from Kutigi Area in Niger state, it was provided and sieved to a particle size of 300 microns and later caluned between 550 – $600^0$C. the catalyst was acidified using 0.1% w/w dilute sulphuric acid 0.15kg of the sample was placed in a beaker where distilled water was added to soak the paste for 60mintues at a controlled temperature range from 60 – $90^0$C. this was later dried at 373k for 12 hours. The stated procedure was carried out since catalyst surface is where the conversion in a catalytic reaction takes place. The surface of the catalyst is non- uniform or heterogeneous and, certain spots or locations on the catalyst that actually participate in the reaction are referred to, as active centres or sites. A regards activity and selectively, active centres have certain activity associated with them. Catalyst activity refers ti the rate at which the catalyst causes a reaction yo proceed towards equilibrium while selectivity's for a certain product of reaction, normally some intermediate product.

The kinetic experiment were carried out in a lagged fluidized bed reactor at high – pressure equipped with a cyclone, thermometer, and a pressure gauge. The effective volume of the reactor is 1100,L (or 1-1Litre). A thermal sensor, an external heating element together with a thermostat provided temperature control in the reactor with an accuracy of ±1$^0$C ( see Appendix I for the experiment set- up). The gas sample was collected through a delivery tube into petroleum ether for adsorption. This was analysed using a gas chromatograph with the liquid – injection method at

Laboratory where the percentage conversion and composition of other product were obtained.

The experiment ere carried out in a fluidized bed operation in a 0.085m diameter reactor with a total height of 0.195m. the distribution plate has hols with diameter of 0.002m and is 0.005m thick. (see appendix I). The gas- phase feed to the reactor is through a manifold gauge connected to the butane cylinder source and volumetric meter the pressure was obtained. Two types of experiment were performed during the kinetic study. The first series of experiment were performed at low gas flow rate of 2500m/hr while the second series were performed at high gas flow rate of 7000ml/hr. both types of experiment were undertaken at temperature range of 353k – 413k and at a constant pressure at 1.5 and at constant pressure of $1.5 \times 10^5 N/m^2$.

The dimensions of the reactor are given above. The fest section of the reactor is made of Pyrex transparent glass in order to visually observe the motion of the particles in the bed. In the experiment, The pressure of supplied gas (butane or air) is measured by a manifold gauge from which the minimum fluidized velocity was calculated. The solid particles adopted in these experiments are alumino sulphates (Zeolite, clay and mica) the physical properties of these particles are given in table 2.0 below. The size of the particles listed in this table is evaluated by the mesh screen analysis. Prior to each run. The particle bed is prefluidized to ensure uniformity of packing. The pressure drop across the bed is measured before and after fluidization.

In a fludizing state, the expansion of the bed is also measures and a relationship between pressure drop and flow arate of gas is examined for several height ranging for 10mm to 100mm.

# CHAPTER FOUR

## 4.0 RESULT

Table below shows the characteristics of clay at a particle size between 150 – 425 $\mu m$. The results showed an increase in the bed expression as the gas flow increases. While it shows an increases in the conversion of butane over the range of temperature considered until a certain time when conversion was observed to decrease.

For mass 100g

| S/NO | Concentration kmol/m$^3$ | Time (min) | Particle size (μm) | Temperature ($^0$C) | Flow rate ( m$^3$/s) |
|---|---|---|---|---|---|
| $C_1$ | 0.063648971 | 5 | 150 | 62 | 1000 |
| $C_2$ | 0.069219093 | 10 | 212 | 63 | 2000 |
| $C_3$ | 0.056413111 | 15 | 300 | 65 | 3000 |
| $C_4$ | 0.045640108 | 20 | 425 | 75 | 4000 |

For mass 150g

| S/NO | Concentration kmol/m$^3$ | Time (min) | Particle size (μm) | Temperature ($^0$C) | Flow rate ( m$^3$/s) |
|---|---|---|---|---|---|
| $C_1$ | 0.058941595 | 5 | 150 | 62 | 1000 |
| $C_2$ | 0.05085681 | 10 | 212 | 63 | 2000 |
| $C_3$ | 0.056413111 | 15 | 300 | 65 | 3000 |
| $C_4$ | 0.037128824 | 20 | 425 | 75 | 4000 |

# CHAPTER FIVE

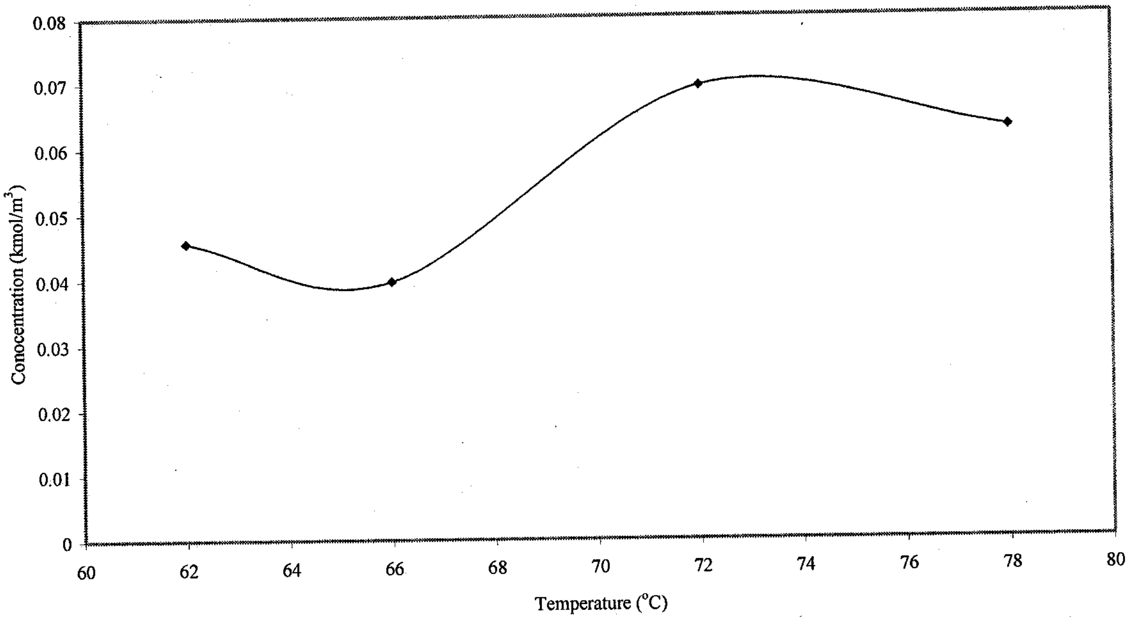


Fig. A1: Plot of concentration against temperature

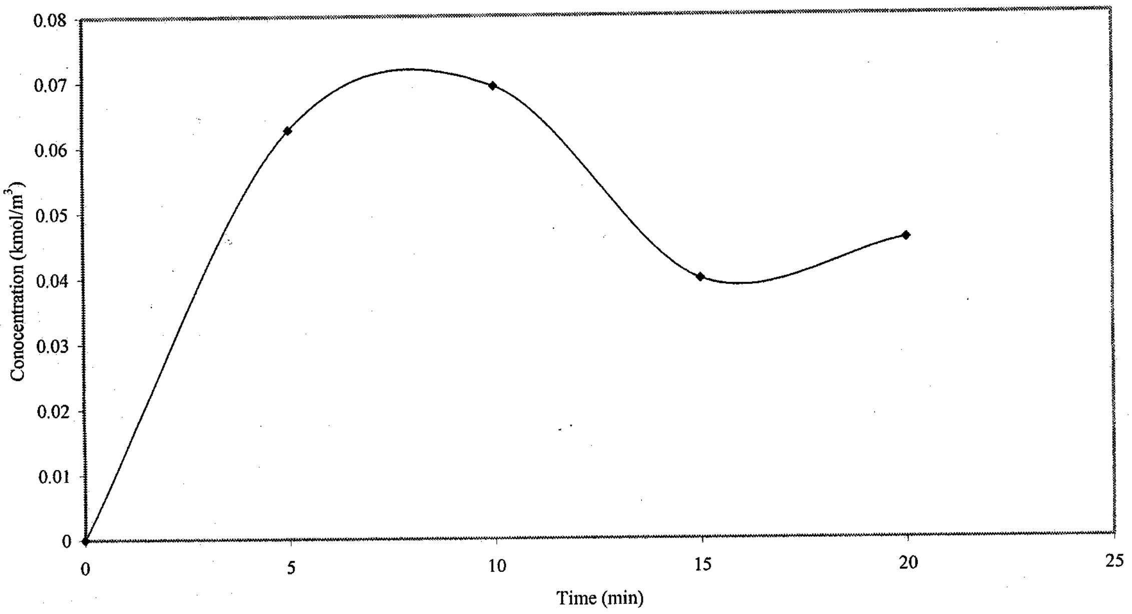


Fig. A2: Plot of concentration against time

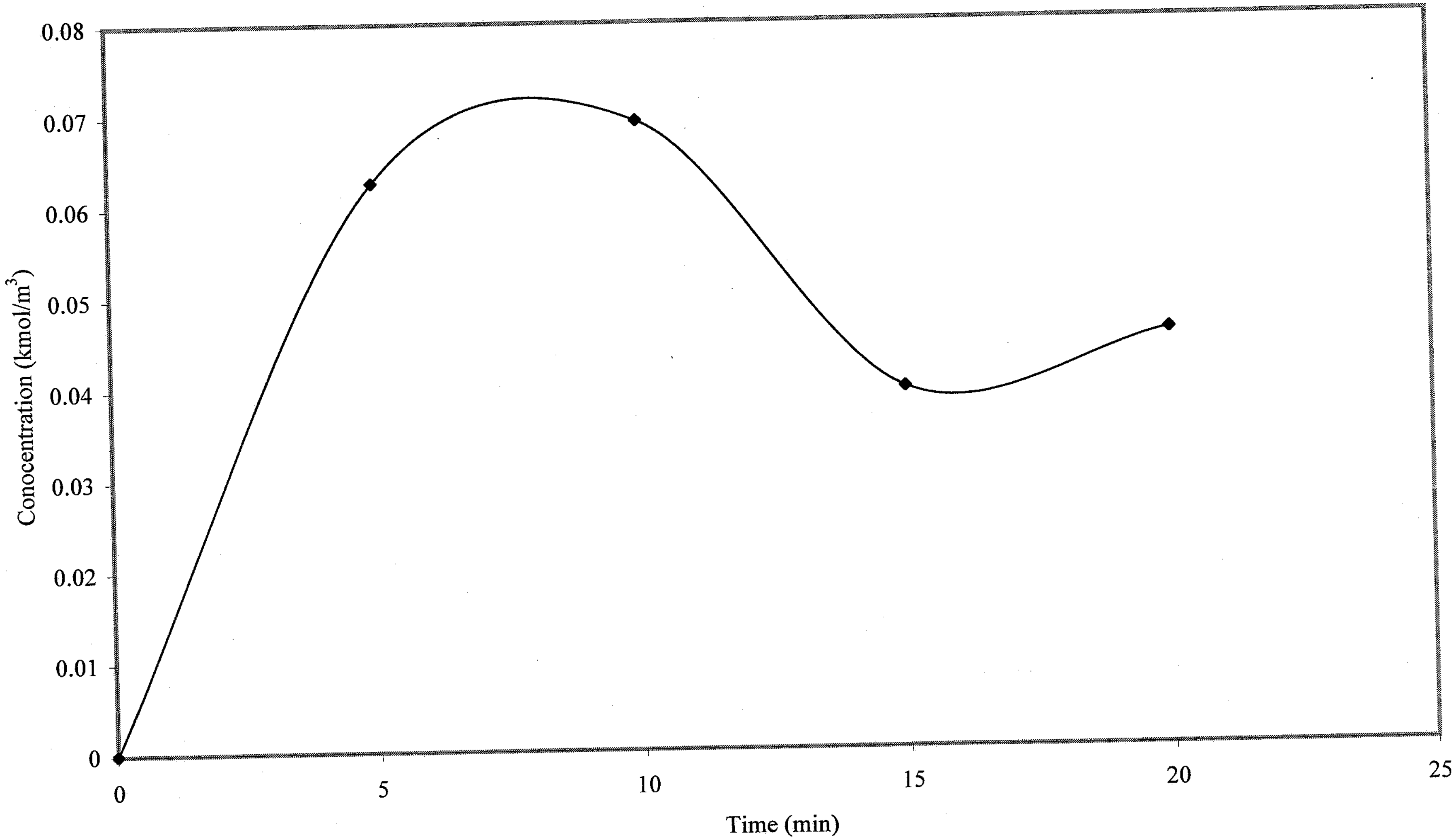


Fig. A2: Plot of concentration against time

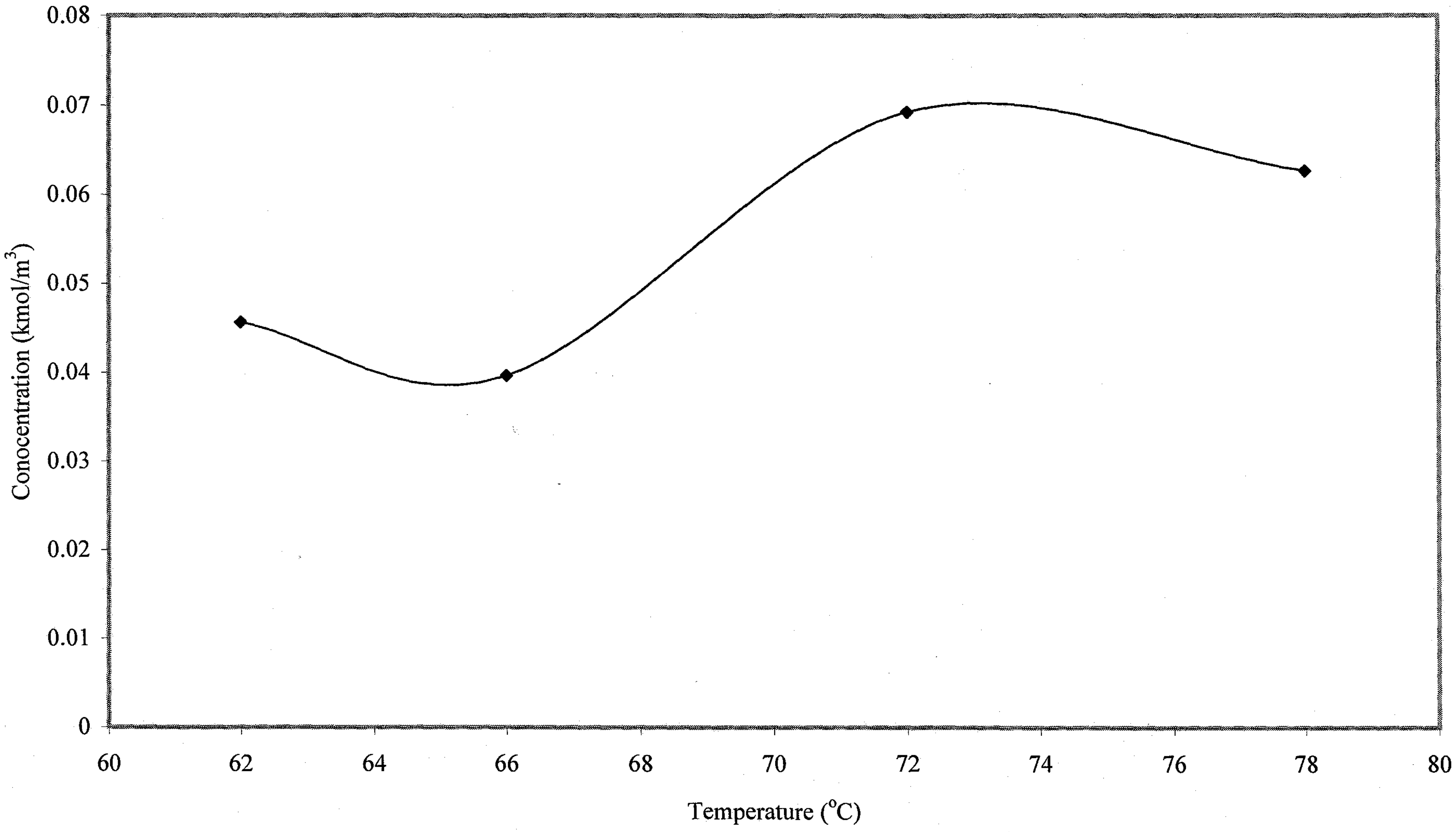


Fig. A1: Plot of concentration against temperature

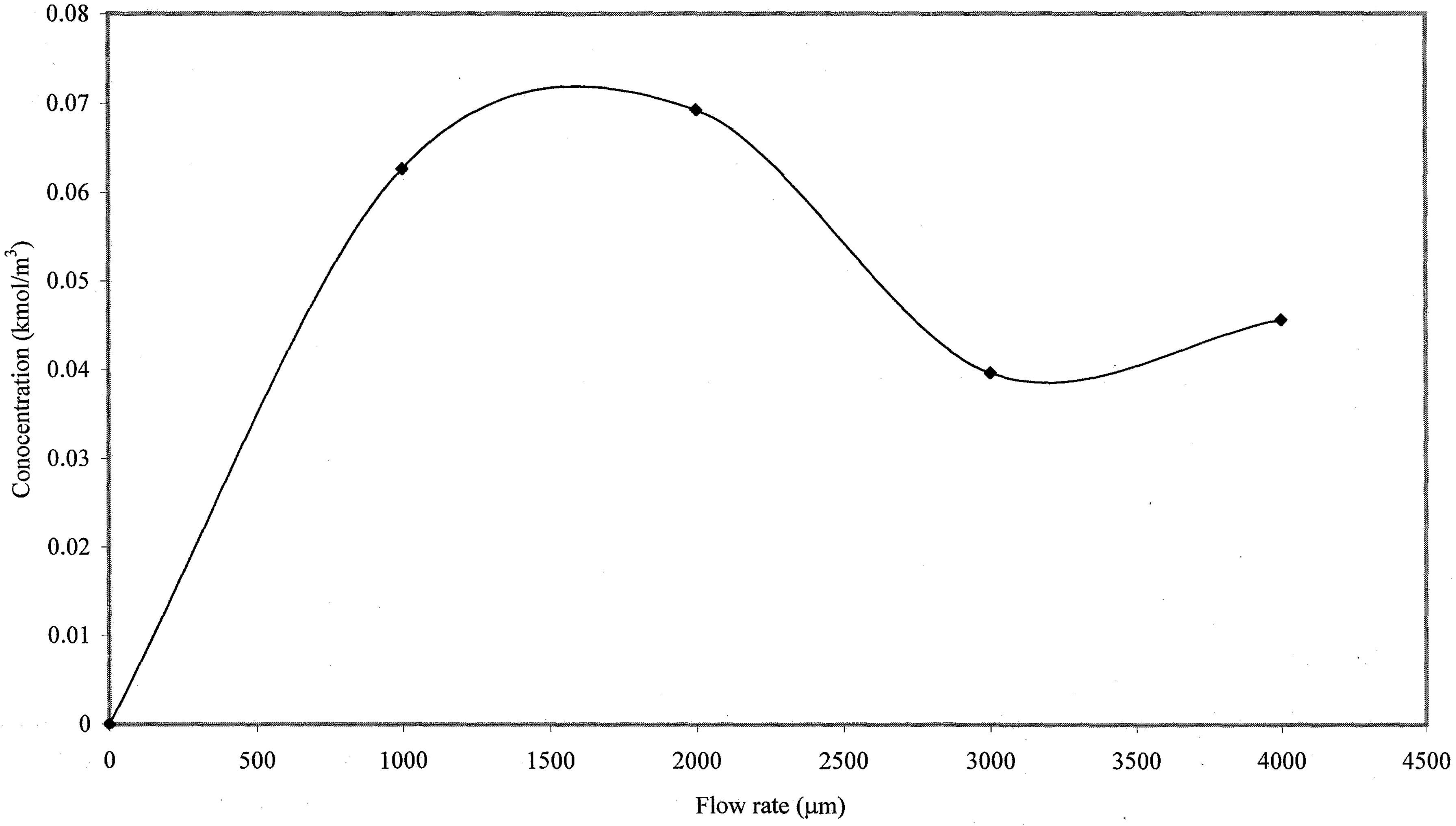


Fig. A4: Plot of concentration against flow rate

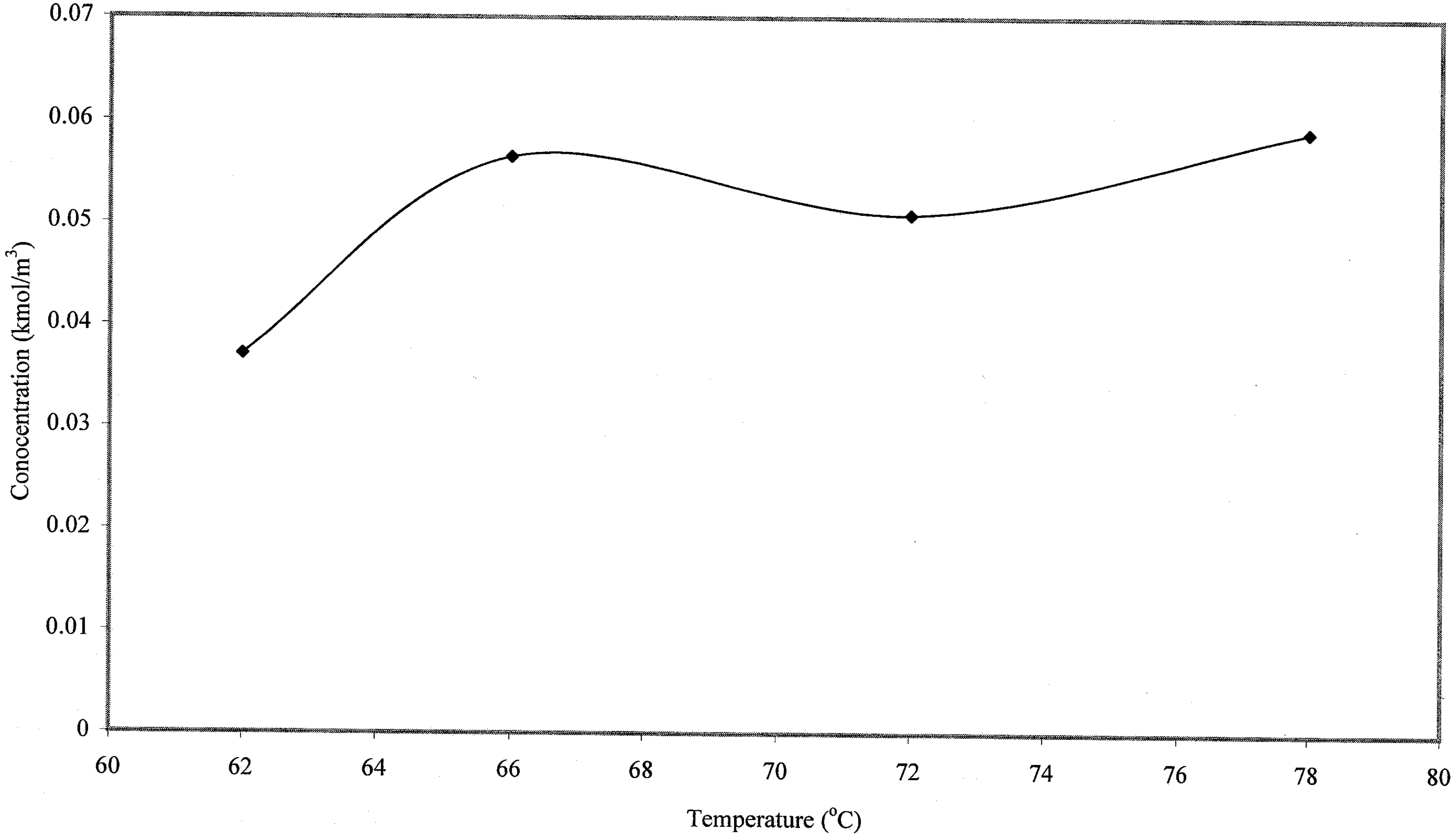


Fig. B1: Plot of concentration against temperature

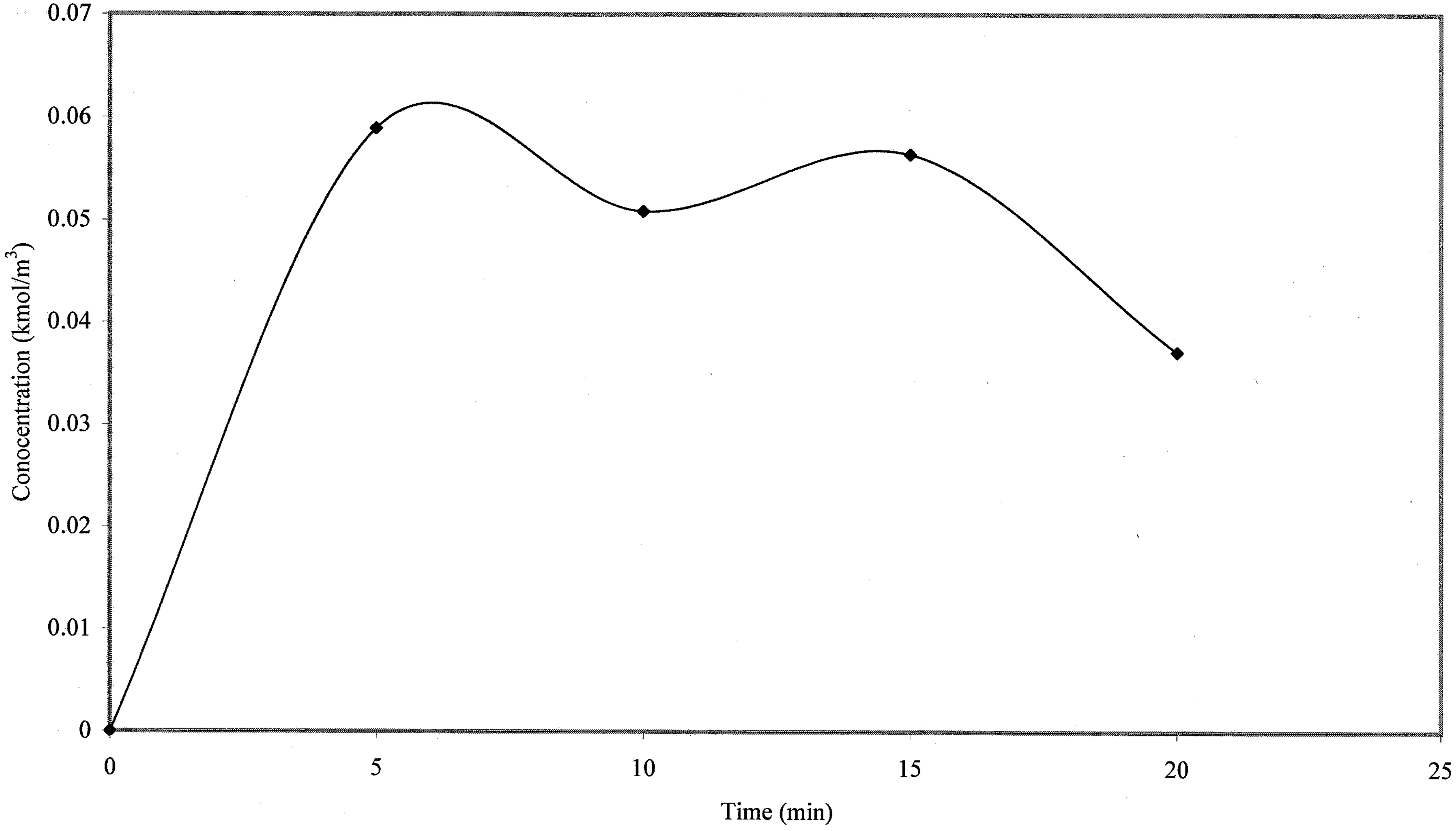


Fig. B2: Plot of concentration against time

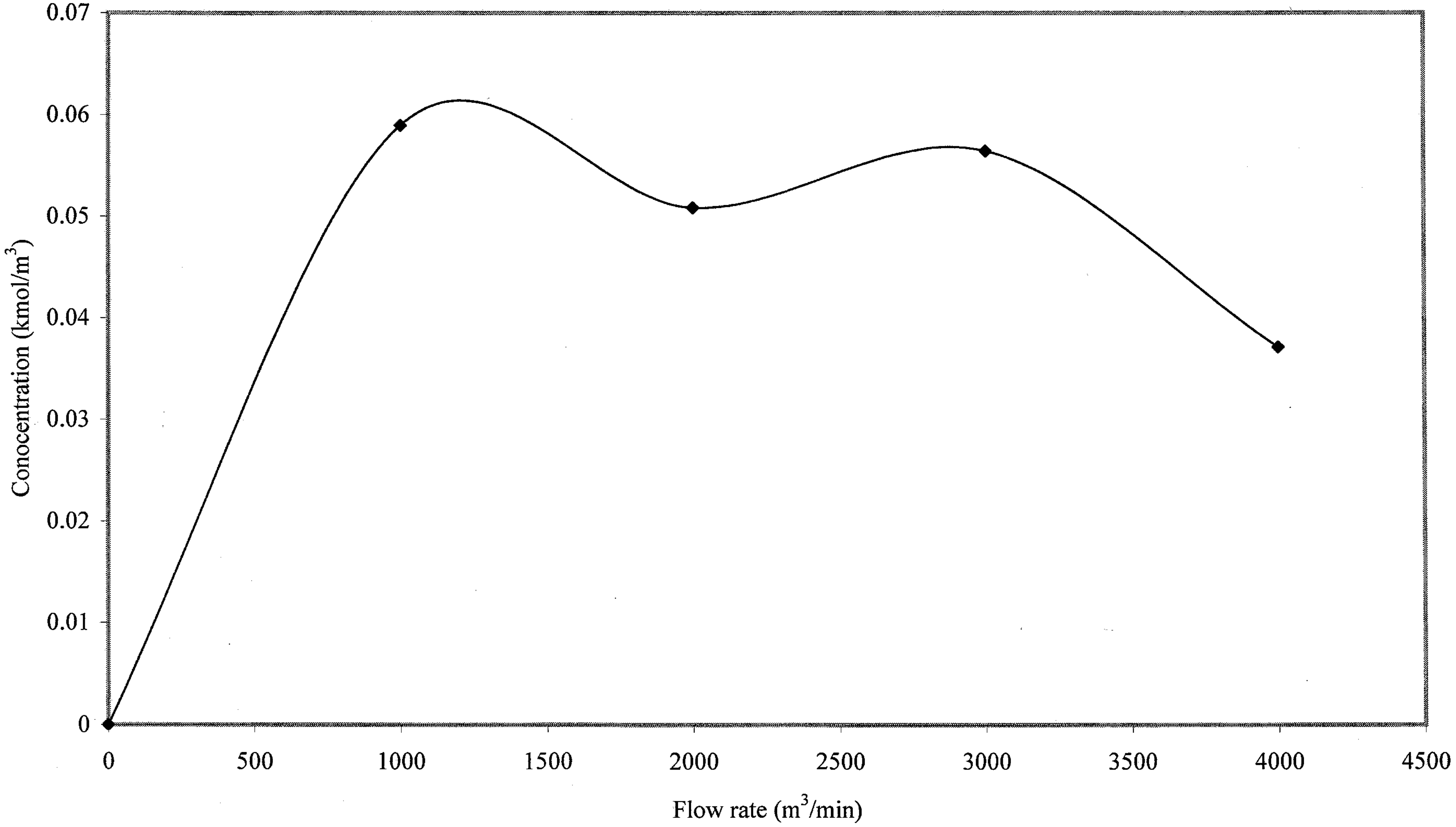


Fig. B4: Plot of concentration against flow rate

## 5.2 DISCUSSION OF RESULT

The data obtained from this investigation, shows that the factors that may influence the magnitude of adsorption characteristics of butane gas over an activated clay catalyst include:

(a) The particle size which the clay on investigation is made up of.

(b) The activating reagent used.

(c) Temperature of the sample under investigation.

(d) Flow rate of the sample under investigation.

(e) Time of the sample under investigation.

(f) Weight of the whole sample under investigation.

These entire aforementioned factors give different concentration value in the result.

The analysis of the clay samples reveals some differences in their constituents. For instance, silicon oxide concentration in these samples might be due to the fact that formation was as a result of decomposed marine and aquatic matters.

In the plots of concentration versus process parameters (i.e. Temperature, Time, Particle size, Flow rate) it was observed that, a curve shaped graph was arrived at in all the plots showing the relationship between each of the following:

(1) Concentration (kmol/m$^3$) Versus particle size(μm)

In this plot for 100g of activated clay that a curved shape was arrived at meaning that they are not directly proportional, rather there is a point of diminishing returns at which a change in the given process variable would have no positive effect on the concentration level. This point may be regarded as optimal value of some sort, and increasing the process parameters beyond this point will lead to a decrease in the value of the concentration and also on the performance of the catalyst.

The concentration increases first then slopes downward and almost at equilibrium.

Also for 150g of activated clay, the plot is similar to that of 100g of activated, except at a point where concentrated diminishes the rises again and ~~groly~~ finally diminishing the second time downward sloping

(ii) Concentration ($\text{kmol/m}^3$) versus flow rate (μm)

in the plot for concentration($\text{kmol/m}^3$) versus flow rate (μm) for 100g of activated clay, a curve was observed which was at optimal condition at flow arte value of about (1600μm) and corresponding concentration of (0.074$\text{kmol/m}^3$)

for 150g of activated clay, the first optimal concentration was about 0.069$\text{kmol/m}^3$ corresponding to about 1200$\text{m}^3$/min flow rate while after diminishing and rising again the optimal concentration was found at 0.06$\text{kmol/m}^3$ corresponding to flow rate of 3100$\text{m}^3$/min.

This curve also demonstrate the behaviour of concentration with floe rate of the sample under investigation.

(iii) Concentration ($\text{kmol/m}^3$) Versus Temperature

this curve shows a slight decrease in concentration corresponding to increase in temperature initially before rising with increase in temperature. The optimal concentration is at 0.07$\text{kmol/m}^3$ corresponding to about $73^0$C of 100g of activated clay.

For 150g of activated clay, the graph is similar to that of 100g.

The optimal concentration was found at 0.057 $\text{kmol/m}^3$ corresponding to $66^0$C

(iv) Concentration ($\text{kmol/m}^3$) Versus Time (min)

The curve shows an increase in concentration with time at first before reaching the optimal position and then diminishing and slightly ridsing later again.

The optimal concentration is 0.074kmol/min corresponding to 7 min time.

Where as the similar behaviour except that it has two optimal points. The first being observed at 0.062 kmol/min corresponding to 7 minutes and the second one is at 0.06 kmol/min corresponding to 17 minutes.

Finally, it has been established from this investigation that for different samples of activated clay in terms of weight cannot give a perfect behaviour. Also parameters like Temperature, Particle size, Time, flow rate play a vital role in the investigation of adsorption characteristics of butane gas over activated clay catalyst

# CHAPTER SIX

## 6.0 CONCLUSION AND RECOMMENDATION

### 6.1 CONCLUSION

The commercial feasibility of this work seems evident since the raw material clay is cheap and readily and naturally available.

Secondly, this research work has indicated that activated clay is suitable for absorbing butane gas.

Also, for different weight of activated clay i.e. 100g and 150g respectively. It concluded that for every 100g of activated clay used one optimal value is observed, but for 150g two optimal value of concentration against the parameter being investigated was observed (i.e. flow arte, particle size, time and Temperature).

Finally, rate of adsorption increases with increase in the parameters earlier mentioned (i.e. Flow rate, Temperature, particle size and Time).

### 6.2 RECOMMENDATION

For economic reasons, it is strongly recommended that activated clay should be used for adsorbing butane gas because it is not only cheap but also naturally readily available.

The use of this catalyst should be encouraged and should also be promoted with immediate effect.

Finally, other naturally available catalyst like termite heap should be utilized optimally to perform the same function as activated clay

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# APPENDIX

## CALCULATION OF THE CONCENTRATION

For 100g $C_1$

$$0.645 \rightarrow 3.466413683\times10^{9}$$

Clay outlet $x_1 \rightarrow 3.366934116\times10^{9}$

$$x_1 \frac{0.0645\times3.366934116\times10^{9}}{3.466413683\times10^{9}}$$

$$x_1 = 0.062648971$$

For 100g $C_2$

$$0.645 \rightarrow 3.466413683\times10^{9}$$

$$x_2 \rightarrow 3.720031191\times10^{9}$$

$$x_2 \frac{0.0645\times3.720031191\times10^{9}}{3.466413683\times10^{9}}$$

$$x_2 = 0.062648971$$

For 100g $C_3$

$$0.645 \rightarrow 3.466413683\times10^{9}$$

$$x_3 \rightarrow 2.130676844\times10^{9}$$

$$x_3 \frac{0.0645\times2.130676844\times10^{9}}{3.466413683\times10^{9}}$$

$$x_3 = 0.039645804$$

For 100g $C_4$

$$0.645 \rightarrow 3.466413683\times10^{9}$$

$$x_4 \rightarrow 2.452829412\times10^{9}$$

$$x_4 \frac{0.0645\times2.452829412\times10^{9}}{3.466413683\times10^{9}}$$

$$x_4 = 0.045640108$$

For 150g $C_1$

$$0.645 \rightarrow 3.466413683\times10^{9}$$

$$x_1 \rightarrow 3.167689176\times10^{9}$$

$$x_1 \frac{0.0645 \times 3.16689176 \times 10^9}{3.466413683 \times 10^9}$$

$$x_1 = 0.058941595$$

For 150g $C_2$

$$0.645 \rightarrow 3.466413683 \times 10^9$$

$$x_2 \rightarrow 2.733189658 \times 10^9$$

$$x_2 \frac{0.0645 \times 2.733189658 \times 10^9}{3.466413683 \times 10^9}$$

$$x_1 = 0.050856807$$

For 100g $C_3$

$$0.645 \rightarrow 3.466413683 \times 10^9$$

$$x_3 \rightarrow 3.031801278 \times 10^9$$

$$x_3 \frac{0.0645 \times 3.031801278 \times 10^9}{3.466413683 \times 10^9}$$

$$x_3 = 0.056413111$$

For 100g $C_4$

$$0.645 \rightarrow 3.466413683 \times 10^9$$

$$x_4 \rightarrow 1.995408916 \times 10^9$$

$$x_4 \frac{0.0645 \times 1.995408916 \times 10^9}{3.466413683 \times 10^9}$$

$$x_4 = 0.037128824$$

# Diagram

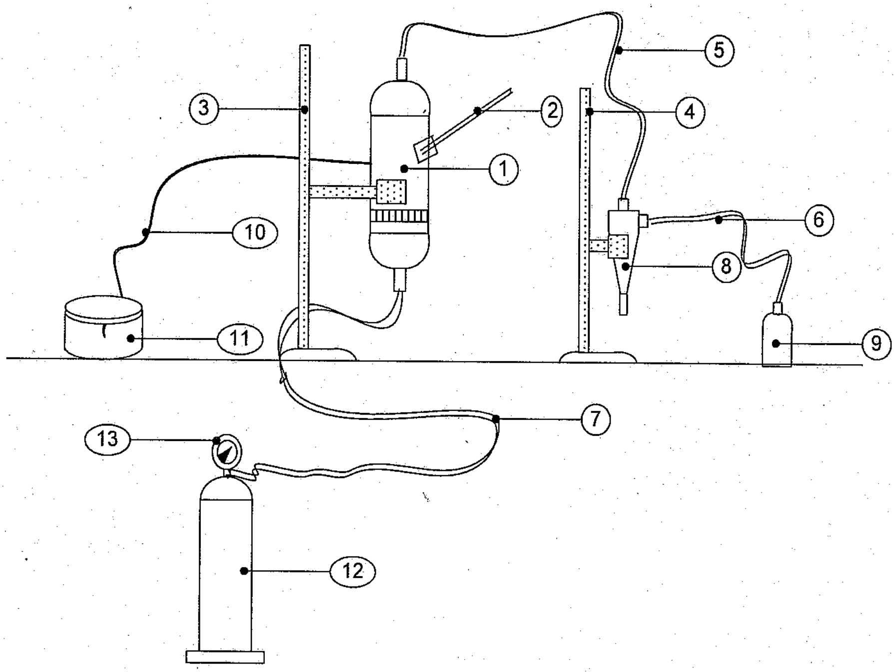

Figure 4.0: Experimental Set-up

1- Prototype Fluidized-bed Reactor

2- Thermometer

3 & 4- Retort Stand

5, 6, & 7- Connecting Tubes

8- Cyclone

9- Collecting Bottle

10- Electric Cord

11- Heating Mantle

12- Gas Cylinder

13- Pressure Gauge