DEODOURIZATION OF KEROSENE USING ACTIVATED CLAY AND RICE HUSK.

BY

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<u>DECLARATION</u>

I, OYEYEMI ABIODUN OYEBIMPE declare that this project presented for the award of Bachelor of Engineering in Chemical Engineering department has not been presented either wholly or partially for any other degree elsewhere.

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Student   Date

<u>DEDICATION</u>

I dedicate this piece of work to the Almighty Jehovah Nissi who is my Banner all through the period of study. And also to my beloved parents, Evang. & Evang. (Mrs.) S.A.B. Oyeyemi for providing me with the education upon which this work is based.

ACKNOWLEDGEMENT

ABSTRACT

The obnoxious odour of Kerosene has diminished its use (apart from domestic purpose) in many industrial processes and so a need for further refining processes which includes deodorization, a process that reduces (or removes) the odour-causing components and improve the smoke point.

The study of the deodorization of Kerosene has been carried out using the 'adsorption' method. Two types of materials were used; Rice husk and Clay. Some part of these materials was activated using Hydrochloric acid and some used without activation. These materials were packed into the glass column as the adsorption bed of a particular height of 25cm; one after the other and the raw domestic Kerosene was run through the column.

The activated clay was found to be most efficient which produced Kerosene with smoke point of 26mm as compared to that of the raw Kerosene with 20mm. The use of acid-treated rice husk gave a better result than raw rice husk with smoke points of 23.67mm and 23mm respectively.

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CHAPTER ONE

1.0   GENERAL INTRODUCTION

Kerosene is a colourless liquid fuel, which is a chemical mixture of hydrocarbons i.e. made of hydrogen and carbon atoms. Kerosene was first made in 1840 by researchers from Europe and North America. They learned how to extract it from coal and shale but in 1859, the first successful petroleum well in United States was drilled and this resulted in large-scale petroleum production and so an abundant source of Kerosene. (2)

Kerosene is a petroleum distillate or fraction, which is obtained in between gasoline and gas oil with boiling range between 140 ^{O}C – 300 ^{O}C. It is less volatile and inflammable than gasoline. Kerosene is predominantly paraffinic with 15 – 20 % aromatics and a small amount of Sulphur, Oxygen and Nitrogen which composition depends on the source.

Kerosene has an obnoxious odour and so the removal of the objectionable odour – causing components from Kerosene, which is, called deodourization of Kerosene. Generally, petroleum fraction which includes gasoline, kerosene, gas oil, diesel oil and Naphtha which are produced by conventional method of refining like distillation, contain components like Nitrogen, Sulphur, Oxygen and aromatic compounds. These compounds are toxic and cause colour instability, corrosion, low pour point, low octane number and the objectionable odour.

The foul odour of kerosene is caused mainly by Sulphur and aromatic compounds, which includes Hydrogen Sulphide, mercaptans, anthracenes, naphthalene, benzene etc.
Naturally, the odour of any petroleum product is very important in its marketability, so, the smallest trace of those certain contaminants and their concentration in the product must be reduced to the minimum.

1.1   KEROSENE DEODOURIZATION METHODS

There are various methods of kerosene deodourization and they include the following:

1. Solvent extraction
2. Oleum treatment
3. Sweetening method
4. Aromatic saturation
5. Catalytic hydrogenation

This project will employ the clay adsorption process to deodourize kerosene. Adsorption involves contacting the raw kerosene with a fixed bed packing of clay in a vertical column and after that tries same method using rice husk in the column. Adsorbents are natural or synthetic materials of microcrystalline structure whose internal pore surfaces are accessible for the selective adsorption of some of the solution components. This method will cost less and give a better-defined control of the quality of kerosene.

1.2   AIMS AND OBJECTIVES

Clay is known to be an adsorbent while rice – husk could also be used as an adsorbent based on some of its composition. The main objective of this project is to determine the potential of using clay and rice husk for the purpose of kerosene deodourization. The effect of both the virgin and acid – treated rice husks on deodourization will also be determined. This objective is focused in order to improve on the economic importance of kerosene as the case may be.

1.3   METHOD AND SCOPE

Raw samples of kerosene are collected from the local commercial vendor and run through a packed column (fixed bed) of clay and rice husk sequentially. The deodourized kerosene samples were collected and deodourization test was carried out on them. Due to the unavailability of some required apparatus, some limitations are expected of this work for example, the use of a burette instead of a

glass column. The scope of this work includes the determination of the effectiveness of adsorbents and test for kerosene quality.

1.4   RELEVANCE OF STUDY

Recent development in the country shows that children have died after being kept in a room fleeted with insecticide due to the toxic compounds. Compound like aromatics present along side with hydrogen sulphide and mercaptans having a particular effect of unpleasant odour and causes corrosion problem at high concentration and hence the need for this DEODOURIZATION, which makes kerosene a good for solvent used in the manufacture of insecticides.

In addition, deodourization is necessary because the kerosene used as burning oil should not give a smoky flame and charring of wick must be minimum on the lamp glasses. The white type kerosene is also used as thinners for paints, varnishes and for dry cleaning, so should be highly treated to avoid unpleasant odour. (4)

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 BACKGROUND

The early application of adsorption refining was for the removal of undesirable, highly coloured material of an asphaltic or resinous nature from petroleum fractions using bone char. (3)

Bone char was later replaced by Fuller's earth, which was found in 1893 by George Taber to be more effective for refining steam cylinder stocks, and the removal of asphaltic or resinous materials from lubricating oil stocks using acid activated bentronite.

Within the last few years, new application of adsorption refining have been proposed which deals not only with the removal of comparatively small amounts of undesirable components from petroleum fractions, but also completely separates certain fractions into constituent classes of hydrocarbon. (9)

2.2 KEROSENE

Kerosene is a petroleum distillate, which is obtained as a fraction between gasoline and gas oil. It boils between 140 $^{\circ}$C and 300 $^{\circ}$C and is predominantly containing paraffinic and aromatic compounds. (2)

Kerosene could either be water white (prime white) or the standard white is the darkest shade. The raw kerosene is subjected to suitable refining treatment according to the uses required which may be classified as follows:

1   Fuels for heating and lighting purposes.

2   Fuels for jet engines (Aviation) and tractors.

3   Thinner in paint industries and insecticides emulsion.

4   Solvents for cleaning.

5   Raw material in the printing ink and metal degreasing industry.

Kerosene with high content of aromatics is not suitable for lighting and heating appliances with wicks (lantern) since they are responsible for the smoke. So for such uses, it is treated to reduce or remove the components e.g. mercaptans.

Chemically, kerosene composition depends on its source but it usually consist about 10 different hydrocarbons; each containing 10 – 14 carbon atoms, which includes n – dodecane alkyl derivatives of benzene, naphthalene and its derivatives. A typical Nigerian kerosene analysis shows an aromatic content of about 7.7 wt % and Sulphur of 0.01973%. This composition has to be highly reduced to extend the use of kerosene.

2.2.1 MERCAPTAN

Mercaptans are hydrocarbon derivatives of Sulphur present in light fractions of crude oil, which includes kerosene. It is one of the organosulphur compounds, which are also called thiols or thio alcohol and have the general structure RSH. They have a characteristic unpleasant odour and its presence in kerosene causes that objectionable odour. Thus, its components have to be minimized in kerosene fraction to make it odourless.

The name thio alcohol suggests that mercaptans are similar to alcohol. Although, some properties are analogous there are decided differences, which are related as follows:

1   Greater acidities of thiols

2   Ease with which mercaptans are oxidized.

3   Ability of mercaptans to enter free – radical reactions.

The second difference probably accounts for the absence of thiols as such in contrast to alcohol in nature.

Some properties of mercaptans include:

1   Formation of salts with bases.

2   Ease of oxidation to disulphides and higher oxidation product such as sulfonic acids.

3   Reaction with chlorine (bromine) to form sulfenyl chlorides.

4   Undergo additions to unsaturated compounds such as olefins, acetylenes, aldehydes and ketones. (14)

The occurrence and removal of mercaptans from petroleum is industrially important. Even the odour of mercaptans also finds use; traces of mercaptans added to dangerous gases acts as a warning agents in case of leaks.

2.2.2 TYPES OF KEROSENE

There are mainly two types of kerosene and these are the domestic kerosene and the aviation turbine kerosene. (4)

I.   DOMESTIC KEROSENE

Kerosene was the major petroleum product used initially just after oil was discovered. It was used mainly for heating and illumination. As time went on, modernization diminished the importance of kerosene but still was used primarily as a source of light in less advanced countries because it is cheap, flexible and portable.

II.   AVIATION TURBINE KEROSENE

Aviation turbine kerosene is a modified development of the illuminating kerosene originally used in gas turbine engines. They are mainly produced by the straight distillation of petroleum. Fuels are released for air – craft flying at a supersonic speed. The various grades of fuel differ in their fractional composition and the overall mercaptan (Sulphur) content. The freezing point for most ATK must not exceed 60 ^{O}C.

The aromatics present are also limited because they don't aid clean burning. Aromatics cause smokiness and carbon deposition in the engines. They also degrade elastomer in fuel system and increase

the illuminoxity of combustion flame, which can adversely affect the life of certain design combustion chamber.

2.2.3 PROPERTIES OF KEROSENE
2.2.3.1 SMOKE POINT

Smoke point could be expressed as the maximum height of flame in millimeters at which the given kerosene will burn without giving off smoke. The different components of kerosene cause the different flame heights that are obtained from the wicks of the lit lamp. (15)

Mainly, aromatics contribute to the smokiness and so the removal would increase the smoke point. Naphthalene with side chains are inevitably retained to give good illumination knowing the percentages of paraffin, napthalenes and aromatics present in kerosene, the smoke point can be predicted as follows:

Smoke Point = 4.48P + 0.32N + 0.20A

P, N and A represent the percentages of Paraffin, Naphthalene and Aromatics respectively.

2.2.3.2 ANILINE POINT

This refers to the lowest temperature at which equal volumes of aniline and kerosene can remain in a uniform solution without separating into phases. This could act as an indication for aromatic hydrocarbon contained in kerosene. (15)

2.2.3.3 POUR POINT

Pour point is the lowest temperature expressed as a multiple of 3 ^{O}C at which kerosene flows when it is chilled without disturbance under specified condition.

2.2.3.4 FLASH POINT

It is defined as the minimum temperature at which the vapour of kerosene heated under definite standard conditions will form an

explosive mixture with the surrounding air and ignite when a flame is brought up to it. This point depends on the distillation range of the product. The lower the range, the lower the flash point. An average flash point of kerosene is between $30 - 60^{\circ}C$ but for marketable kerosene, it should be found to be above $49^{\circ}C$. (15)

2.2.3.5 SPECIFIC GRAVITY (5)

Kerosene has a specific gravity or relative density of range between $0.8 - 0.86$ at $20^{\circ}C$. It depends upon the temperature and it decreases when kerosene is heated. The specific gravity can be calculated at a certain t $^{\circ}C$ temperature if that at $20^{\circ}C$ is known using the formula below:

$$d_t = d_{20} - Y(t - 20)\ ^{\circ}C$$

Where d_t = Specific gravity at t $^{\circ}C$

d_{20} = Specific gravity at $20^{\circ}C$

Y = Coefficient of volume expansion

2.2.3.6 VISCOSITY

This refers to the internal resistance of a fluid to its movement. It is regarded as the internal friction in liquid, which is attributed to the liquid particle. The higher the viscosity of the liquid, the lower its mobility or fluidity. The viscosity of liquid petroleum products is influenced by the presence of resinous substances. (15)

Kerosene has a very low viscosity and so it is highly mobile.

2.2.3.7 FIRE OF IGNITION

This is the temperature at which kerosene vapour heated under definite condition ignites when a flame is brought up to it, and burns for at least 5 seconds. The ignition point is naturally always higher than the flash point.

2.3 ADSORBENTS

Adsorbents are natural or synthetic materials of micro – crystalline structure whose internal pore surfaces are accessible for selective association of solid and solute.

Adsorption of a substance involves its accumulation at the interface between two phases, such as a liquid and a solid or a gas and a solid. The molecule that accumulates or adsorbs at the interface is called an adsorbate and the solid on which adsorption occurs is the adsorbent. (11)

Usually, the attractive forces of adsorbents are weaker and less specific than those of chemical bonds and the large surface area is a property, which distinguishes it from other solid substances. This surface area depends on the method of preparation or the origin of the product and not the chemical composition. Adsorption depends on the numerous minute pores, which permeates the individual particles and are selective on molecule shape. There is also a particular affinity for unsaturated and polar molecules during adsorption. (6)

The application of an adsorbent in engineering processes depends on the magnitude of its attractive force. The common adsorbents used in petroleum industry include silica gel, clay, fuller's earth, activated carbon, molecular sieves and bone char.

Generally, an industrial adsorbent is required to possess a high adsorbing capacity, thermal endurance, ease of regeneration, selectivity for the solute and have a long service life without change in structure or surface properties.

The adsorption process in kerosene purification although originally utilized by industries mainly in the deodourization of liquids, it is also being applied to the separation of aromatic hydrocarbons and numerous applications in catalytic processes many of which employ adsorbents for support of the catalyst.

In general, there are three methods:

1   Percolation through a long column of coarse earth.

2   Contact at a high temperature with finely powdered clay.

3   Contact in the vapour phase with loosely packed clay.

The removal of odour in kerosene is governed by the desorption isotherm of Freundlich expressed by: (5)

$$\frac{\text{Log x}}{\text{m}} = \text{Log n} + (1/n \ \text{log c})$$

Where n = unit of impurities removed

    m = quantity of adsorbent used

    c = concentration of impurities

    x = quantity of kerosene to be deodourized

2.3.1 SILICA GEL

This is a hard granular and very porous product made from the gel precipitated by normal acid like sulphuric acid or hydrochloric acid and treated with sodium silicate solution. The resulting gel precipitated is allowed to set then leached with water to remove salt and excess acid. This is then dried and screened to size. Its moisture content will vary between 4% and 7%. Silica gel looses its adsorbing capacity rapidly if it is heated to the temperature required to burn off adsorbed components.

2.3.2 FULLER'S EARTH

These are natural clays chiefly anhydrous magnesium and aluminium silicates in form of minerals or a pulgite and montmorillonite. It is heated and dried during which it develops a porous structure then ground and screened. They are particularly useful in decolourizing, neutralizing and stabilization of light distillates by removal of gum – forming substances and further processing of lubricating oil.

2.3.3 MOLECULAR SIEVES

These are porous synthetic Zeolite and metal aluminosilicates. The 'cages' of the crystal cells can entrap adsorbed matter and the diameter of the passage ways, controlled by the crystal composition, regulates the size of the molecule, which can enter.

The sieves can be separated by adsorption according to molecular polarity and degree of unsaturation. The molecular sieves could be in form of pellets, beads or powder and are used for dehydration of gases and liquid hydrocarbon mixtures.

2.3.4 ACTIVATED CARBON

Adsorptive carbon is derived from a wide variety of sources and characteristics of these differ very appreciably depending on the method of preparation.

This particular carbon is prepared from coal, charcoal or other carbonized materials by a process of activation. Activated carbon is employed in the vapour phase separation and recovery of hydrocarbon gases. Its main advantage in the process of adsorption is the large surface area they offer at relatively low price.

2.4   CLAY

Clay could be described in two ways; as a rock term and as a particle size term.

As a particle size term, it refers to that fraction of the earthly material containing the smallest particle in the mechanical analysis of the sedimentary rock and soil. Earthly material is normally of three types based on size, which are sand, silt and clay. Clay usually is less than $2\mu m$ in size and its mineral includes shale and argillites.

In a rock term, it is a material that has been deposited as a sediment and has formed due to hydrothermal action or by actions of weathering. It could also be described as an earthly fine graded material, which develops plasticity when moistened, or with limited amount of water. (10)

Chemical analysis of clay shows that it is composed mainly of silica, alumina and water. The commercial value of clay is related to its mineralogical and chemical composition and the presence of a little amount of mineral of soluble salt impurities can restrict its use. The common impurities include carbonates iron oxide, mica, quartz, feldspar etc.

2.4.1 TYPES OF CLAY

Based on their formation, clay is classified into three main types as follows:

1   Montmorillonite
2   Kaolinite
3   Illite

FORMATION OF CLAY BY WEATHERING. (1)

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┌─────────────────────────────────────┐          ┌──────────────────────────────┐   - K
│   FERROMAGNESIAN MINERAL             │          │   MONTMORILLONITE            │ ◄────────┐
│                                      │          │                              │          │
│   Olivine                            │ ───────► │   (Al, Mg, Fe) 2 (Si, Al) 4 O10 │        │
│   (Mg, Fe) 2 Si O4                   │          │   (OH) 2 . n H2O, O, Ca, Na  │          │
│   Pyroxenes                          │          └──────────────────────────────┘          │
│   (Ca, Mg, Fe) 2 Si2 O6              │                    ▲       │  + Si O2               │
│   Amphiboles                         │                    │       ▼                        │
└─────────────────────────────────────┘                                                     │

┌─────────────────────────────────────┐          ┌──────────────────────────────┐          │
│           FELDSPAR                   │ ─────────┐│       KAOLINITE              │          │
│                                      │          ││                              │          │
│   KAlSi3O8                           │ ────────►│   Al2 Si2 O5 (OH) 4          │          │
│   NaAlSi3O8    In varying proportions│          │└──────────────────────────────┘          │
│   CaAl2Si2O8                         │          │         ▲   - K                          │
│                                      │ ─────────┘         │   - Si O2                       │
└─────────────────────────────────────┘                    │                                 │

┌─────────────────────────────────────┐          ┌──────────────────────────────┐          │
│            MICAS                     │          │         ILLITE               │ ◄────────┘
│                                      │          │                              │   + K
│   Biotite                            │ ───────► │   K Al2 (Al, Si3) O10 (OH)   │
│   K (Fe, Mg) 3 Al Si3O10 (OH) 2      │          └──────────────────────────────┘
│   Muscovite                          │
│   K Al3 Si3 O10 (OH)                 │
└─────────────────────────────────────┘
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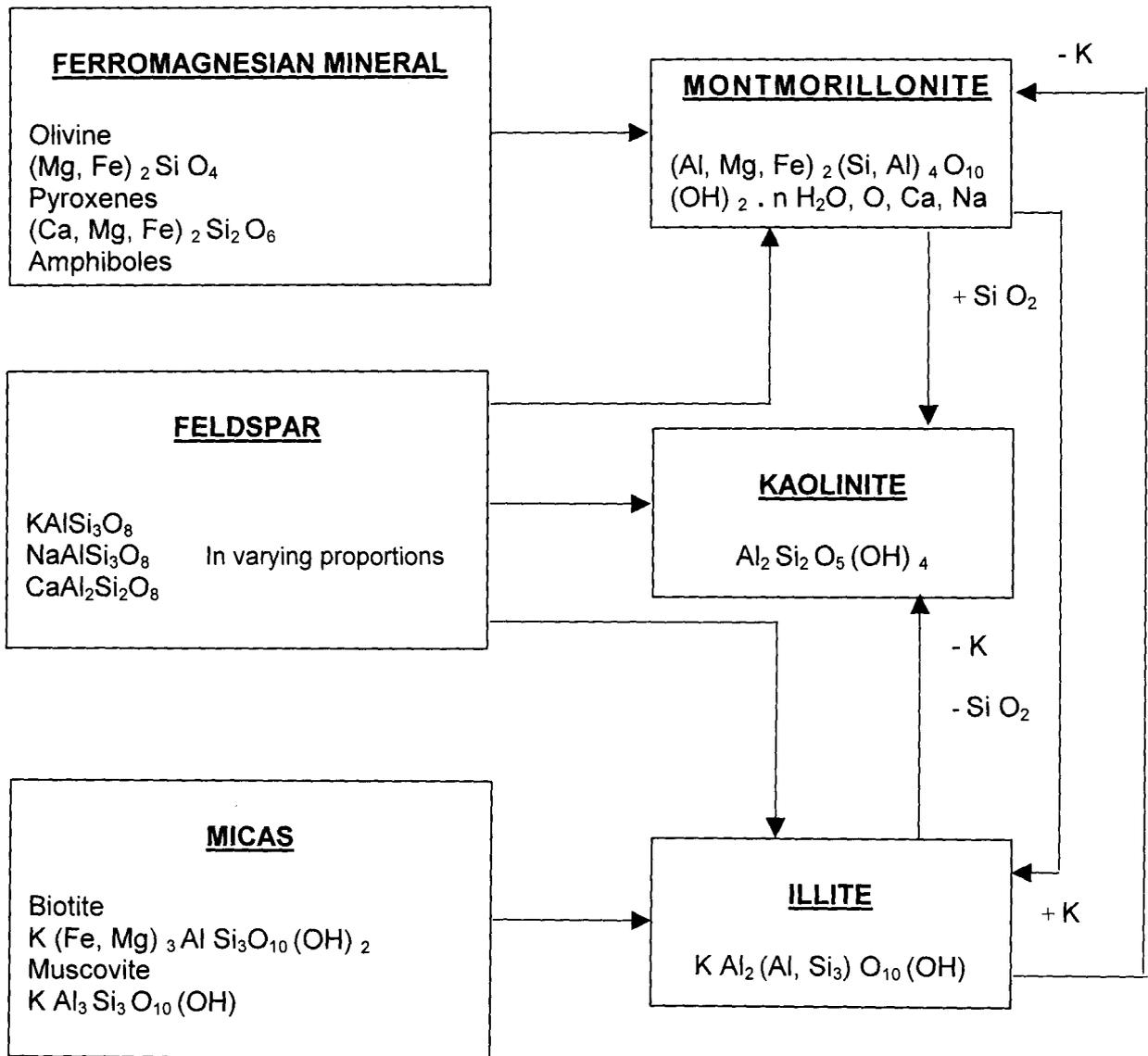
So far, the most abundant primary rock-forming mineral is the feldspar. Potassium and sodium feldspar forms the granitic composition and calcium – sodium feldspar forms the basaltic composition. Kaolinite occupies a central position in the clay mineral and its formation by decomposition of potassium feldspar (orthoclase) is represented as follows:

$$2KAlSi_3O_8 + 3H_2O + 2CO_2 \longrightarrow$$

Potassium feldspar   Acid Rain

$$Al_{12}Si_2O_5 (OH)_4 + 2K_4 + 2HCO_3 + 4SiO_2$$

Kaolinite + Ion and silica in solution
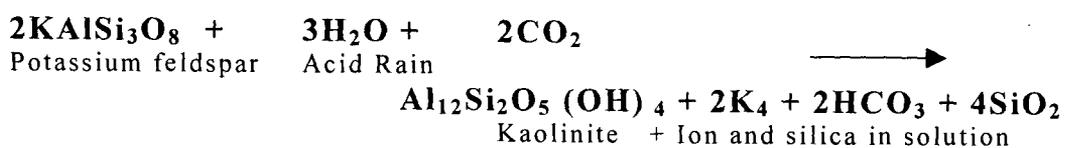
In the reaction above, some water goes into the structure of the clay mineral as hydroxyl ions (OH). Some silica is removed in solution and so is all the potassium. However, in some situation, not all the potassium is removed in solution and so Illite is formed.

$$3KAlSi_2O_2 \quad + \quad 2H_2O \quad + \quad 2CO_2 \longrightarrow$$
$$KAl_{12}(Al_{12}Si_2)O_{10}(OH)_2 \quad + \quad 2K_4 \quad + 2HCO_3 \quad + \quad 6SiO_2$$
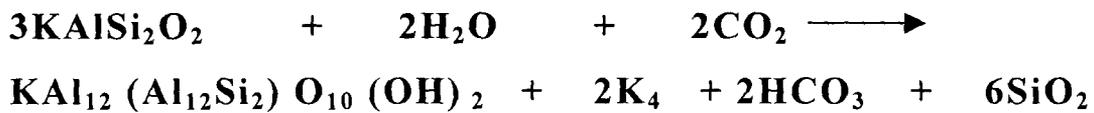
In general, ferromagnessian minerals and calcium – sodium feldspar (Plagioclase) weather initially to montmorillonite, potassium feldspar to Illite or Kaolinite and micas to Illite. Balite is both a mica and a ferromagnessian mineral and its weathering product include montmorillonite as well as illite.

2.4.2 KAOLINITE CLAY

Kaolinite is a common clay is composed of a silicate sheet ionically bounded to a sheet of AlO (OH) $_2$, producing thin platelets of clay with the formula $Al_2Si_2O_5(OH)_4$.

Kaolin is a hydrated aluminium silicate and a good example of a layer lattice. The structural formula is written thus $Al_2O_3.2SiO_2.2H_2O$.

Sheet Structure of Kaolinite Clay. (14)

```
            HO    OH    OH
              \    |    /
               \   |   /
                \  |  /
                 2Al
                 / | \
                /  |  \
               /   |   \
            HO     O     O
                   |
                   |
                  2Si
                 //|| \\
                // || \\
               //  ||  \\
              //   ||   \\
            O      O      O
```
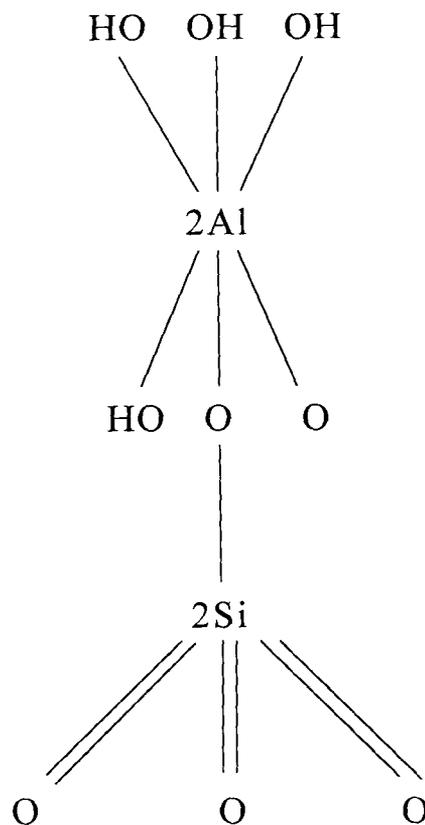
2.4.3 PROPERTIES OF CLAY

The properties of clay materials are determined by at least five factors: texture, organic materials, non-clay mineral composition and soluble salt with exchangeable ion.

2.4.3.1   COLOUR

The maintenance of a uniform colour is very important in most structural clay. This colour is influenced by the state of oxidation of iron (Fe), the firing temperature, and division of the iron mineral and the degree of vitrification. In addition, the composition of lime, alumina and magnesia in clay mineral could also affect the colour.

2.4.3.2   PLASTICITY

The plasticity of a material is the ability of the material to undergo permanent deformation in any direction without rupture under a stress beyond that of elasticity yielding.

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Most clay become plastic when mixed with varying proportion of water. Clay could be very plastic i.e. fat clay or rarely plastic i.e. lean clay.

2.4.3.3 VITRIFICATION

Vitrification is due to a process of gradient fusion in which some of the more easily melted constituent begins to produce an increasing amount of liquid, which makes up the glassy bonding material in the fired product. The temperature at which it is carried out is important in the clay structural product. The degree of vitrification depends on time of firing and the temperature (max) attained.

2.4.3.4 STRENGTH

The clay must possess a green strength i.e. strength of the clay mineral when wet and plastic. The green strength is very important because most structural clay products are handled at least once and must be strong enough to maintain shape. The dry strength is that which the clay has after firing and drying.

2.4.3.5 SHRINKAGE

Shrinkage could be of either firing or drying and are both important properties used for structural clay product. Drying shrinkage is high in most very plastic clays but low in the sandy clays or clay with low plasticity and tends to produce weak porous clay.
Firing shrinkage depends on the amount of volatile material present in the clay and the dehydration characteristics of the clay mineral.

2.4.3.6   SOLUBILITY

The solubility of clay mineral in acid varies with the structure of the acid, acid concentration, acid to clay ratio and the temperature duration of the treatment.

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Acid will first attack the adsorbed cation and then the component of the octahedral part of the clay mineral structure.

2.4.3.7 ORGANIC REACTIONS

Organic materials occur in clay as discrete particles and as reaction compound with the clay mineral. Ionic organic compounds such as amine may replace in - organic ions on the surface of the clay mineral. These may be held in inner layer position within the expandable clay mineral and organic molecules may be one or thick several layers on the clay mineral surface.

2.4.3.8 ION EXCHANGE

The ion exchange property of clay is what makes it an adsorbent. The exchange capacity of clay varies with particle size, the nature of the adsorbed ion and the perfection of crystallinity. Clay minerals are able to adsorb certain positively and negatively charged particles (Cation and Anions) and retain them around the external part of the structure unit in an exchangeable state. (11)

Anion exchange capacity depends on the replacement of OH^- at the edge of the lattice structure and due to adsorption because of the geometry of the anion in relation to that of the clay mineral.

For the cation, exchange capacity may be due to the substitution within the lattice structure and the hydrogen or exposed hydroxyl.

2.5 RICE HUSK

According to the statistics of the Food and Agriculture Organisation (FAO) of the United Nations (1974 – 1975), the world annual paddy rice (Oryza Sativa) production is estimated to be about 341,000,000mega tones. Most of this tonnage is produced in S.E. Asia. (7)

A minor derivative of the rice crop is the 'Husk': a fibrous non-digestible commodity, representing some 20% of the dried paddy on

stalk. According to findings, dried paddy on stake yielded 52% by weight – white rice, 20% husk, 15% stalk and 10% bran, the rest 3% is lost in the conversion process. (8)

If all the paddy rice available were commercially milled 68 X 10^6 Mega tones of husks can be produced. They would occupy 600 million m^3 of storage space. Due to their abrasive character, poor nutritive value, low bulk density and very high ash content, only a little of the husk can be disposed for a certain low value. Applications such as chicken litter, juice processing aid and animal roughage among others. The remaining rice husks are transported to the fields for disposal using by open field burning. (8)

2.5.1   PHYSICAL PROPERTIES OF RICE HUSK

Most rice husks are gold or straw in colour. Some may be white, reddish brown shades of purple or sooty black. The length of rice husk is about 5 – 10 mm and the width varies from 2.5 – 5 mm. Bulk density of rice husk is 0.100g/ml. Other reports indicated bulk density values ranges from 96 – 160 Kg/m^3 and the husk can be compressed to 400 Kg / m^3. (8)

Grinding can also raise the bulk density from 192 or 208 to 384 or 400 Kg/m^3.

2.5.2   CHEMICAL PROPERTIES OF RICE HUSK

The major carbohydrates of husks are cellulose and hemicellulose. Hemicellulose, a chiefly pentosan is a glucoxylan, which can be hydrolyzed to xylose. Percentage composition of pentosan that is a good source of furfural (an important chemical, which finds many uses in the oil refining including deodourization (14)) varies between 16 – 19.8 %. The crude protein content of rice husk is about 3 %. A higher protein value undoubtedly reflects some bran contamination in it.

Other major chemical components are lipid content of rice husk (ranges from 0.39 – 2.98 %) and lignin. There is evidence that large

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part of lignin is chemically combined with hemicellulose and that the middle lamella of the cell wall may contain 70% of the lignin associated with pentosan and a little cellulose.

The major inorganic component of rice husk is ash, which varies between 13.2 – 29.0 % of the weight of rice husk.

2.6 FURFURAL

Furfural is a colourless liquid heterocyclic aldehyde $C_5H_4O_2$, obtained by the distillation of the pentose sugar occurring in corn cobs, hulls, rice husks and other agricultural waste products; widely used as a solvent and reagent in the dye stuffs, plastics and other industries. (10)

When pure, a colourless liquid aldehyde boiling at $161.7^{o}C$ are also called furfuraldehyde, fural, 2-furaldehyde or 2-furnacarboxaldehyde. It is obtained mainly for different uses as will be discussed later.
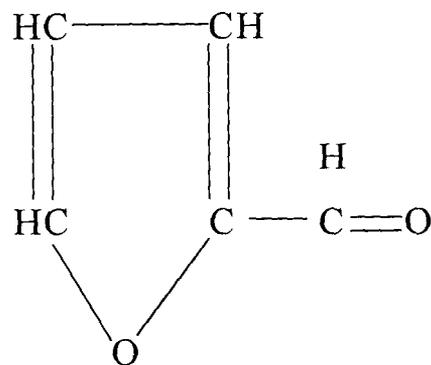
Furfural Structure (12)

2.6.1 CHEMICAL PROPERTIES OF FURFURAL

Furfural has the structural formula shown in the figure. It contains not only an aldehyde group but also an ether linkage (C-O-C) and a system of alternating single and double bonds (diene structure). These provide several sites in the molecules for reaction with other compounds. It is similar to benzaldehyde in most of its reaction as an aldehyde and in its ability to undergo substitution reactions for hydrogen atoms on the ring.

Resin formation can take place by reaction at the aldehyde group or through the diene – aldehyde system (also known as resinophore grouping). The other linkage provides a point at which the ring can be opened to give straight chain compounds.

Three general routes to furfural derivatives are employed in the chemical industry. It can react as an aldehyde with phenols, ketones, and esters to produce resins and can react with thiols. Its reaction with thiols (mercaptans) brings about the deodourization in kerosene. (3)

Catalytic removal of the aldehyde group from furfural gives furan C_4H_4O that can be hydrogenated to tetrahydrofuran. The latter is a widely used solvent and as an intermediate in the preparation of polytetramethylene. Catalytic hydrogenation of furfural gives furfuryl alcohol. (14)

CHAPTER THREE

3.0 EXPERIMENTAL PROCEDURE

3.1 (a) EQUIPMENT AND APPARATUS

1. Sieve shaker and sieves model
2. Mortar and Pestle
3. Weighing balance
4. Oven
5. Dessicator
6. Measuring cylinder (50 ml, 25 ml)
7. Volumetric flask (250 ml)
8. Beaker (100 ml)
9. Funnel
10. Glass wool
11. Filter paper
12. Burette (50 ml)
13. Stirrer
14. Crucible
15. Sample bottles
16. Blender

(b) REAGENTS

1. Hydrochloric acid (2M HCl)
2. Distilled water

(c) MATERIALS

1. Clay sample
2. Rice husk
3. Kerosene

3.2   PRE – TREATMENT OF MATERIALS

3.2.1   CLAY PROCESSING

The clay has to undergo various processing in order to prepare it for the adsorption process. The unit operations that were involved include; grinding, drying, sieving and acid treatment.

GRINDING

The raw clay sample was taken from Kuta, Niger state and was identified to be the light gray kaolin clay. It was majorly lumps and so needed to be grinded into finer particles to aid drying and sieving operations.

DRYING

After the clay sample has been properly grinded, it was sun – dried for about two weeks after which it was checked for proper dryness. Molding with the palms did this check, if no coagulation then clay is dried and if not, drying continued.

SIEVING

The clay sample was poured into the sieve shaker, which was arranged using the 250 μm, 150 μm and the collector in the downward manner. The particle size of the sample, which remained in the 150 μm, was gathered and kept for the experiment.

ACID TREATMENT OF CLAY

Hydrochloric acid, which is a mineral acid, was used for the treatment of the clay. 2M HCl was prepared, 500 cm^3 of the acid solution was measured into the beaker, and 400 g of the sieved clay sample was mixed together with it. The mixture was allowed to properly react for about 24 hours after which it would have settled and so decanted and filtered.

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The filtered acid – treated clay was spread into a crucible and the oven dried at 100 ^{O}C to aid fast drying. After, the clay has been confirmed dried, it is noticed to have congealed and so had to be grounded again into fine powder and then poured into a beaker and kept in the dessicator to avoid the clay absorbing moisture from the atmosphere due to its hygroscopic nature. The clay was noticed to have turned into a greenish yellow from light gray after the acid – treatment.

3.2.2   RICE HUSK PROCESSING

Rice husk, which is also used as an adsorbent in this work also, undergoes some unit operations before its use and these include grinding, sieving and acid – treatment.

GRINDING

Grinding of the rice husk, which is collected from the local rice sellers in the market, was grinded into finer particles and then sent for sieving.

SIEVING

The sieve shaker was used for the sieve analysis and the fine rice husk particles in 150 μm sieve was collected and kept for the use of this work. Two 400 g sample was collected with one part sent for acid – treatment and the other part kept as it is.

ACID TREATMENT OF RICE HUSK

One part of the 400g sieved rice husk sample was mixed together with 500 cm^{3} of 2M HCl, which was stirred for about 15 minutes and kept for about 24 hours.
After 24 hours, the acid – treated rice husk sample was filtered and oven – dried at about 100°C. It also congealed after drying and was pounded using the mortar and pestle. The colour of the rice husk,

which was formerly light brown, turned into dark brown after the acid – treatment.

3.3   PREPARATION OF 2M HCl

A 2M HCl acid was prepared from a concentrated hydrochloric acid with the assay shown below on the bottle:

Density = 1.18g/cm

Percentage purity = 36 %

The molecular weight of HCl was calculated as follows:

HCl ⇒ (H = 1, Cl = 35.46)

HCl = 35.46 + 1 = 36.46

The molarity of this concentrated HCl was calculated to be 11.65 M and the volume needed to be 171.67 cm^3 to be made up with 828.33 cm^3 of distilled water to make the 2M HCl.

The concentrated acid was added to the already measured distilled water and not vice – versa. This is done to avoid explosive fumes being given off during mixing.

Comprehensive calculations on preparation of 2M HCl are shown at the appendix.

3.4   PACKING OF ADSORBING COLUMN

A burette was used as the adsorbing column and this was first stocked with glass wool to a height of about 2cm from the lower tip of the burette to prevent the loss of adsorbents during the process.

The column is now packed with the adsorbents (clay, rice husk) to a height of 25 cm. The materials were properly stocked by pressing it tightly using a glass rod after filling to every 8cm. This was done to obtain and maintain a tightly packed column for the process.

The operation was carried out using the acid – treated clay, acid – treated rice husk and the non acid – treated rice husk and the raw kerosene was subsequently run through it.

3.5   ADSORPTION PROCESS

The adsorption column was set on a retort stand and the 25 ml measuring cylinder was place to collect the deodourized kerosene below the burette.

The kerosene was filled into the burette and was allowed to flow down, penetrate and wet the packed column. The time from the pouring of the kerosene to the first drop into the measuring cylinder was noted and recorded. The bulkiness of the packed column and the material used for the column has an effect on the rate of flow of the kerosene through the column and invariably time taken (retention time). This will therefore have an effect on the extent of reaction or adsorption of mercaptan and other Sulphur compounds in the kerosene will occur.

During this adsorption process, it is expected that the mercaptans and Sulphur compounds causing the odour in kerosene will be adsorbed on the surfaces of the clay material and rice husk due to their composition and adsorptive ability as the case may be.

FUNNEL

RAW KEROSENE

ABSORBING COLUMN

GLASS WOOL

RETORT STAND

MEASURING CYLINDER

DEODORISED KEROSENE SAMPLE
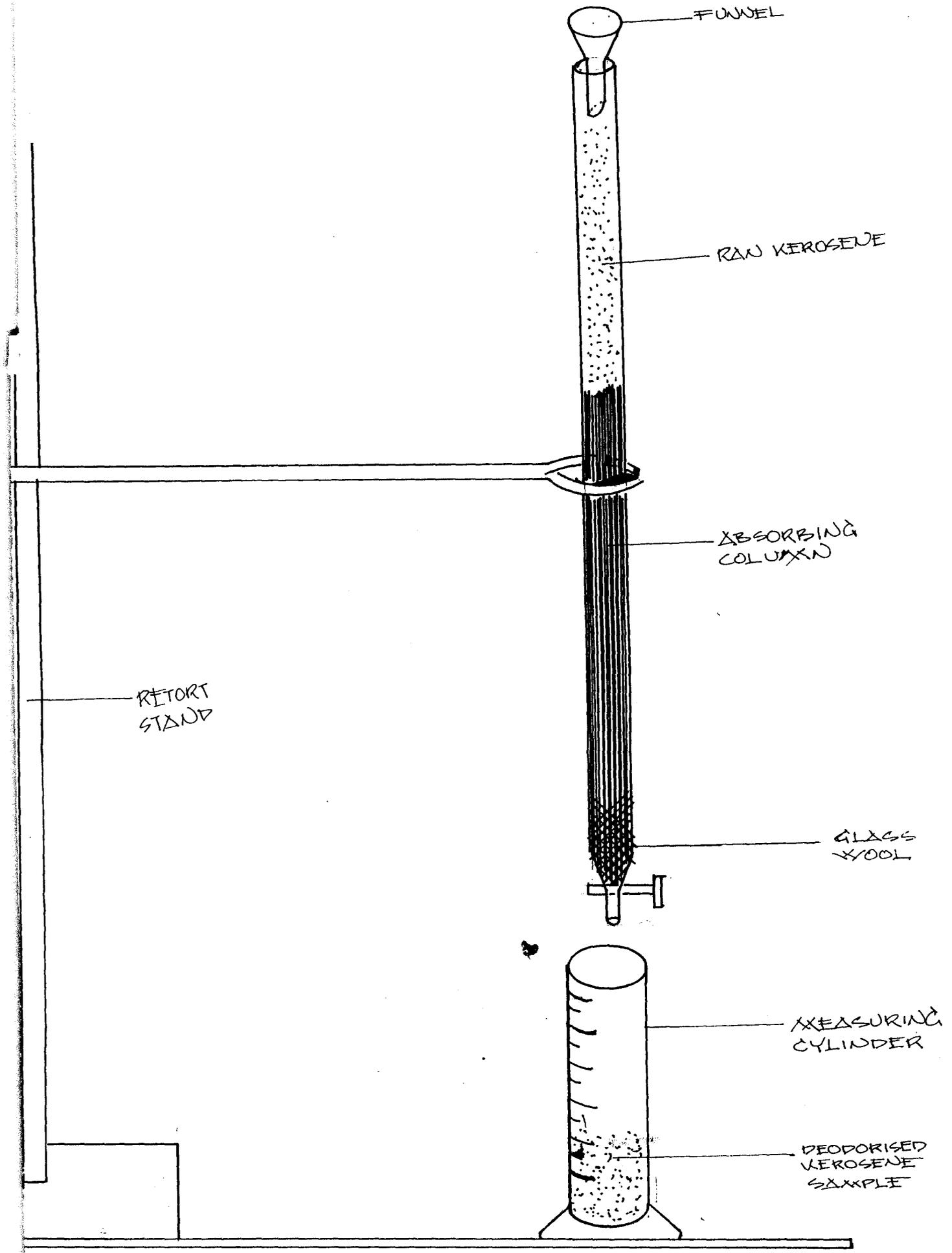
Fig. SHOWING SET-UP FOR ADSORPTION PROCESS

3.6   CONFIRMATORY ANALYSIS

3.6.1   DETERMINATION OF SMOKE POINT

This experiment was carried out at normal room temperature determined to be $27^{O}C$ using a kerosene lamp. About 50mls of a particular kerosene sample was introduced into the dry oil container of the lamp and about 120mm long new wick was also soaked into the sample and fixed into the wick – holder carefully easing out any twists arising from the fixing.

The wick holder was fixed to the lamp and left for about 10 minutes to allow for proper soaking. The lamp was lit and allowed to burn for about 5 minutes continuously and then the wick is adjusted to give smoky flames and then lowered until the smoky tail just disappears.

The height in mm of the flame at that point where the smoky tail just disappears is noted and recorded and this same procedure is carried out for the subsequent deodourized kerosene sample and the different smoke points recorded.

In order that the flame heights are easily measured, a plane white paper is masked at the wall behind the kerosene lamp and on it points corresponding to flame heights are marked and later properly measured with a ruler.

CHAPTER FOUR

4.0　EXPERIMENTAL RESULTS

4.1　RESULTS OF DEODOURIZATION

Tables1, 2 and 3 show the effect of adsorbing materials on the flow rate of kerosene during deodourization.　The operating conditions are as listed below;

Height of column = 25 cm

Particle size = 150µm

Temperature = 27 °C (Room Temperature)

Table 1: ADSORBENT: ACID TREATED CLAY

Time for kerosene to wet the adsorbent of height 25cm = 83 min.

Volume (ml)	Cumulative Deodourization time (Min.)
0	0
5	40
10	87
15	135
20	188
25	232
30	274
35	314
40	354
45	394
50	434

Average outflow rate = 434 min. / 50 ml

= 8.68 min. / ml

Table 2: ADSORBING MATERIAL: ACID TREATED RICE HUSK

Time for kerosene to wet adsorbent of height 25 cm = 77 min.

Volume (ml)	Cumulative Deodourization time (Min.)
0	0
5	31
10	57
15	83
20	110
25	140
30	170
35	198
40	227
45	257
50	285

Average outflow rate = 285 min. / 50 ml

= 5.7 min. / ml

Table 3: ADSORBENT: RAW RICE HUSK

Time for kerosene to wet adsorbent of height 25 cm = 42 min.

Volume (ml)	Cumulative Deodourization time (Min.)
0	0
5	22
10	48
15	70
20	90
25	112
30	132
35	152
40	173
45	192
50	212

Average outflow rate = 212 min. / 50 ml

= 4.24 min. / ml

4.1.2   SMOKE POINT ANALYSIS

The following shows the result of the smoke point analysis, which is carried out on the deodourized kerosene samples, and that of the raw kerosene.

Table 4

| Sample	Smoke Point Readings (mm)			Average Smoke Point (mm)
	1st	2nd	3rd	
A	20	21	21	20.66
B	26	26	26	26.00
C	24	24	23	23.67
D	23	23	23	23.00

A – Raw kerosene

B – Deodourized kerosene using acid – treated clay

C – Deodourized kerosene using acid – treated rice husk

D – Deodourized kerosene using raw rice husk

Note: From literature, raw kerosene should have smoke point which ranges between 20 – 22 mm. (9)

Graphs 1, 2 and 3 show the plot of deodourized kerosene volume against the cumulative deodourization time for each adsorbent sample that was used and graph 4 represent the smoke point determinations.

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FIGURE 4.10:GRAPH SHOWING ABSOPTION USING ACID TREATEDCLAY

2

FIGURE 4.10:GRAPH SHOWING ABSOPTION USING ACID TREATED RICE HUSK

VOLUME (ml)

CUMMULATIVE DEODOURIZATION TIME (min)
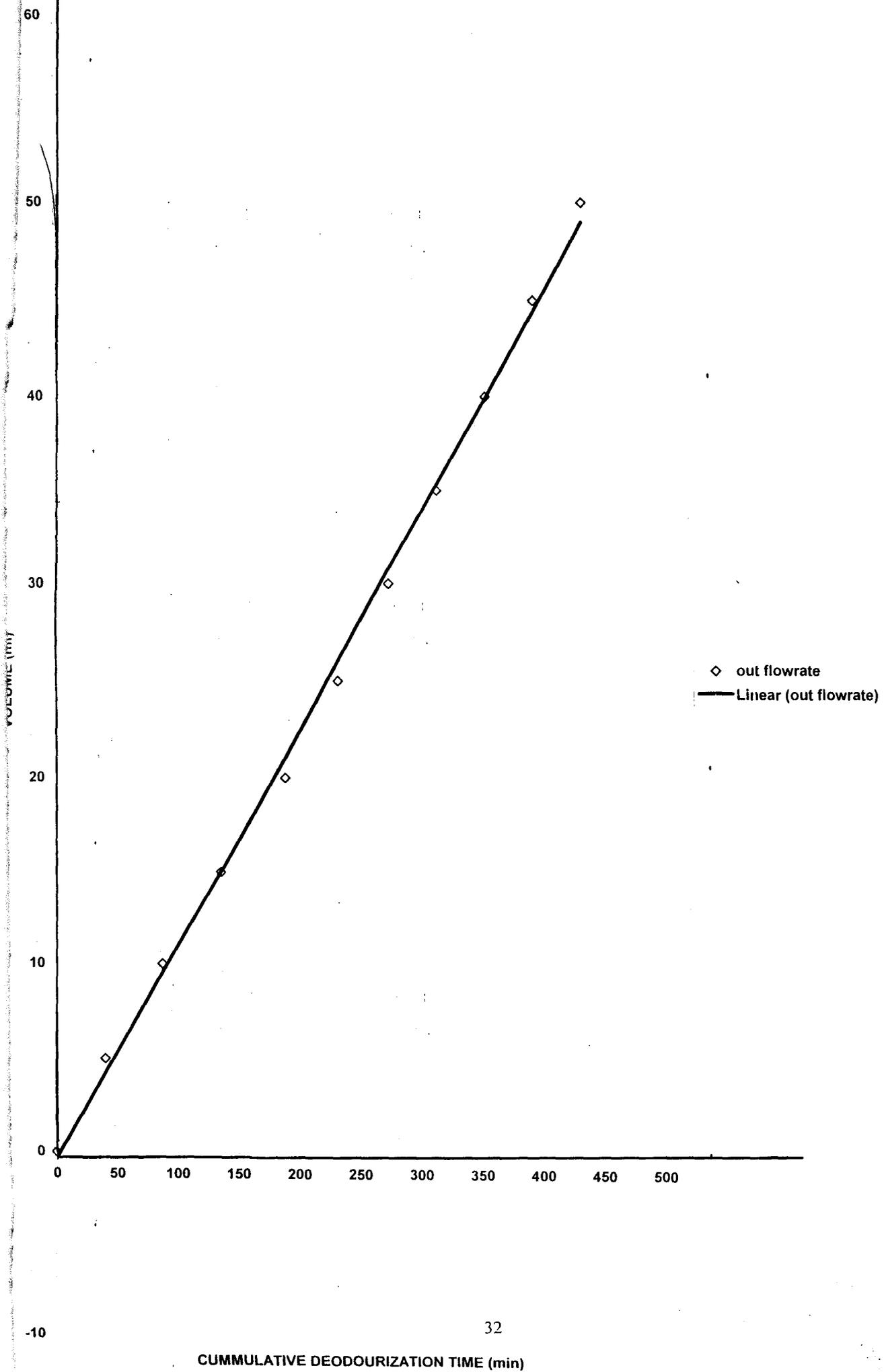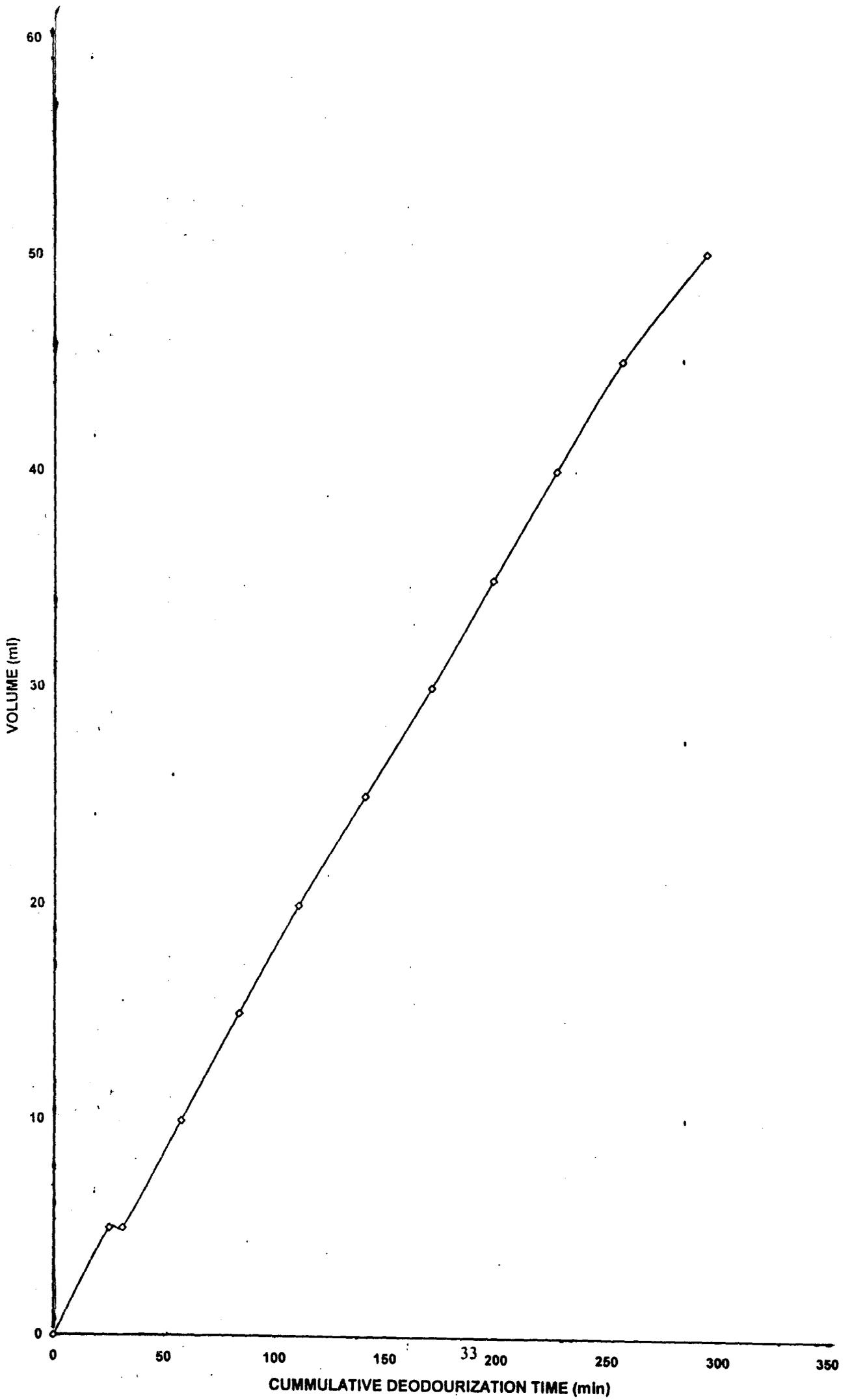
FIGURE 4.30:GRAPH SHOWING ABSOPTION USING ▮▮▮▮ ▮▮▮▮▮▮ RICE HUSK

CHANGE IN FLOWRATE BEFORE STEADY STATE

VOLUME (ml)

CUMMULATIVE DEODOURIZATION TIME (min)
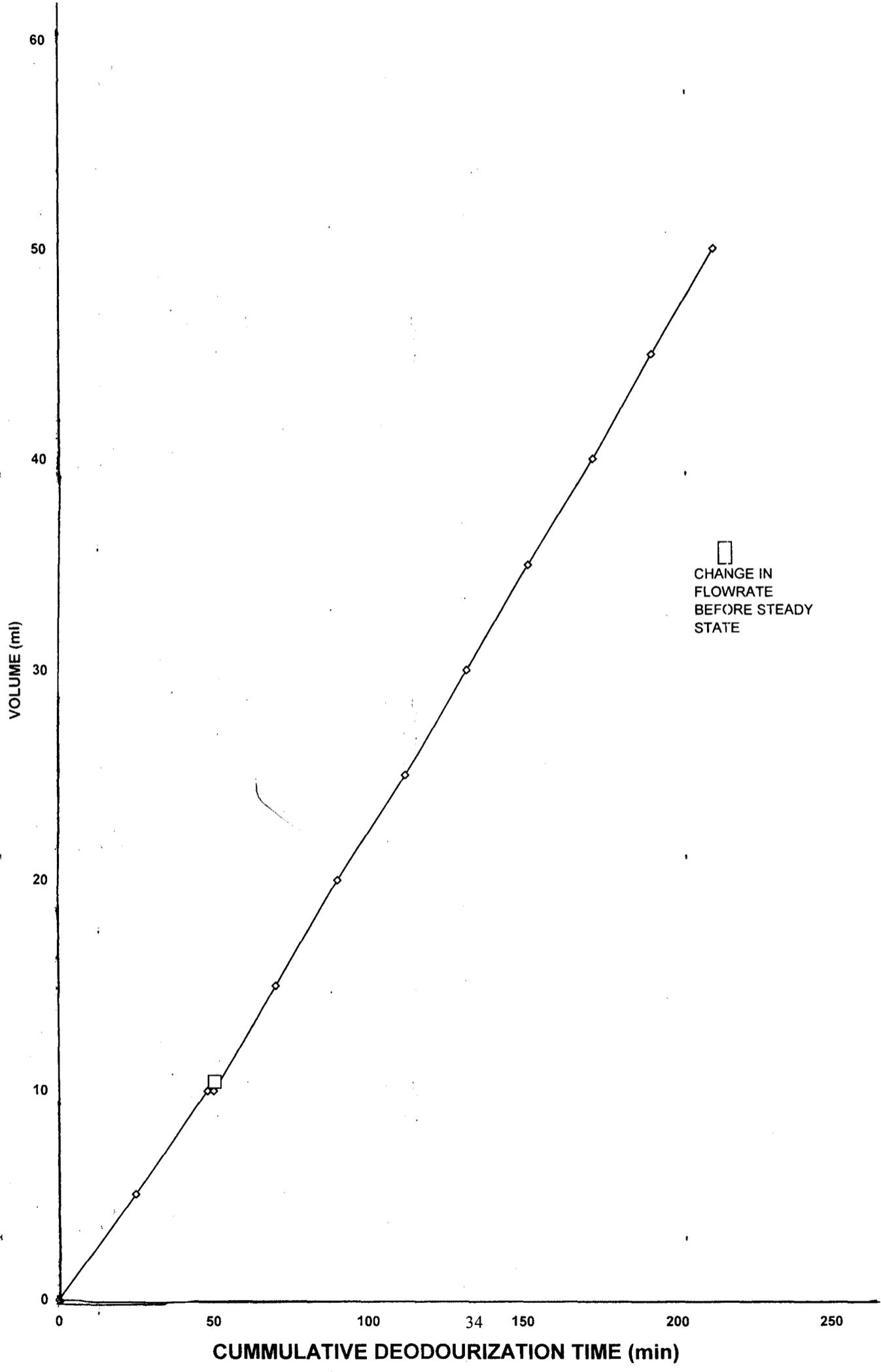
FIGURE 4.40 : CHART SHOWING SMOKE POINT OF DEODOURISED KEROSINE USING DIFFERENT ADSORBENTS

A - RAW KEROSINE SAMPLE
B - DEODOURIZED KEROSINE
  (ACID TREATED CLAY SAMPLE)
C - DEODOURIZED KEROSINE
  (ACIS TREATED HUSK SAMPLE)
D - DEODOURIZED KEROSINE
  (RAW HUSK SAMPLE)

AVERAGE SMOKE POINT IN (mm)

35
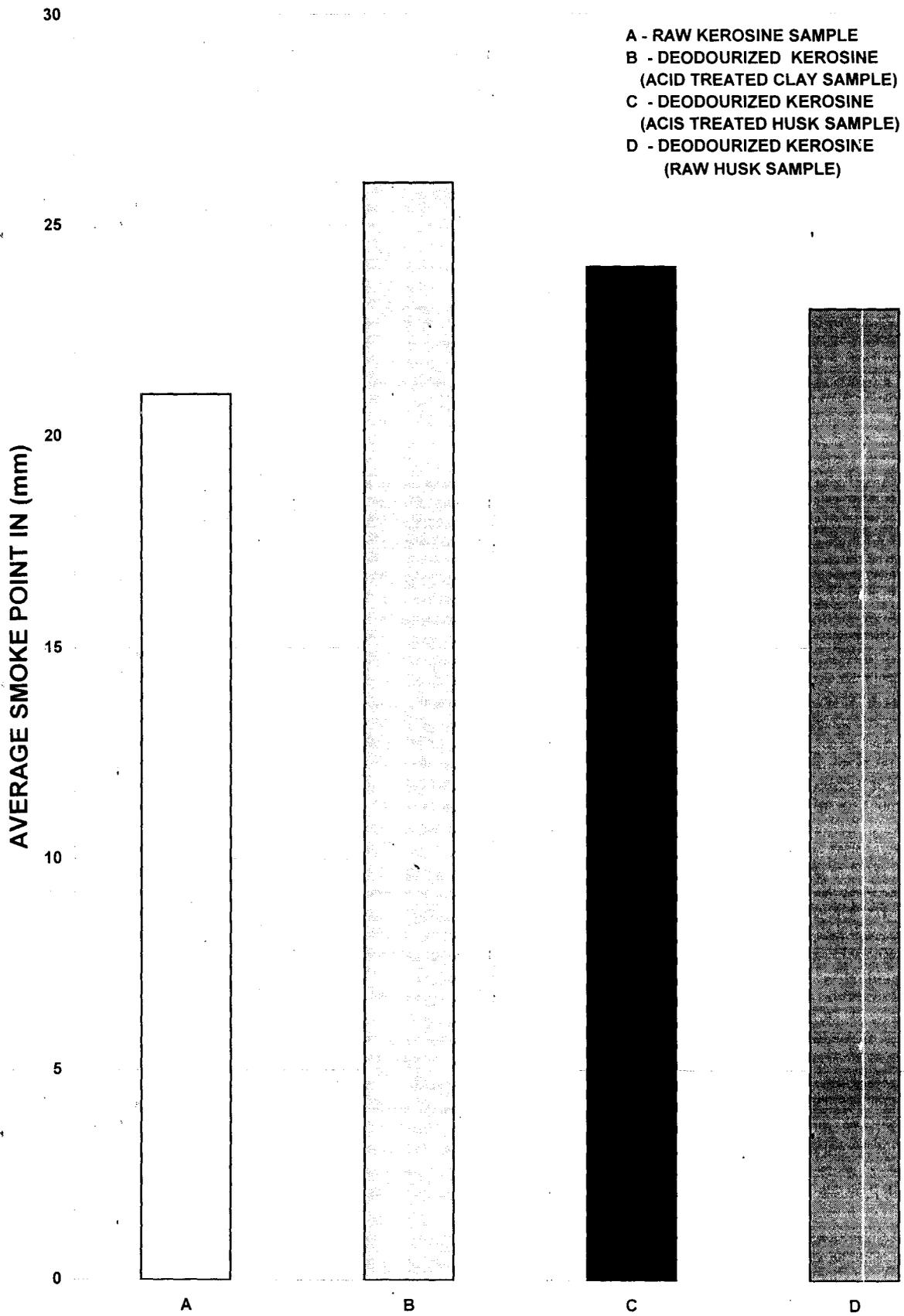
4.2   DISCUSSION OF RESULTS

From the work carried out in 1997 by Adeoti R.A. (89/1376) who tried deodourization of kerosene using different clay samples and varying the height of packed column. His deduction then was that the kaolin clay sample best deodourized and the most effective height of 20 cm which then concluded that the higher the height, the better the adsorption and justified the deodourizing capacity using Aniline point determination.

This work considered the best parameters of the previous work using clay sample and compared with rice husk. A better height was also chosen (25 cm) and the deodorizing capacity was justified using smoke point determination.

It was observed that the colour of the acid treated clay and rice husk differ slightly from their original colour and there was a fume of hydrochloric acid during the process of drying the acid – treated samples. The clay turned from light gray to yellowish green while the rice husk from the light brown to very dark brown.

The time for the kerosene to wet the packed column differ from one material to another with the largest to be 83 min. for acid treated clay, 77 min. for acid treated rice husk and 42 min. for the raw rice husk.

The plot of volume of deodourized kerosene against the cumulative deodourization time shows the flow rate of kerosene though the column before and after attainment of a steady state. Before steady state, flow rate fluctuates with time but after steady state, it becomes constantly flowing.

The outflow rate of the acid treated clay was the highest showing strong intermolecular bonds between the particle material and less porous than rice husk.

Smoke point determination for the effluent kerosene shows the capacity of deodourization for each adsorbing material used. The higher the smoke point, the lower the aromatic content and the better the deodourization. The smoke points of raw kerosene was 20.66 mm

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which is still in line with the standard range value of 19 – 21 mm, the acid treated clay gave 26 mm and usually like acid treated rice husk which gave 23.67 mm, raw rice husk is 23mm.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1   CONCLUSION

The degree of activation of the clay by acid treatment, which is quite high in this work, gave a better performance of the clay as compared with the old work. The acid – treatment actually activates the sample and gives it a better adsorption capacity as the case may be.

The effectiveness of adsorption of aromatics increases with increase in the height of packed column and surface area available for adsorption, which is in accordance with the theoretical knowledge of adsorption process.

Conclusively, clay sample proved a better adsorbent than rice husk based on their adsorption capacity, which is determined from the smoke points of their respective kerosene effluents.

5.2   RECOMMENDATION

Considering the time, resources and information available to carry out this work, I suggest that the work be splitted into two parts. One to compare different adsorbents for deodourization and the other to vary the different parameters for each adsorbent. This will help to conclude firmly on the adsorbent and parameters, which best deodourizes.

Charcoal, which is neutral in terms of polarity and with a very good adsorption capacity, can be used as adsorbent. Its result with that of clay and rice husk can be compared.

The use of sulphuric acid (H_2SO_4) instead of hydrochloric acid (HCl) should be considered for the activation of the adsorbent, as this is a better mineral acid.

Lastly, I recommend that equipment like gas chromatography be made available which will analyze the aromatic content as this will give better and accurate amount of aromatic present and state all other molecules present in the kerosene.

The lower the aromatic content, the higher the smoke points. Amongst the adsorbents used, activated clay (kaolin sample) is the most efficient which gave a smoke point of 26 mm.

For this process to be put into practice commercially, a high length of column and a very slow flow rate is required to give a better performance.

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APPENDIX I

The preparation of a 2M Hydrochloric acid was from a concentrated hydrochloric acid with the following assay on it.

Density = 1.18 g/cm

Molecular weight = 36.46 g/mol

Percentage purity = 36 %

The molarity of the concentrated HCl was calculated as follows:

$$\frac{\text{Specific gravity}}{\text{Molecular weight}} \times \% \text{ purity} = \text{Molarity}$$

$$\frac{1.18 \times 1000}{36.46} \times \frac{36}{100} = 11.65 \text{ M}$$

Therefore, the volume required to make 1000 cm^3 of 2M HCl was calculated as follows:

$M_1 V_1 = M_2 V_2$

M_1 = Molarity of concentration acid (11.65 M)

V_1 = Volume of concentration acid (?)

M_2 = Molarity of diluted acid (2 M)

V_2 = Volume of concentration acid (1000 cm^3)

$$V_1 = \frac{M_2 V_2}{M_1}$$

$$V_1 = \frac{2 \text{ M} \times 1000 \text{ cm}^3}{11.65 \text{ M}}$$

$V_1 = 171.67 \text{ cm}^3$

171.67 cm^3 of concentrated acid was measured and made up to 1000 cm^3 i.e. adding 828.33 cm^3 (1000 − 171.67) of distilled water.

APPENDIX II

STANDARD PROPERTIES OF KEROSENE

Calorific Value $\Rightarrow$ 11,060 Kcal / Kg

Flash Point $\Rightarrow$ 30 – 60 $^{\circ}$C

Self-Ignition Point $\Rightarrow$ 235 – 290 $^{\circ}$C

Explosive Limit $\Rightarrow$ 1.4 – 7.5 (% Vol)

Latent heat of vaporization $\Rightarrow$ 50 – 52 Kcal / Kg

Smoke Point $\Rightarrow$ 19 – 22 mm