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PRODUCTION OF OXALIC ACID FROM THE BARK OF EUCALYPTUS CAMALDULENSIS

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DEDICATION

This work is dedicated to my late father Alhaji Alfa Adamu Lawal
and my mother Mallama Aishetu Adamu.

ACKNOWLEDGEMENT

CERTIFICATION

I hereby certify that I have supervised, read and approved this project work, which is adequate in scope and quality for the partial fulfilment for the award of Bachelor Degree in Chemical Engineering.

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   Project Supervisor   Head of Deparmtment

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   External Examiner

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ABSTRACT

This work was done in order to investigate the effect of particle size, time variation and increase in volume of dilute H_2SO_4 acid on the yield of oxalic acid from the bark of Eucalyptus Camaldulensis. 4% dilute sulphuric acid was used, while the reaction was carried out at 50°c. Two experiments are performed on each particle size for 3 hours and 6 hours. At the end of the investigation, it was found that the yield of oxalic acid decreases with increase in particle size of the bark of Eucalyptus Camaldulensis. The particle size range of 0.25mm - 0.5mm gave an average yield of 1.669g for 3 hours and 1.045g for 6 hours, 0.5mm - 0.71mm gave an average yield of 1.413g for 3 hours and 0.893g for 6 hours, 0.71mm - 0.85mm gave an average yield of 1.046g for 3 hours and 0.593g for 6 hours, 0.85mm - 1.00mm gave an average yield of 0.809g for 3 hours and 0.454g for 6 hours and 1.00mm - 1.40mm gave an average yield of 0.780g for 3 hours and 0.394g for 6 hours.

The average yield of oxalic acid was also found to decrease as the reaction time increases from 3 hours to 6 hours for each particle size. Using particle size of 0.25mm - 0.5mm as reference, the corresponding average yield for 3 hours and 6 hours are 1.669g and 1.045g respectively. The investigation also shows that increase in the volume of H_2SO_4 acid used, results in an increase in the average yield of oxalic. When 750 ml of H_2SO_4 acid was used, an average yield of 2.594g and 2.208g were obtained for 3 hours and 6 hours respectively, 500ml of H_2SO_4 acid gave 2.05g and 1.789g for 3 hours and 6 hours respectively and 250ml of H_2SO_4 gave an average yield of 1.669g and 1.045g for 3 hours and 6 hours respectively, all using a size range of 0.25mm - 0.5mm of the bark of Eucalyptus Camaldulensis.The percentage purity of the acid produced was found to be 82.004%.

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CHAPTER ONE

INTRODUCTION

Organic acids are of enamous important to human life, as most of them are used as raw materials in various chemical and petrochemical industries. They are classified as either carboxylic or dicarboxylic acids, that is possessing one and two carboxyl group (COOH) respectively. Example of carboxylic acids are: formic acid, Acetic acid, Buteric acid e.t.c. While that of dicarboxylic acid is oxalic acid.

Oxalic acid is the first member of the dicarboxylic acids and has a lot of commercial importance such as in the manufacture of sodium oxalate used in blue printing, in the manufacture of paints and vernishes, as a dye-stuff intermediate in the manufacture of plastics etc. Because of this, there is an increasing demand of the acid by various chemical and petrochemical industries.

This write up is specifically aimed at investigating the production of oxalic acid from a naturally occuring tree known as eucalyptus camaldulensis, in order to meet the increasing demand of the acid by the various chemical and petrochemical industries that utilizes it as raw material and other various uses to which it is put.

The idea of producing the acid from the bark of eucalyptus camaldulensis came from the fact that, the bark of eucalyptus camaldulensis is known to contain calcium oxalate from which oxalic acid can be produced by reacting it with a mineral acid that will best produce oxalic acid.

A lot of work has been done by the final year students of Chemical Engineering Department of Federal University of Technology, Minna, on the account to investigate the yield of the acid from the bark of eucalyptus camaldulensis with each student varying the parameters such as particle size range, temperature, raction time, concentration of acid, volume of acid, and mass of sample; so as to see at what specific parameters can oxalic acid be best produced from the bark of eucalyptus camaldulensis.

This work is aimed at using 4% dilute sulphuric acid with 25 grams of the bark at a temperature of 50°c. It investigates the effect of variation of the reaction time, and the change in volume of the acid on the average yield of oxalic acid from the bark.

CHAPTER TWO

LITERATURE REVIEW

2.1 ORGANIC ACIDS

These are generally acid that are obtained or derived from alcohols

or aldehydes which are organic compounds. They are usually formed
by the replacement of the OH or C=O group from alcohols and

aldehydes respectively by a carbonyl group $C=O$. The most important
$\diagdown OH$

classes of organic acids to be discussed are carboxylic and

dicarboxylic acids.

2.2 CARBOXYLIC ACIDS

Carboxylic acids are organic acids with one carboxyl group i.e. $C=O$
$\diagdown OH$

which are obtainable from the process of oxidation of primary

alcohols or aldehydes.

Carboxylic acids has wide range of commercial applications and also

has high degree of natural occurance. Formic acid (a carboxylic

acid) is partly responsible for the irritation resulting from

contact with stinging nestles, and from ant and bee stings. It was

first made by distillation of red ants. This asociation with ants

accounts for it's name since formica is the latin word for an ant.

Acetic acid is a product of fermentation and arises from the

souring of alcoholic materials such as wines and beers. It was

once made by distillation of wood. Vinegar is a dilute aqueous

solution of acetic acid. Butanoic acid, sometimes also called

butyric acid, is present in rancid butter and is partly responsible

for its smell. Longerchain acids are widely distributed in

vegetable and animal fats, often in the form of esters.

PREPARATION OF CARBOXYLIC ACIDS

The simpler carboxylic acids are made industrially by oxidation of

the appropriate alcohol or aldehyde. Formic acid is also made from

carbonmonoxide and sodium hydroxide.

	Heat	HCOONa Mineral	HCOO H
CO + NaoH	---->	(Sodium) ---->	(Formic acid)
	Pressure	(Formate) acid	
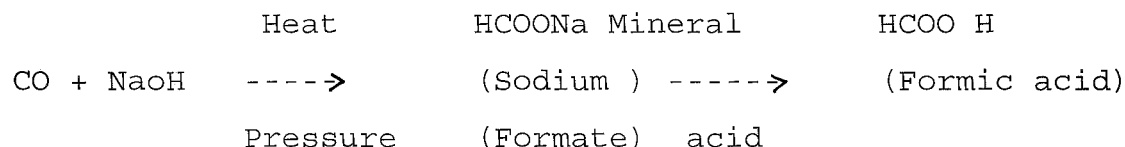
It has use industrially as an expensive weak acid and solvent.

Laboratory method of preparation is by oxidation of prmary alcohols

and aldehydes.

$$RcH_2OH \xrightarrow{\text{Oxidation}} RcHo \xrightarrow{\text{Oxidation}} RCooH.$$
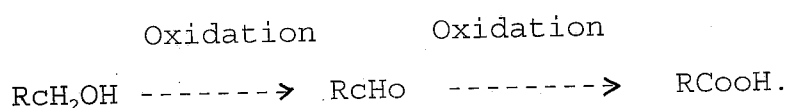
PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

(1) The lower members of carboxylic acids are soluble in water.

(2) They have higher melting points and boiling points than alcohols with the same number of carbon atoms, e.g. Formic acid, Boiling point 100°c and methanol, with boiling point of 65°c. Acetic acid has a boiling point of 118°c and melting point of 17°c. Compare with ethanol, boiling point of 78°c and melting point of -177°c.

(3) They are more acidic than alcohol. For example, the dissociating constant Ka for acetic acid is 1.8×10^{-5} and that of ethanol is 10^{-8}.

CHEMICAL PROPERTIES OF CARBOXYLIC ACID

(1) Formation of acid chlorids:-
Carboxylic acids are converted to an acid chloride or acyl chloride when reacted with thionyl chloride or phosphorus pentachloride:

(a) $RCOOH \xrightarrow{Socl2} \underset{\underset{cl}{|}}{R=O} + So2 + Hcl$

$RCOOH \xrightarrow{pcl5} \underset{\underset{cl}{|}}{R=O} + POcl3 + Hcl$
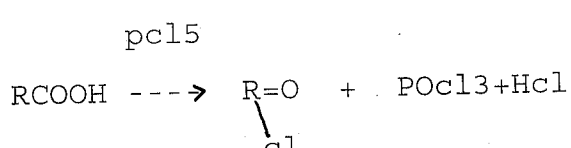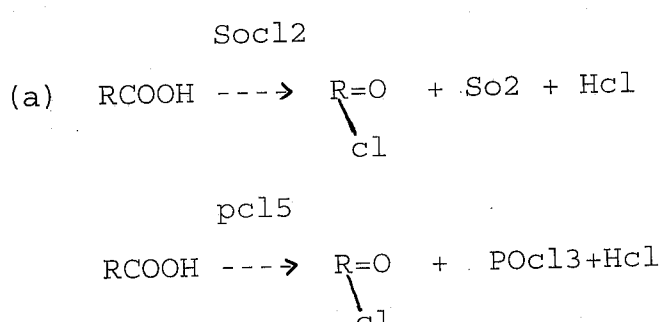
An acid chloride or acyl chloride.

(2) Reactions of carboxylic acids with derivatives of Ammonia.
Caboxylic acids reacts with the drivatives of ammonia, to give ammonium salts:

$RCOOH + NH_2X \longrightarrow RCo_2^- {}^+NH_3X$
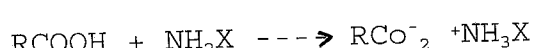
(3) Reactions with alcohols:
Carboxylic acids reacts with alcohols to give esters

$R - \underset{\underset{oH}{|}}{C=O} + R^1OH \longrightarrow R - \underset{\underset{OR^1}{|}}{C=O} + H_2O$
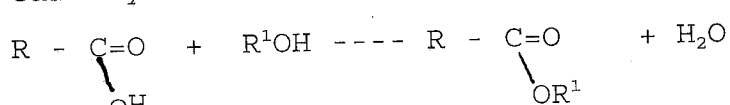
(4) Oxidation of carboxylic acids:

3

In general, carboxylic acids are not easily oxidized, but formic acid is exceptional and is readily oxidized to carbondioxide.

Oxidation

$$H - C=O \quad ------> \quad H_2O + CO_2.$$
$$\quad\quad \backslash H$$
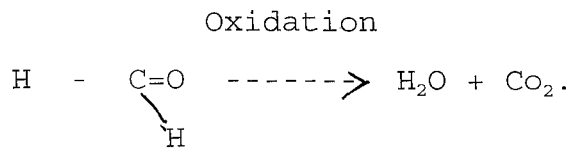
2.3 DICARBOXYLIC ACIDS

Dicarboxylic acids are organic acids with two carboxyl group with a general formula $HOOC(CH_2)n\ COOH$, many of which occur naturally.

2.4 OXALIC ACIDS

Oxalic acid or ethanodoic acid has a formula as HO_2CCO_2H, and is the simplest member of the dicarboxylic acids. It is one of the strongest organic acids. Its potassium and calcium salts are present in many plants. It can be found naturally in some leafy vegetables such as spinach and rhubarb. The acids and its salts are poisonous, but cooking destroys most of the acids.

2.4.1 COMMERCIAL PREPARATION OF OXALIC ACID

Oxalic acid is prepared commercially by heating sodium formate:

heat

$$2HCo_2\ Na+ \quad -----> \quad Na\ +-O_2C-CO_2-\ Na+$$
$$\quad\quad\quad\quad \text{sodium oxalate.}$$
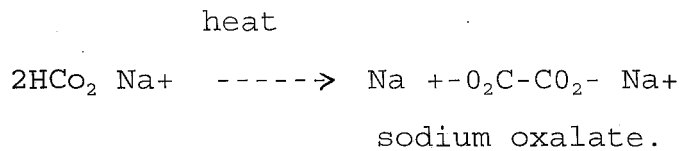
Sodium oxalate can be converted to oxalic acid by the addition of mineral acid.

2.4.2 PHYSICAL PROPERTIES OF OXALIC ACID

1. Oxalic acid crystals is colourless and has 2 moles of water of crystallization $(H_2C_2O_4.2H_2O)$.

2. The hydrated form has a melting point of 101.5^0c while the unhydrated form has a melting point of 189.5^0c.

3. Oxalic acid when hydrated loses water at a temperature of $100-105^{\circ}c$.

4. It has a specific gravity of 1.9.

5. It is poisonous.

2.4.3   **CHEMICAL PROPERTIES OF OXALIC ACID**

1.   It becomes dehydrated when reacted with concentrated sulphuric acid giving Co_2, Co and H_2O.

$$H_2C_2O_4 \xrightarrow[H_2SO_4]{Conc} Co + Co_2 + H_2O.$$
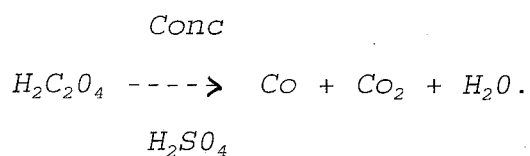
2.   It acts as a reducing agent and it is easily oxidized to carbondioxide and water with warm acidified solution of pottasium pamanganate ($KMNO_4$).

$$H_2C_2O_4 \xrightarrow[KMnO_4]{(O)} 2CO_2 + H_2O$$
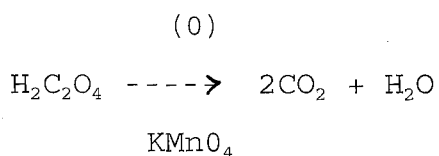
3.   When anhydrous oxalic acid is reflux with methanol or ethanol, it yields esters with stronger acid as catalyst.

4.   Acid chloride formation: Oxalyl dichloride with a boiling point of 64°c is obtained by the action of phosphurus pentachloride and similar reagents on oxalic acid.

2.4.4   **USE OF EXALIC ACIDS**

1.   Crude oxalic acid is used for the cleaning of floors and toilet wears.

2.   It is used in the production of oxalate salts especially sodium oxalate used in blue printing.

3.   It is used in the manufacture of diethyl oxalate which is used as a solvent.

4.   It is also used as a dye-stuff intermediate in the manufacture of plastics.

5.   It is used as an acid rinse in laundries where it is used in the rmoval of rust and ink stains by converting the insoluble lorn (III) ions to soluble Iorn (II) ions. Similarly, it is also used

for the removal of scals from automobile radiator.

6.   It is mostly used as analytical reagent in the laboratories.

7.   It is used as monoglyceryl oxalate in the manufacture of allyl alcohol and formic acid.

8.   It is used as an important raw material in the production of varnishes and paints.

9.   It is used as reagents for condensation and dehydration reactions.

10. It is used in the bleaching of straw and wood.

2.4.5 CONDITIONS FOR THE PRODUCTION OF OXALIC ACID FROM THE CALCIUM OXALATE IN THE BARK OF EUCALYPTUS CAMALDULENSIS

1.   The concentration of the dilute sulphuric acid should not exceed 7%.

2.   The soaked calcium oxalate should be heated at low temperature.

3.   The filtrate containing oxalic acid should not be concentrated to more than 1/3 of the original volume.

2.5   ORIGIN AND STRUCTURE OF EUCALYPTUS

Eucalyptus is a large genus of trees and shrubs native of Australia, Newzealand, Tasmania, Malaysia etc. There are 650-700 species and sub-species of eucalyptus. The height of the eycalyptus tree varies from species to species. The smallest species may be less than 6.5 feet (2 meters) tall, while the tallest may be about 330 feet (100 meters) tall.
The leaf of many species contain an aromatic oil called eucalyptus oil which has a very high economic importance. The leaves are hard, oblique or vertical. The young leaves are usually opposite, not stalked and covered with whitish bloom. The margins are smooth, but the edges of few species are wavy or slightly toothed. The fruits of the eucalyptus are capsules surrounded by a wood, cap-shaped receptable and contains numerous minute seeds. The

capsules is tapped by a disc that breaks up into two to seven valves depending on the species. Some seeds are permanently winged while others are smooth or sculptured, possibly the largest fruits are from 5 to 6 centimenters in diameter and are known as mottle can or silver leaf eucalyptus.

2.5.1 CULTIVATION OF EUCALYPTUS IN NIGERIA

Eucalyptus has been cultivated in large number in Nigeria especially in the savannah region of the country. The cultivation of eucalyptus amounts up to 4000 hectares at the end of 1973 and the cultivation was extended to about 8000 hectares per year. A wide range of species were experimented. Several species choosen have a wide range of natural occurance in Australia.

Some areas of Nigeria where eucalyptus is cultivated includes Minna in Niger State, Jos Plateau State, Kaduna State and Kano State.

Eucalyptus camaldulensis species was introduced to Nigeria in 1916 which grew fairly successfully. The hausa people call it Bishiyar tulare (scent tree) while the nupe people call it Era.

2.5.2 EUCALYPTUS SPECIES IN NIGERIA

1. Eucalyptus Camaldulensis: This species is widely cultivated in plantations and from self sowned seed; variable and hybridizing with other species. The bark is smooth, ash coloured and peeling. Leaves are narowly lanceoted up to 25 cm long and 1.5 cm broad.

2. Eucalyptus Citriodora: This is widely grown in towns. The bark is smooth and purlished. The leaves are lanceolate; which are 16 cm long and 2 cm broad, and strongly lemon-scented.

3. Eucalyptus Cloeziana: This has a dark-brown stringy bark. The leaves are lanceolate and are up to 12 cm long and 3 cm broad.

4. Eucalyptus Deghipta: This is a large tree with smooth redish bark. The leaves are ovate-lanceolate which are up to 14 cm long and 7cm broad.

5. Eucalyptus Tereticornis: This specie has an irregular blotched bark. The leaves are narrowly lanceolate which are up to 20cm long and 2.5cm broad.

6. Eucalyptus Torelliana: This specie has a dense crown, which is usually planted for shade. The bark is scaly and persistent below, smooth and peeling above. Yong leaves narrowly to broadly lanceolate which are up to 12cm long and 4cm broad.

2.5.3 VALUABLE PRODUCTS OBTIANED FROM EUCALYPTUS SPECIES

Essential Oil: The essential oils found in all eucalyptus species are called eucalyptus oil which are normally distillable. The essential oils used as raw materials in and leaves of eucalyptus citiodora, eucalyptus robusta, eucalyptus smittii and eucalyptus globulus.

Among the terpene and ketone derivatives in the oils are cineole used as stain remover and also used in vertinary medicine, and piperitone used in the manufacture of synthetic thymol. The oil is also used in the manufacture of perfumes and soaps.

Timber: Eucalyptus are also grown to serve as timber which vary in properties and uses. Such uses may be for construction of furniture and carbinet work. Because of its tallness it can also be used as electric and telephone poles. The wood can also be used for making ships. The important timber species are Eucalyptus Macillata and Eucalyptus Citriodora.

Fuel Wood: Eucalyptus trees are also used as fuel wood. The wood of most eucalyptus burns well when air-dried and leaves little ash. Eucalyptus plantations and other forest resources can supply a substantial part of the household fuel needed in middle and low classes. One of the most importnat advantage of using eucalyptus as a fuel wood is that it does not smoke.

> **Tannin:** This is usually contained in the bark of eucalyptus species. It is a complex aromatic compound. Some have been shown to be glucosides, containing glucose combined with various phenols and hydroxyl acids. The tannin can be exploited for commercial purposes. It can be sold to various tannaries, foot wear and leader factories which at present depend on imported mineral tannins.

> **Alkanoids:** Alkanoids are obtained commercially from eucalyptus leaves or barks as drug rutin. Rutin is an important drug for the repeatic. Alkanoids are also chemcially basic compounds with an imporant physiological activity in medicine for example as an analgestics.

> **Charcoal:** A part from the use in the production of bread by the supply of heat in most African countries, must eucalyptus carbonized easily, providing good commercial charcoal. It

yield a substantial amount of energy of about 7,900 calories per kilogram against 4,700 kilograms for wood.

Honey and Ornamentals: Eucalyptus honey has been a major source of income in Australia and a total of about 17 million kilogram is being exported annually. It is also used for domestic consumption. Some species are important source of nectar and pollen for honey bees and also as ornamentals.

Pulp and Paper: Many paper industries uses the bark of many eucalyptus species as raw material for the production of paper. The world production of pulp from eucalyptus is over one million tonnes annually.

Other Uses: Most of the eucalyptus are used locally as medicine for the treatment of asthma in some part of northern Nigeria. It is also used as an important additive in the production of scent and also used in the production of local ink. It is also used as forest tree for wind break, as handle for tools e.g. hoe; and also in railway constructions.

2.6 FACTORS AFFECTING THE RATE OF CHEMICAL REACTION

2.6.1 THE EFFECT OF CONCENTRATION ON THE RATE OF CHEMICAL REACTION

On the basis of elementary kinetic theory, a chemical reaction will occur only if the particles of reacting substances are allowed to come in contact. The rate of reaction will therefore depend on the frequency with which the particle collide, which will in turn depend (among other factors) on their density i.e. on their concentration. The more crowded the particles are, the more often we should expect them to bump into one another. Thus concentration changes can reasonably be expected to lead to changes in the rate of reaction.

In conclusion, if the reagents involved in a chemical reaction have their concentrations increased in a homogenous mixture, more frequent mollecular collisions will occur and the rate will thereby be increased.

2.6.2 THE EFFECTG OF TEMPERATURE ON THE RATE OF CHEMICAL REACTION

When temperature of a reaction is increased, heat is supplied to the particles involved, in the reaction and thereby increasing the kinetic energy of the particles. If the particles travel at a greater speed when the temperature is increased then they will collide with one another at more frequent intervals, and we could therefore expect the reaction to proceedd at a faster rate. With respect to the above, an increase in temperature within a definate limit will increase the rate of reaction.

2.6.3 THE EFFECT OF SURFACE AREA OF REACTANTS ON THE RATE OF REACTION (I.E. PARTICLES SIZE)

Particle size or surface area affects the rate of chemical reactions in heterogenous reaction. For example, alluminium foil reacts moderately with dilute sodium hydroxide solution when warmed. But powdered alluminium reacts rapidly from cold and will usually froth out of the test tube spontenously. This occur because for a given mass of metal, powder offers a much greater area to the reacting liquid than does foil.

In general, the smaller the particle size the greater the rate of chemical reaction.

2.6.4 THE EFFECT IF CATALYST ON THE RATE OF CHEMICAL REACTION

A catalyst is any substance which if added to a reaction mixtures, increases the rate of reaction and become unchanged in amount and chemical nature at the end of the reaction. The catalyst, usually reduces the activation energies of the reactants involved, and by so doing makes the rate of reaction to be increased.

2.7 CRYSTALLIZATION

This is a process by which a substance in a liquid state is converted to a solid state. Crystallization occured when the liquid is cooled. As the liquid cools, the kinetic motions of the particles decreases, and the attractive forces becomes more and dominant. As cooling continues, the attractive

forces become more and more dominant and the kinetic motion diminishes to such an extent that the particles begin to occupy relatively fixed positions in space. In fact as the liquid cools, a point is reached where the particles are arranged in a three dimensional pattern in which they occupy definite spartial positions. When the particles are arranged in fixed positions, the liquid is said to have changed to solid or crystal.

2.8 FILTRATION

This is a simple separation process whereby a solid is separated from a liquid. Simple laboratory filtration process involves the use of a filter paper folded twice to obtain a conical structure; which is then fit closely into a funel. The funel is then placed on a beaker and the mixture is poured into a filter paper. It will be found that, the solid particles called the residue are retained in the funel while the lquid portion is collected in the beaker as filtrate.

2.9 EXTRACTION

This is the process of separating two or more components of a mixture by treating it with a solvent that preferentially dissoves the required components; thereby separating it from the mixture. The types of extration are given below.

2.9.1 LIQUID/LIQUID EXTRACTION

In liquid/liquid extration, separation is possible when the solubilities of the homogenous liquids mixture are sufficiently different. This type of extration is also called solvet extraction. It is used in separating components of lubricating oil from crude oil fraction. Because it depends in different in chemical potential, it is more sensitive to chemical type than to molecular size.

2.9.2 SOLID/LIQUID EXTRATION

This is the extraction of a soluble component which may be a liquid from an insoluble solid by means of a solvent. This process is utilized in everyday life during the use of a lipton tea bag. It is also used in sugar and vegetable

industries. The process may be carried out in batch or continous process. The leaching process i.e. solid/liquid extration will produce two output streams, one being a solution of solute or solvent (extract), the other containing the inert solute mixed with some solvent. (Raffinate).

2.9.3. EXTRACTIVE DISTILLATION

This process is used in separating aromatics from aliphatics. It is developed by universal oil production companies. In this process, the solvent is recovered by extractive distillation and the raffinate is cleaned up by a wash. A light aliphatic fraction is used as the wash solvent in the extractor.

2.9.4 CHOICE OF SOLVENT

The selection of solvent is very important as it offer a best balance for any extraction process. The characteristics to be considered for solvent selection includes, high saturation limit and selectivity for the solute to be extracted, the solvent should be of low viscosity, low vapour pressure, low toxicity, non flamability, low density, low surface tension, ease and economy or recovery from extracted streams and price.

2.10 PRODUCTION PROCESSES

Production or processing of raw materials to give the desired finished products are classified into 3 main categories, which is batch, semibatch and continuous production processes.

2.10.1 BATCH PRODUCTION PROCESS

This is a stagewise proccess or operation whereby some quantity of feed is charged into the equipment for a period of time and after the completion of the reaction, the product is discharged. In this process, there is no flow in or out of the system, but there may be relative motion within it. Since the process is uniform throughout the reacting medium it's unsteady state and the composition change with time.

2.10.2 SEMI-BATCH PROCESS OF PRODUCTION

This is an intermediate between the batch and continous process. There are different ways in which semi-batch process can operate.

(1) Change in composition with constant volume. In this case there is inflow and outflow of materials in both. Since reactant A is already in the reaction, reactant B is charged into it and at the same time the product is being formed.

(2) The volume and composition changes with time. Reactant B is charged into a system having rectant A already. There is only inflow and no outflow of material in the system.

(2) As time increase, the volume changed with constant composition. That is at the same time, both A and B are charged into the system.

2.10.3 CONTINOUS PRODUCTION PROCESS

Because of economic consideration, this occurs mainly in a large scale production. At any point the composition is unchanged with time. The process continous as the feed is charged into the equipment and a steady state process is maintained.

2.11 THE EFFECT OF RISK DUE TO EXPOSURE TO OXALIC ACID

Presently, there are various type of solid product that are produced by chemical and other allied industries. Toxic product such as oxalic acid are used in various chemical and petrochemical industries. It combine with calcium and magnesium ions in blood tissues inhibiting the action of enzymes depending on those ion for their activity.

Many human motalities have been recorded following ingestion of little as 5g of oxalic acid. The symptoms appear rapidly and are marked by a shock like state, collapse and convulsive seizures. A marked renal damage with precipitation of calcium oxalate in the renal tabules may appear. The results of convulsive seizures are thought to be of hypocaemia. Exposure of oxalic acid solution or potassium oxalate to skin, may cause a localised pain and cyanosis.

Oxalic acid in solid form or in concentrated solution can cause burn in the skin, eyes or mucous membranes. It concentration within the range of 5 to 10% are irritating, if prolonged exposure was experienced. Oxalic acid or it's

oxalate occurs in certain edible plants, notably spinach which o.9% and may not be poisonous, but can serve to reduce the body's calcium supply through its own oxalic acid content. The rhubarbs leaves contain as much as 1.2%. Cases of fatal poisoning by ingestion of larger quantities of rhubarb leaves have been recorded even though the stalk are safe.

The safety of any individual working with oxalic acid is important, as such protective glasses and wear must be provided to avoid contact with eyes and skin. If oxalate salts concentrated are present in the atmosphere or in hot solutions, adequate ventilation should be given to the victim or proper respiratory or protective device have to be worn. Calcium oxalate crystals appear in natural or alkaline urine, and in some cases, these will cohere to form slowly growing jagged-shaped (and consequently painful) urinary calculi, or kidney stone. Oxalic acid has non-poisonous calcium chalk (e.g. chalk, plaster or whitish wash) as its antidotes. Injury from inhalation of oxalic acid dust appears to be very rare.

Oxalic acid is a strong acid in nature, exposure due to dust must be carefully controlled and work areas concentrations held within an acceptable health limit.

CHAPTER THREE

PRODUCTION OF OXALIC ACID FROM THE BARK OF EUCALYPTUS CAMALDULENSIS

3.1 APPARATUS AND EQUIPMENT USED

The apparatus and equipment used during the production of oxalic acid from the bark of eucalyptus camaldulensis are:

1. Hot plate
2. Electric heating mantle
3. Sieve sharker
4. Locally fabricated stirrers
5. Beakers
6. Measuring cylinders
7. Filter papers
8. Funels
9. Weighing balance (electronic)
10. Oven

3.2 EXTRACTION OF TANNIN

The weighed sample of the bark of eucalyptus was soaked in a reasonable quantity of water and allow to stand over night. This process enables the tannin and other soluble substances to be dissolved. The resulting solution was then decanted and tested with feric chloride and a blue-black colouration was observed which signifies that the tannin has been removed.

3.3 DRYING

After the removal of the tannin from the bark, the bark is weighed and the initial weight was noticed, after which it was dried under the sun for five consecutive hours. At the end of the drying it was then weighed again. The drying process continues untill a constant weight of 3.725kg was obtained on the 6th day. The analysis of the drying is shown in table 4.1 in the next chapter.

3.4 SIZE REDUCTION

The dried sample of the bark was placed in a wooden motar and crushed into various sizes using a wooden pistle. The sample was then taking to the laboratory for screening.

3.5 SCREENING OF PARTICLE SIZE

After size reduction, the sample was placed on the upper mesh of a sieving machine consisting a series of meshs of different size ranges. The machine was then started and allowed to operate untill a considerable amount of the sample is obtained in each mesh. Five different size ranges were selected for the experiments and these are: 0.25-0.5mm, 0.5mm-0.71mm, 0.71mm-0.85mm, 0.85mm-1.00mm and 1.00mm-1.4mm.

3.6 EXPERIMENTAL PROCEDURE

About 25g of the sample of the bark of eucalyptus camaldulensis was placed in a beaker and 250ml of 4% sulphuric acid was added to it. The beaker was then transferred to an electric heating mantle operating at 50°c. The content of the beaker was continously stirred with the aid of a locally fabricated electronic stirrer for three hours or six hours. After the time alloted, the content of the beaker was filtered and the filtrate was weighed. After that, a second filtration was again carried out and the filtrate was again weighed. The filtrate so obtained is then concentrated to about one-third of its original volume in an ovum operating at 70oc for one hour. The concentrated solution was allowed to cool after which the final filtration was done and the filtrate weighed. The final filtrate so obtained was then placed in a refrigerator over night. The following monring it was always found that crystals of oxalic acid are always formed at the bottom of the beaker. The supernated water was then decanted and the oxalic acid is dried and weighed.Four experiments were carried out on each size range two for three hours and the other two for six hours. Another set of experiment was carried out in order to investigate the effect of increase in volume on the yield of oxalic acid during which four experiments were carried out using 500ml of dilute acid and another four using 750ml of the acid.

3.7 PROCEDURE FOR THE DETERMINATION OF PERCENTAGE PURITY

Preparations of Standard Solutions

0.5479 of NaOH crystals was dissolved in 100ml of distilled water forming a standard solution of 0.138m NaOH.

0.6g each of pure and impure oxalic acid crystals were also dissolved in 100ml of distilled water separately.

PROCEDURE

The pure oxalic acid was first back-titrated against 25ml of the 0.138m NaOH using phenophthalein as indicator. The volume of the acid used at end point was recorded. The same procedure was carried out using the impure oxalic acid. The volumes obtained are used to calculate the percentage purity which was found to be 82.004%.

3.8 Flow diagram for the production of oxalic acid from the bark of eucalyptus camaldulensis using batch process.

```
┌─────────────────────┐
│ Raw bark of         │
│ eucalyptus camal-   │─────────┐
│ dulensis            │         │      ┌──────────────────────┐
└─────────────────────┘         └─────▶│ Agitation and heating│
                                       │ at 50° c  for six    │
┌─────────────────────┐         ┌─────▶│ hours or three hours │
│ 4% Dilute H₂SO4     │         │      └──────────────────────┘
│ Acid                │─────────┘                 │
└─────────────────────┘                           ▼
                                       ┌──────────────────────┐
                                       │   First Filtration   │
                                       └──────────────────────┘
                                                  │
                                                  ▼
┌─────────────────────┐         ┌──────────────────────┐
│ Concentration at    │◀────────│  Second Filtration   │
│ 70°c and cooling    │         └──────────────────────┘
│ the concentrated    │
│ solution            │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐         ┌──────────────────────┐
│ Final Filtration    │────────▶│   Crystallization    │
└─────────────────────┘         └──────────────────────┘
                                            │
                                            ▼
                                ┌──────────────────────┐
                                │       Drying         │
                                └──────────────────────┘
```

TABLE 4.1.5
Results obtained using 250ml of dilute 4% sulphuric acid with
0.85mm - 1.00mm size range of eucatyptus bark.

Duration for heating at 50°C	3 hours	3 hours	6 hours	6 hours
Mass of sample (g)	25.00	25.00	25.00	25.00
Mass of the acid (g)	259.859	258.783	260.305	250.510
Mass of acid + sample (g)	264.859	263.783	285.305	285.510
Mass of first filtrate (g)	203.850	204.173	173.222	179.886
Mass of the second filtrate (g)	193.153	194.913	159.234	168.023
Mass of the concentrated solution (g)	179.168	183.039	149.817	160.561
Mass of the final filtrate (g)	176.915	181.540	146.380	155.365
Mass of the oxalic acid obtained (g)	0.840	0.778	0.428	0.479
Average mass of oxalic acid (g)	0.809		0.454	

TABLE 4.1.6
Results obtained using 250ml of dilute 4% sulphuric acid with
1.00mm - 1.4mm size range of eucatyptus bark.

Duration for heating at 50°C	3 hours	3 hours	6 hours	6 hours
Mass of sample (g)	250.00	25.00	25.00	25.00
Mass of the acid (g)	259.235	258.722	258.375	283.049
Mass of acid + sample (g)	284.235	283.722	283.375	283.049
Mass of first filtrate (g)	189.800	197.015	179.970	171.143
Mass of the second filtrate (g)	181.759	188.008	169.227	160.943
Mass of the concentrated solution (g)	169.146	179.457	157.367	150.656
Mass of the final filtrate (g)	167.154	176.125	155.058	148.038
Mass of the oxalic acid obtained (g)	0.798	0.801	0.391	0.397
Average mass of oxalic acid (g)	0.780		0.394	

TABLE 4.1.7
Results obtained using 500ml of dilute 4% sulphuric acid with
0.25mm - 0.5mm size range of eucatyptus bark.

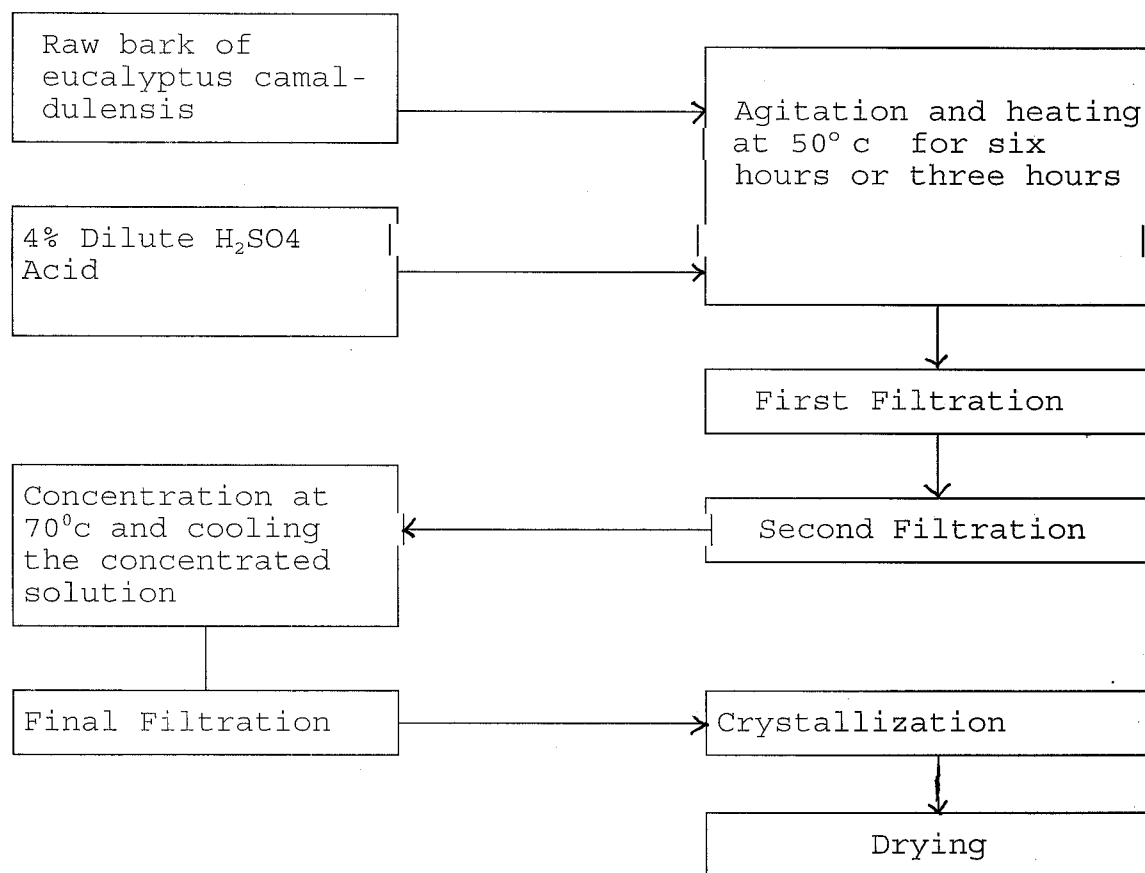| Duration for heating at 50°C	3 hours	3 hours	6 hours	6 hours
Mass of sample (g)	25.00	25.00	25.00	25.00
Mass of the acid (g)	525.498	526.020	525.096	525.821
Mass of acid + sample (g)	550.498	551.020	550.096	550.821
Mass of first filtrate (g)	464.851	465.998	445.303	446.001
Mass of the second filtrate (g)	450.047	451.672	427.268	426.972
Mass of the concentrated solution (g)	435.539	436.006	414.307	412.998
Mass of the final filtrate (g)	429.037	431.008	409.023	408.971
Mass of the oxalic acid obtained (g)	2.011	2.099	1.823	1.754
Average mass of oxalic acid (g)	2.05		1.789	

TABLE 4.1.8
Results obtained using 750ml of dilute 4% sulphuric acid with
0.25mm - 0.5mm size range of eucatyptus bark.

Duration for heating at 50°C	3 hours	3 hours	6 hours	6 hours
Mass of sample (g)	25.00	25.00	25.00	25.00
Mass of the acid (g)	784.733	784.099	785.002	784.918
Mass of acid + sample (g)	809.733	809.099	810.002	809.918
Mass of first filtrate (g)	753.733	754.125	735.021	732.917
Mass of the second filtrate (g)	738.215	739.712	720.421	719.987
Mass of the concentrated solution (g)	718.402	720.011	701.511	702.019
Mass of the final filtrate (g)	715.127	713.419	688.212	685.021
Mass of the oxalic acid obtained (g)	2.578	2.610	2.102	2.314
Average mass of oxalic acid (g)	2.594		2.208	

SECTION 4.2   TABLES FOR ANALYSIS OF RESULTS

TABLE 4.2.1
The following table shows the percentage yield of oxalic acid from each size range of the samples of eucalyptus bark.

Particle size range (mm)	volume of acid (ml)	mass of sample (g)	Yield of oxalic acid (g)		Percentage yield of oxalic acid %	
			3 hours	6 hours	3 hours	6hours
0.25-0.5	250	25	1.669	1.045	6.676	4.180
0.5-0.71	250	25	1.413	0.893	5.652	3.572
0.71-0.85	250	25	1.046	0.593	4.184	2.372
0.85-1.00	250	25	0.809	0.454	3.236	1.816
1.00-1.4	250	25	0.780	0.394	3.120	1.576

TABLE 4.2.2
The following table shows the effect of increase in volume of acid on the yield of oxalic acid (i.e percentage yield).

Particle size range (mm)	volume of acid (ml) ·	mass of sample (g)	Yield of oxalic acid (g)		Percentage yield of oxalic acid %	
			3hours	6 hours	3 hours	6 hours
0.25-0.5	250	25	1.669	1.045	6.676	4.180
0.25-0.5	500	25	2.050	1.789	8.20	7.156
0.25-0.5	750	25	2.594	2.208	10.376	8.832

TABLE 4.2.3
The table below shows the particle sizes and their corresponding average yields:-

Particle size (mm)	Average Yield (g)	
	3 Hours	6 Hours
0.25 - 0.50	1.669	1.045
0.50 - 0.71	1.413	0.893
0.71 - 0.85	1.046	0.593
0.85 - 1.00	0.809	0.454
1.00 - 1.40	0.780	0.394

TABLE 4.2.4

The table below shows the effect of time variation and the volume
of H_2SO_4 acid used on the yield of oxalic acid obtained:

Particle size (mm)	Volume o H_2SO_4 Used (ml)	Average Yield (g)	
		3 Hours	6 Hours
0.25 - 5.00	250	1.669	1.045
0.25 - 5.00	500	2.050	1.789
0.25 - 5.00	750	2.594	2.208

TABLE 4.2.5

The table below shows the results obtained for the titrations for
determination of percentate purity of the oxalic acid produced:-

	Volume of Oxalic Acid (ml)	Volume of NaoH Used (ml)		Average Volume of NaoH Used (ml)
		1	2	
Pure	25	21.7	22.6	22.15
Impure	25	18.24	18.22	18.23

ABLE 4.2.6

he following table shows the values obtained for linear
correlation and regression graph for 6 hours:-

Experimental Values		Arbitrary Values	
X	Y	X	Y
250	1.641	400	1.9186
500	2.104	650	2.381
750	2.568		

TABLE 4.2.7

The following table shows the values obtained for linear correlation and regression graph for 6 hours;-

Experimental Values		Arbitrary Values	
X	Y	X	Y
250	1.101	300	1.2166
500	1.681	600	1.9132
750	2.262		

Fig 4.3.1: Relationship b/w Particle Size & Average Yield of Oxalic Acid
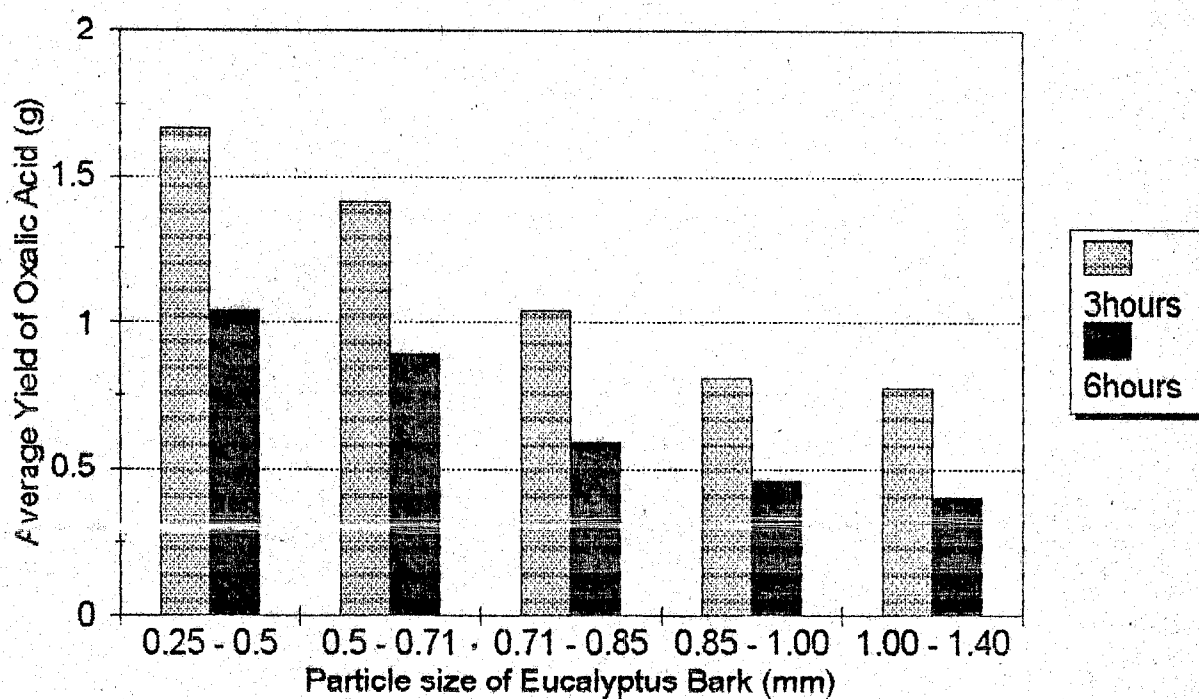
Fig 4.3.2: The effect of Incr. In Vol of H_2SO_4 acid on avg. yield of Oxalic A
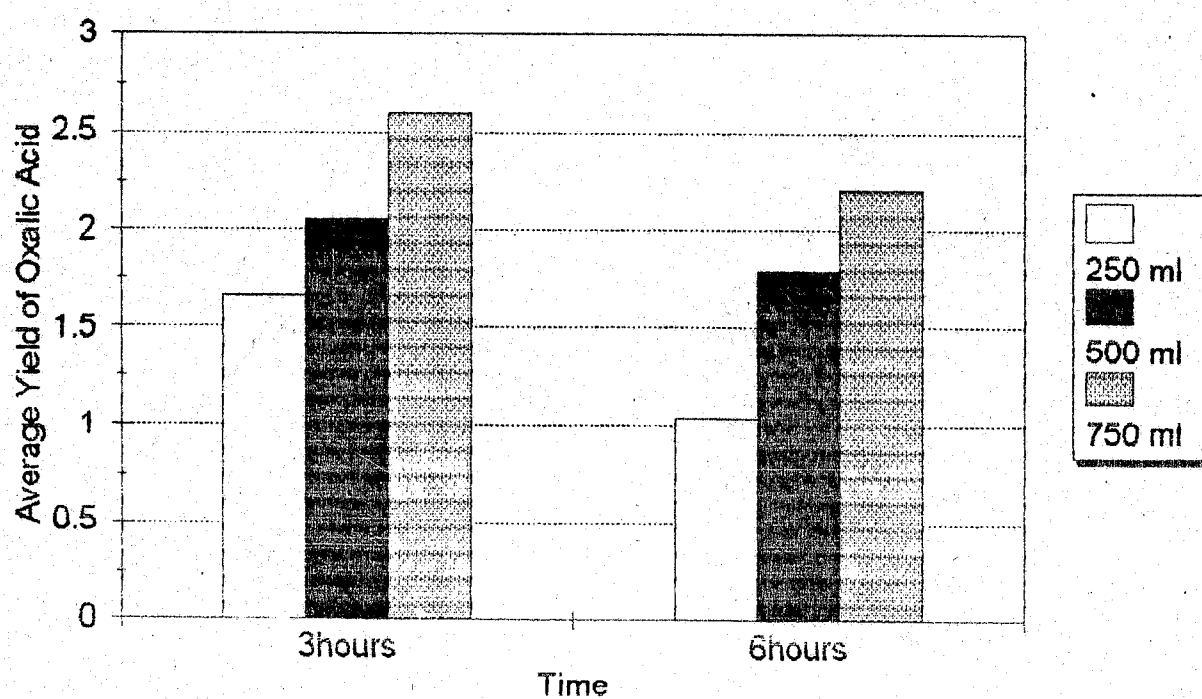
Fig 4.3.3 Linear Correlation and Regression for 3 hours

Legend:
■ Exp. Point
Arbitrary Point

X-axis: Volume of H_2SO_4 acid used (ml)
Y-axis: Average Yield of Oxalic Acid (g)
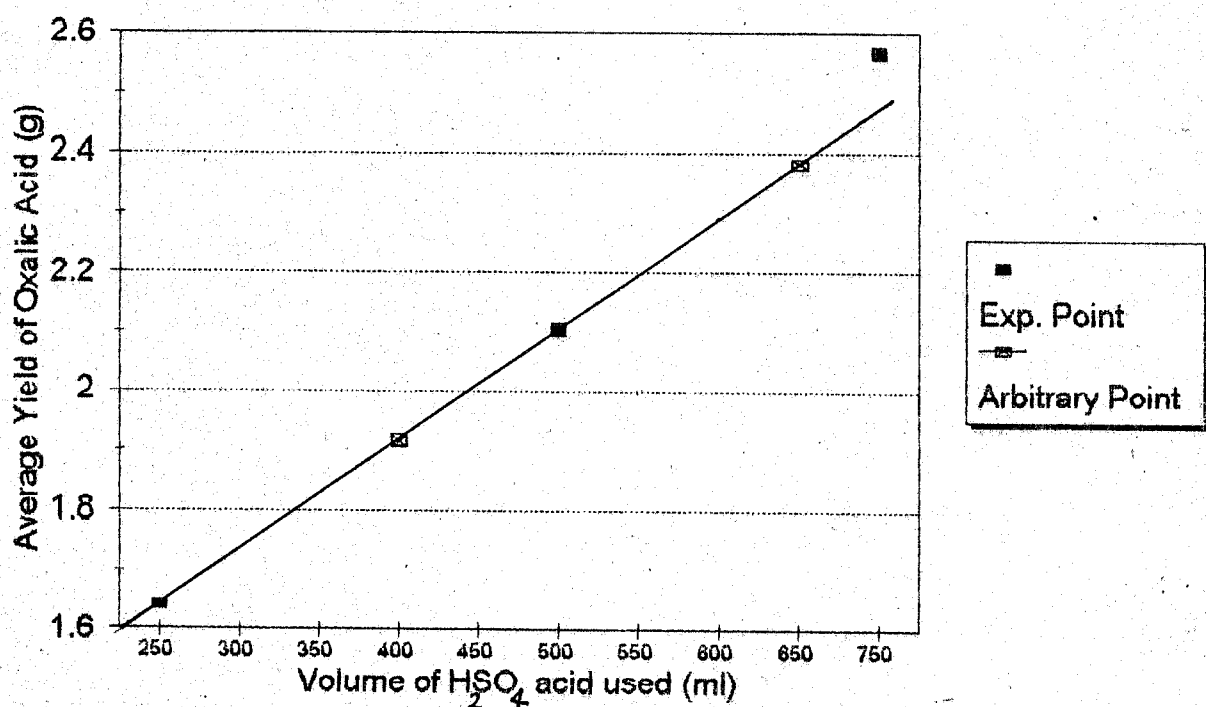
Fig 4.3.4 Linear Correlation and
Regression for 6 hours

Chart plotting Average Yield of Oxalic Acid (y-axis, 1 to 2.4) against Volume of H_2SO_4 acid used (ml) (x-axis, 250 to 750).

Legend:
- ○ Exp. Point
- ▣ Arbitrary Point
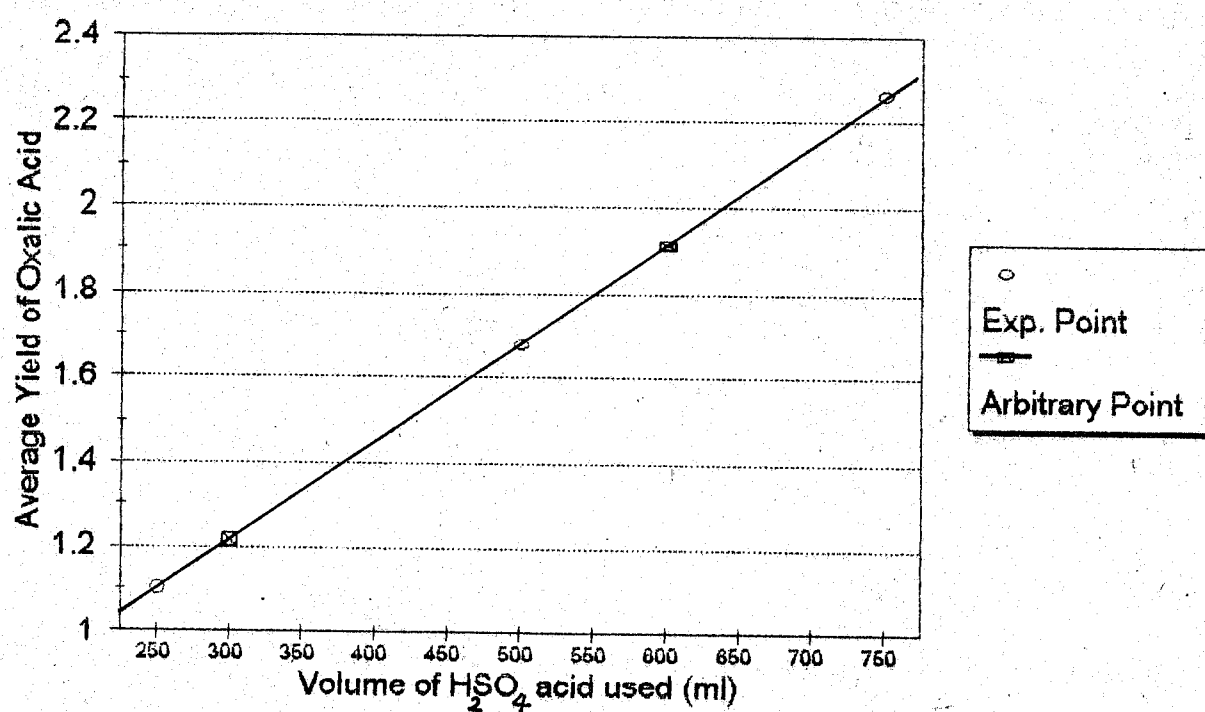
CHAPTER 5

5.1 DISCUSSION OF RESULTS

Since the scope of this work is to investigate the effect of particle size of the bark of eucalyptus camaldulensis, the variation of reaction time, and the effect of increase in volume of H2S04 on the yield of oxalid acid from the bark of eucalhyptus camaldulensis, the results will be discussed based on the three major parameters.

Five different particle siae ranges were used, which are: 0.25mm - 0.5mm, 0.5mm - 0.71mm, 0.71mm - 0.85mm, 0.85mm - 1.00mm and 1.00mm - 1.4mm. Table 4.2.3 of section 4 summarises all the results obtained on the experiments carried out on all the particle siae ranges using 250ml of dilute 4% H2S04 acid. The table gives all the five different size ranges and their corresponding average yields of oxalic acid. For the size range of 0.25 - 0.5mm, the yield was 1.669g for 3 hours and 1.045g for 6 hours. For 0.5mm - 0.71mm, the yield was 1.413g for 3 hours and 0.893g for 6 hours, for 0.71mm - 0.85mm the yield was 1.046g for 3 hours and 0.593g for 6 hours for 0.85mm - 1.00mm, the yield was 0.809g for 3 hours and 0.454 for 6 hours, and for 1.00mm - 1.4mm the yield was 0.780g for 3 hours and 0.394g for 6 hours. From the analysis of the yield obtained for both 3 hours and 6 hours reaction time, it is clearly seen that the yield of the oxalid obtained decreases with increase in particle size of the bark of eucalyptus camaldensis. This is totally in agreement with the theory on the effect of surface area (i.e. particle sieze) on the rate of chemical reaction which states that the smaller the surface area the greater the rate of chemical reaction. The relationship between the particle sizes and their corresponding average yields is also represented by figure 4.3.1.

Following the above results, it will also be seen that the average yields obtained for 6 hours is always lower than tghat of the 3 hours, for all the particle size ranges. This can be clearly seen in figure 4.3.1., considering particle size range 0.25mm - 0.5mm the yield for 3 hours is 1.669g and that for 6 hours is 1.045g. This reduction in yield in the case of 6 hours compared to that of 3 hours is as a result of reduction in volume of the final filtrate from which the oxalid acid is obtained. This reduction in volume is as a result of evaporation of the solution during constant stirring and heating at 50°c, and since the stirring takes a longer time in

terms of 6 hours it lead to more evaporation compared to that of 3 hours. The reduction in volume of the final filtrate can be seen in Table 4.1.2 for the particle size range of 0.25mm - 0.5mm. For the two 3 hours experiments, the mass of the final filtrate was 141.189g and 130.737g and their corresponding yields were 1.935g and 1.402g respectively. On the other hand, the mas of the final filtrate for the two 6 hours are 101.643g and 102.560g and their corresponding yields are 1.043g and 1.047g respectively.

Increase in volume of the dilute H_2SO_4 acid used has a remarkable effect on the yield of the oxalid acid obtained. This was justified by repeating the experiment using the smaller particle size range of 0.25mm - 0.5mm and increasing the volume of acid from 250ml to 500ml and 750 ml. Considering figure 4.3.2, it can be seen that for 3 hours experiment,m 750ml of acid produced an average yield of 2.594g, that of 500ml of acid produced an average yield of 2.050g and that of 250ml of acid gave an average yield of 1.669g. Moreso, the 6 hours experiment, 750ml of acid gave an average yield of 2.208g, that of 500ml of acid gave an average yield of 1.789g and finally the 250ml of acid gave an average yield of 1.045g.

Figures 4.3.3 and 4.3.4 shows the linear correlation and regression with the volume of H_2SO_4 used as the independent variables and the average yields of oxalic acids as the dependent variables for 3 hours and 6 hours respectively. The figures clearly reveals a linear relationship between the volume of H_2SO_4 used and the average yield of oxalic acid obtained.

Finally, the percentage purity of the oxalid acid obtained was calculated to be 82.004%, and this may be as a result of some impurities that may have escaped the filtration processes carried out during the experiment. This makes the oxalic acid obtained to be brownish in colour as against its natural colourless appearance.

5.2 CONCLUSION

At the end of this work it has been found that the average yield of oxalic acid decreases with increase in particle size range of the bark of eucalyptus camaldulensis, with the particle size ranges, 0.25mm - 0.5mm giving a corresponding yield of 1.669g for 3 hours and 1.045g for 6 hours, 0.5mm giving a corresponding yield of 1.669g for 3 hours and 1.045g

for 6 hours, 0.5mm - 0.71mm gave a corresponding yields of 1.413g for 3 hours and 0.893g for 6 hours, 0.71mm - 0.85mm gave a corresponding yield of 1.046g for 3 hours and 0.593g for 6 hours, 0.85mm - 1.00mm gave a corresponding yield of0.809g for 3 hours and 0.454g for 6 hours of 0.780g for 3 hours and 0.394g for 6 hours.

It has been found also that the longer the ractants are allowed to react and stirred the lesser the average yield of the oxalic, with the particle siae 0.25mm - 0.5mm given rise to an average yield of 1.669g for 3 hours and 1.045g for 6 hours, and all other particles sizes follows the same trend.

It is also obvious that increase in volume of H2S04 acid used results in increase in the average yield of oxalic acid obtained and that the two has a linear relationship. The 750ml of H2S04 gave an average yield of 2.594g for 3 hours and 2.208g for 6 hours,500ml of H2S04 gave an average yield of 2.05g for 3 hours and 1.789g for 6 hours and 250ml of H2S04 gave an average yield of 1.669g for 3 hours and 1.045g for 6 hours. The percentage purity of the oxalic ac id produced is 82.004%.

5.3 RECOMMENDATIONS

1.   I recommend that the reaction should be allowed to take place in a close system so as to reduced the evaporation of the reaction mixture during stirring and heating as part of the final products may also evaporates. This will also enables us to know the real effect of time variation on the yield of the oxalic acid, as the 6 hours reaction time may give rise to larger average hields of oxalic acid if not because of the longer time take for evaporation.

2.   I also recommend that more investigations should be carry out on the effect of volume on the yield of the oxalic acid by keeping on increasing the volume of acid used for particular mass of the sample of eucalyptus bark used, so as to enable us know the maximum volume at which the average yield becomes constant. The optitmum volume at which optimum amount of oxalic can be obtained should also be determined.

3.   Students should also take on project work on the feasibility studies for the commercial production of oxalic acid from the bark of eucalyptus camaldulensis. These studies should include the cost of producing the raw materials i.e.

eucalyptus camaldulensis, and the cost of H2S04 acid from our indegenous refinaries that will give a reasonable yield of oxalic acid for year. It should also includes the cost for the design of the equipment to be used and also the cost of labour. The expected return should then be compared with that obtained from the one obtained from the petrochemical industries.

CALCULATIONS FOR AVERAGE YIELD OF OXALIC ACID

From Table 4.1.2

The amounts of oxalic acid obtained for 3 hours are, 1.935 and 1.402.

. . Average yield of oxalic acid is $\underline{1.935 + 1.402}$ = 1.669
$$2$$

The amount obtained for 6 hours are, 1.043 and 1.047.

. . Average yield of oxalid is = $\underline{1.043 + 1.047}$ = 1.045
$$2$$

All other values are calculated as above.

CALCULATIONS FOR THE PERCENTAGE YIELD OF OXALIC ACID

The percentage yield of oxalic acid is given by

% Yield = $\underline{\text{Average yield of oxalic acid}}$ x 100
Mass of sample of eucalyptus bark

From Table 4.1.2

Average yield for 3 hours is 1.669 and the mass of sample used is 25

. . % Yield = $\underline{1.669}$ x 100 = 6.676%
$$25$$

Average yield for 6 hours is 1.045 and mass of sample is 25

. . % Yield = $\underline{1.045}$ x 100 = 4.18%
$$25$$

APPENDIX II

CALCULATIONS FOR THE DETERMINATION OF PERCENTAGE PURITY

Percentage purity is giveb by:

% Purity = <u>Concentration of impure oxalic acid</u> x 100
                    Concentration of pure oxalid acid

0.138 M of NaoH solution was back-filtrated against both the pure and impure oxalic acids, and the results on table 4.2.5 were obtained.

The equation for the reaction between the NaoH slution and the oxalic acid (H2C204) solution is given by:

$$2 \text{ NaoH} + C_2O_4H_2 \ ---\rightarrow \ Na2C204 + 2H20.$$

The concentration of the acids are calculated using:

Concentration = Molarity of acid x Molar mass of acid.

The standard molar mass of oxalic acid is 90.04.

The molarities of both the pure and impure oxalic acid can be caulculated using the following formular:

$$\frac{M_A \ V_A}{M_B \ V_B} \ = \ \frac{A}{B}$$

Where: M_A = Molarity of the aid

   V_A' = Volume of the acid

   M_B = Molarity of the base

   V_B = Volume of the base

   $\frac{A}{B}$ = Ration of number of moles of acid to that of the number of moles of base.

For Pure Oxalic Acid

   $\frac{M_A \ V_A}{M_B \ V_B}$ = $\frac{A}{B}$ Where M_B = 0.138M

From table 4.2.5

N_A = 25ml, V_B = 22.15ml

From the equation for the reaction, $\underline{A}$ = 1/2
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ B

. . $\dfrac{M_A \times 25}{0.138 \times 22.15}$ =   1/2

. . M_A = $\dfrac{0.138 \times 22.15}{2 \times 25}$ = 0.061M

Concentration = M_A x Molar mass

$\qquad\qquad$ = 0.061 x 90.04 = 5.49g/dm^3

. .   Concentration of the pure oxalic is 5.49g dm^{-3}

For Impure Oxalic Acid

M^B = 0.138M, $\underline{A}$ = 1/2

From table 4.2.5

V_A = 25, V_B = 18.23

. . $\dfrac{MA \times 25}{0.138 \times 18.23}$ = 1/2

. .   MA = $\dfrac{0.138 \times 18.23}{2 \times 25}$ = 0.05M

Concentration = M_A x Motar mass

$\qquad\qquad$ = 0.05 x 90.04 = 4.502 gdm^{-3}

. .   Concentration of impure oxalic acid is 4.502 gdm^{-3}

Percentage purity of oxalic acid = $\dfrac{4.502}{5.490}$ x 100 = 82.004%

Calculations for Linear Correlation and Regression for 3 hours duration, using the results for particle size 0.25 - 5.00mm

Let X = Volume of dilute H_2SO4 acid used

   Y = Average yield of oxalid acid.

n	x	y	xy	x^2
1	250	1.669	417.25	62500
2	500	2.050	1025	250000
3	750	2.594	1945.5	562500
	ΣX= 1500	ΣY = 6.313	ΣXY=3387.75	ΣX^2=875000

$\overline{X}$ = $\Sigma \dfrac{x}{n}$ = $\dfrac{1500}{3}$ = 500, $\overline{X}^{-2}$ = $(500)^2$ = 250000

$\overline{Y}$ = $\Sigma \dfrac{Y}{n}$ = $\dfrac{6.313}{3}$ = 2.104

Let the equation for Linear graph be

$\overline{Y}$ = $M\overline{X}$ + C

Where M = Slope and C = Intercept

The Slope (M) is given by the formular

$M = \dfrac{\Sigma\ XY - n\overline{X}\ \overline{Y}}{\Sigma\ X^2 - n\overline{X}^2} = \dfrac{3387.75 - 3(500 \times 2.104)}{875 - 3(250000)} = \dfrac{231.75}{125000}$

. . M = 1.854×10^{-3}

The intercept C is given by

C = $\overline{Y}$ - $M\overline{X}$ = 2.104 - 1.854×10^{-3} (500) = **1.177**

. . C = 1.177

Subtituting 'm' and "c" in the linear regression equation above

$\overline{Y}$ = $M\overline{X}$ + C

$\overline{Y}$ = $1.854 \times 10^{-3} + 1.177$

Let the new formular for regression be

$\hat{Y}$ = $1.854 \times 10^{-3}x + 1.177$

For X = 250

$\hat{Y}$ = 1.854×10^{-3} (250) + 1.177

. . $\hat{Y}$ = 1.641

All other values are calculated as above and the following table is generated

n	x	$\hat{Y}$
1	250	1.641
	500	2.104
	750	2.568
	$\Sigma X = 1500$	$\Sigma \hat{Y} = 6.313$

The variation is calculated as

$$V^2 = \Sigma(\hat{Y}-\bar{Y})^2 \text{ and } V^2 = \Sigma(Y-\bar{Y})^2$$

Where

$\hat{Y}$ = Estimated point of dependent variable

$\bar{Y}$ = Average of dependent variable

Y = Dependent variable

For n = 1

$(\hat{Y}-\bar{Y}) = 1.641 - 2.104 = -0.463$

$(\hat{Y}-\bar{Y})^2 = (-0.463)^2 = 0.214$

$(Y-\bar{Y}) = 1.669 - 2.104 = -0.435$

$(Y-\bar{Y})^2 = (-0.435)^2 = 0.189.$

Following the above calculation for n = 2 and n = 3 the following table is generated:

n	Y	$\hat{Y}$	$(\hat{Y}-\bar{Y})$	$(\hat{Y}-\bar{Y})^2$	$(Y-\bar{Y})$	$(Y-\bar{Y})^2$
1	1.669	1.641	-0.463	0.214	-0.4355	0.189
2	2.050	2.104	0	0	-0.054	0.003
3	2.594	2.568	0.464	0.215	0.490	0.240
	$\Sigma Y=$ 6.313	$\Sigma \hat{Y}=$ 6.313	$\Sigma(\hat{Y}-\bar{Y})=$ 0.001	$\Sigma(\hat{Y}-\bar{Y})^2=$ 0.249	$\Sigma(Y-\bar{Y})=$ 0.001	$\Sigma(Y-\bar{Y})^2=$ 0.432

The correlation coefficient is given by

$$r^2 = \frac{\Sigma(\hat{Y}-\bar{Y})^2}{\Sigma(Y-\bar{Y})^2} = \frac{0.429}{0.432} = 0.9931$$

$\therefore r = +\sqrt{0.9931}$ and this implies the graph is Linear.

500	1.101
750	1.681
$\Sigma X=1500$	2.262

The variation squared is calculated as

$$V^2 = \Sigma (Y-\bar{Y})^2 \text{ and } V^2 \text{ and } \Sigma (Y-\bar{Y})^2 \text{ Where } \bar{Y} = 1.681$$

For n = 1

$(Y-\bar{Y}) = 1.101 - 1.681 = -0.580$

$(Y-\bar{Y})^2 = (-0.58)^2 = 0.336$

$(Y-\bar{Y}) = 1.045 - 1.681 = -0.636$

$(Y-\bar{Y})^2 = (-0.636)^2 = 0.404$

Following the above calculation for n = 2 and n = 3 the following table is generated:

n	Y	$\hat{Y}$	$(\hat{Y}-\bar{Y})$	$(\hat{Y}-\bar{Y})^2$	$(Y-\bar{Y})$	$(Y-\bar{Y})^2$
1	1.045	1.101	-0.580	0.336	-0.636	0.404
2	1.789	1.681	0	0	0.108	0.012
3	2.208	2.262	0.581	0.338	0.527	0.278
	$\Sigma Y =$ 5.047	$\Sigma \hat{Y} =$ 5.044	$\Sigma (\hat{Y}-\bar{Y}) =$ 0.001	$\Sigma (\hat{Y}-\bar{Y})^2 =$ 0.674	$\Sigma (Y-\bar{Y}) =$ 0.001	$\Sigma (Y-\bar{Y})^2 =$ 0.694

The correlation coeffient is given by

$$r^2 = \frac{\Sigma (\hat{Y}-\bar{Y})^2}{\Sigma (Y-\bar{Y})^2} = \frac{0.674}{0.694} = 0.971$$

$$\therefore r = \pm \sqrt{0.971}$$

This applies that the graph is Linear.

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