

**KINETICS OF ACID HYDROLYSIS OF MILLET COBS  
FOR GLUCOSE PRODUCTION**

*By*

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# CERTIFICATION

This report has been read and approved as meeting the requirements of the Department of Chemical Engineering in the School of Engineering and Engineering Technology, Federal University of Technology, Minna, for the award of Bachelor of Engineering B. Eng. (HONS) Degree in Chemical Engineering.

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**Kinetics of Acid Hydrolysis of Millet Cob for Glucose Production [By: Ogunjobi, A. Taiwo]**

## DEDICATION

This project is dedicated to "Peace World Over." and to all the serious souls conscious of keeping our environment pollution free

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## ACKNOWLEDGMENT

I give my humblest gratitude to the Almighty Creator, the Most Merciful and Most Beneficent for the privilege, grace and strength which he has afforded me to partake of this great experience.

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I am thanking all my friends and every other well wishers who have contributed in their own way to this my success. May the Lord reward you all accordingly.

## ABSTRACT

This work determined the kinetics of the acid hydrolysis of millet cob.

The sample was pretreated by means of pulverizing for size reduction. The extractive contained in it were then removed with diethylether.

Lignin isolation was carried out with 6M sulphuric acid which dissolves the cellulose contained. 8M (NaOH) Sodium hydroxide was used to precipitate  $\alpha$  - cellulose.

Hydrolysis of cellulose to D - glucose was carried out using 5M, 2.5M and 3.5M solutions of 1.8 specific gravity sulphuric acid at temperatures of 65, 70, 75 and 80°C.

The hydrolysis rate follows a first order kinetics with an activation energy  $E_a$  of 74.25KJ/gmol.

A chemical process for the production of the D-Glucose from cellulosic materials e.g millet cob was designed. The detail design of the hydrolysis reactor was then conducted.

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## PHYSICAL PROPERTIES OF MATERIALS.

## CHAPTER ONE

### 1.0 GENERAL INTRODUCTION

1.1 Glucose; a monosaccharide sugar belonging to the aldohexose group has been an indispensable source of energy, both for human and animal consumption.

Domestically, it has served as a diet supplement most especially in the recuperation during sickness and industrially, it is very essential as a raw material for the production of other products e.g in food and pharmaceutical industries.

Going by this high demand for glucose which has not really been met by current production processes, efforts are being intensified to develop new methods of production to supplement the ones being used.

Technological advances and researches have highlighted the possibilities of producing glucose from agricultural wastes which is one of the most abundant renewable resources.

Several cellulosic agricultural waste materials like; maize cobs, saw dust, rice husk and host of others have been hydrolysed for glucose production.

This project sets to introduce millet cob as a by product of millet cultivation into the genera of glucose production from agricultural by-products.

This work is designated "Kinetics of Acid Hydrolysis of Millet Cobs for Glucose Production".

The economic viability of using millet cobs for glucose production is thus evaluated by determining the percentage glucose yield from this hydrolysis process.

### 1.2 MILLET CULTIVATION

Millet cob is the main raw material used in this work. The millet cob is obtained as an agricultural waste.

Agricultural wastes depict those liquids or solids parts which are usually by-products in agricultural practices, for example plant residues, stalks, cobs, husks etc. and animal wastes.

Millet is widely grown in the tropics and subtropics in regions of limited rainfall. It completes its growth circle within 90 to 120 days. It is usually interplanted with sorghum

which is taller. Because of its short height, it prevents the surface soil of farmland being washed away by erosion. Millet is generally more tolerant to drought and low soil fertility than majority of other cereals.

The naked seeds are yellowish to whitish in colour and about wheat grain size. The mature plant is about 1 to 4 feet tall and an inch thick.

Millet is being cultivated mainly in the northern part of Nigeria where rainfall is adequate enough to sustain its growth. Barnyard millet which thrives well in swampy areas has not really be explored in Nigeria, hence millet cultivation has not been practiced in the rain forest vegetational zones of this country. Response to riding varies from -70 to +240kg grain per hectare.

### 1.2.1 MILLET VARIETY

Globally, there are about six varieties of millet being cultivated. The two widely grown varieties in Africa are : the Japanese barnyard millet (Echinochloa frumentacea ) and the Raggee or Fingeu millet ( Eleusine corocana )

Fingeu millet has the highest yield of all millet varieties. It yields about 800 - 1,800kg grain per hectare.

In India hybrids give up to 50% increase in yield over local varieties. The hybrid variety is vulnerable to dowly mildew (Sclerospora graminicola ).

### 1.2.2 GROWING SEASON

Millet is grown at altitudes between 1000-2000m. Annual rainfall of between 900-1250mm. With less rainfall (lower than 800mm) irrigation is required. Thomas (1970) says the crop grows best with minimum temperature not falling below 18°C. It is grown on free draining sandy loam soil and cannot tolerate water logging.

### 1.2.3 AREA, PRODUCTION, YIELD

The highest yielding of all millet varieties is the Finger millet with 800 - 1800 kg grain per hectare about 26 million tons were produced annually in the 1970's.

In Nigeria, production has increased over the years most especially when there has been annual drop in rainfall. Hence, millet cultivation has been substituted for maize which requires more rainfall.

Because of the increasing demand for millet as food for human consumption (considering its nutritious value), livestock feed and as an alternative grain for brewing industry, millet cultivation is now more harnessed in the savanna belts of the country and even in some areas in the forest zones (through planted when the rainfall has meaningfully reduced i.e between August and September). The plant residue is as well used as silage for animal feeding.

### 1.3 MILLET COB

Millet cob is a cylindrical rachis which harbours the grains on it. It is found at the apex of the mature plant and remains as waste after threshing, pounding and winnowing. Rachis is 0.4 - 1.0mm wide base. Spikelets 4-5 x 2-2.5mm. Grains are enclosed in florets and Spikelets.

The cobs consists principally of Crude protein 4.29% of dry matter, N - free extract 41.39%, Crude fibre 43.60%, Total ash 9.32% (French M. H. 1943 b).

Uses of the cobs include the following:

**Agricultural Uses:** Mulching and soil conditioner, animal feeds, diluents and carriers for insecticides when ground to flour finess.

**Industrial Uses:** Considering the physical properties, it is used for cleaning, as an abrasive for soaps, manufacture of roofing materials, fillers for explosives, glues, adhesive etc. Taking the chemical properties into consideration, it is used in the manufacture of furfural, fermentable sugars, solvents and liquid fuels, single cell production. etc. In addition, this work centres around production of glucose from millet cobs.

### 1.4 CELLULOSE

Cellulosic materials which is the most abundant and renewable resources is presently being explored as biomass energy resources for conversion into a variety of useful materials.

It has in the past being used as animal feed and bedding, ploughing under soil to maintain fertility and a whole lot been pyrolysed during bush clearing. This last method of disposal has really constituted a great threat to our atmosphere and environment.

Efforts are now being harnessed in turning this abundant and excellent energy source into commercial products.

Millet cobs contain cellulosic materials (cellulose, hemicellulose and lignin) in a considerable amount. This ligno cellulosic matrix of plant material is being studied for the releasing of bound cellulose from the lignin component.

Cellulose is always associated with a variety of other polysaccharides such as starch, pectin and a variety of hemicellulose. The purest form of cellulose found in seed hairs of cotton, contains about 6% by weight of non-cellulosic polysaccharides, proteins and mineral elements (Cowling and Kirk, 1976).

Hemicellulose is a term coined by Schulze (1891). It is the non-cellulosic polysaccharide other than starches and fructosans found in the aerial, and normally lignified parts of the organs of higher land plants. Hemicellulose and lignin form a protective cover for cellulose from the attack of micro-organisms. The hemicellulose can be extracted by dilute aqueous alkali after the removal of lignin.

The treatment of hemicellulose yields xylose which can be fermented to produce ethanol.

Lignocellulosic biomass consists of cellulose (50%), hemicellulose (28%) and lignin and other materials (22%).

Hemicellulose are those polysaccharides non-covalently associated with cellulose.

The current attempts to produce fuel and chemical products from cellulose in urban trash and residues remaining from forestry, agricultural and food processing operations will result in the following as stated by Cowling *et al.* (1976).

1. Help solve modern waste - disposal problems
2. Diminish pollution of the environment
3. Brings an increase in food and animal feeds.
4. Produce alternative fuel to fossil fuels.

5. Help improve forest managements by providing markets for low-quality hardwood and other green junks.
6. Assist in the development of life-support systems for deep space and submarine vehicles.
7. Create job opportunities.

That an eager market is awaiting cheap glucose production from waste lignocellulose materials was suggested by mandels *et al.* (1974). The crude glucose syrup would be a suitable substrate for single cell protein production; a source of fermentable chemicals such as fuel alcohols or as chemical feedstock.

Two main problems are being encountered considering the features of natural cellulosic materials; these are crystallinity and lignification. (Cowling, 1975; Cowling *et al.*, 1976; Fan *et al.*, 1980, 1981). These two factors limit the accessibility and susceptibility of cellulose to acid and other hydrolytic agents.

Lignin restricts acid and microbial access to the cellulose while crystallinity restricts the rate of various mode of attack on the cellulose.

Several physical, chemical and microbial pretreatment for enhancing the conversion of lignocellulosic materials to glucose have been reported. (Millett *et al.*, 1975, 1976; Nesse *et al.*, 1977; Dunlap *et al.*, 1976; Kumakura *et al.*, 1978, 1982; Macdobald *et al.* 1979; Beardmore *et al.*, 1980; Kesley *et al.*, 1980, Chang *et al.*, 1981; Nelson *et al.*, 1982; Ander *et al.*, 1983; Hatakke, 1983; Rexen, 1983; Khan *et al.*, 1986.)

Pretreatment of cellulose opens up the cellulose structure and removes interaction between glucose chains.

Acid hydrolysis being a method of cellulose conversion to glucose is either done with dilute or concentrated acids. Using concentrated acid makes the process to proceed at low temperature, the sugar formed are not degraded by heat. But a large amount of acid is required to soak the feedstock. Acid recovery is thus necessary and this capital intensive.

Hence, virtually all recent process development work has been done with dilute acids. Cellulose hydrolysis in dilute acids requires higher temperature, atleast 180°C. This makes the glucose produced to be charred. (Harris *et al.*, 1963).

Hydrolysis of purified raw materials especially commercial cellulose such as soika floc, avicel, sweco, sigmacell, walseth absorbent cotton and viscose rayon fibres. Unfortunately, these do not give the real nature and properties of the naturally existing raw materials.

### 1.5 OBJECTIVES AND SCOPE.

Millet cob is being investigated as material for acid saccharification. Millet cobs represent a renewable, low-cost energy resources available in significant amount in this country. Pretreatment to increase the availability of the cellulose in millet cob were carried out.

The main objectives of this work are :

- a. To isolate cellulosic materials in millet cobs
- b. Investigation of the effect of temperature on the initial rates of acid hydrolysis of millet cobs
- c. To determine the kinetic of acid hydrolysis of millet cobs using sulphuric acid.

To achieve these objectives, various pretreatment were carried out. These include size reduction, delignification using diethyl ether. The pretreated millet cobs was hydrolysed at different temperatures using varying concentration of sulphuric acid.

Samples of hydrolyze were collected at regular intervals of time and analysed for reducing sugar from which the hydrolysis rate could be determined.

A detail design of the hydrolysis reactor is to be carried out.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1.1 SOURCES OF CELLULOSIC MATERIALS

Cellulose is the main polysaccharide in plants. It forms the skeletal structure of the plant cell wall. Occurring with other polysaccharide and hemicellulose derived from other sugars such as xylose, arabinose and mannose. In woody part of plants, it is intimately mixed and some times covalently linked with lignin.

Wood contains 40-50% cellulose, 20-30% lignin and 10-30% hemicellulose as well as mineral salts, proteins and other biochemical compounds.

The most abundant natural sources of cellulose are (cowling *et al* , 1976)

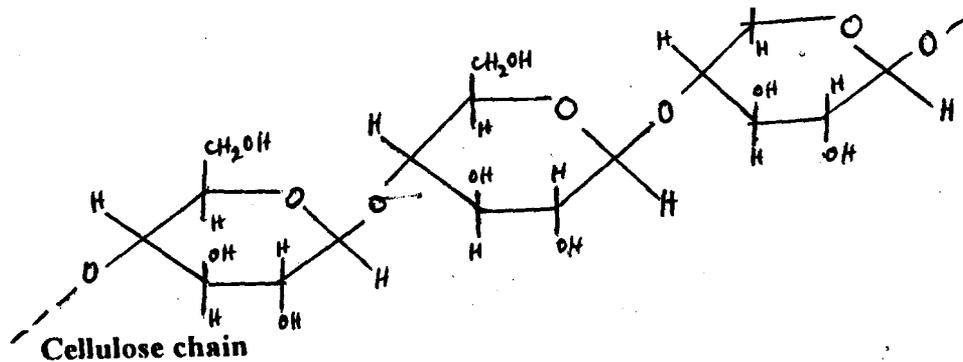
- I. the stems of woody angiosperms (hard woods)
- ii. the stems of woody gymnosperms (soft woods)
- iii. the stems of monocotyledons (palm, bamboo, wheat, millet, sugarcane etc)
- iv. non-lignified parenchyma cells of most leaves or partly lignified fibres such as seed hairs, seed shafts etc.

#### 2.1.2 CHEMICAL AND MOLECULAR STRUCTURE OF CELLULOSE

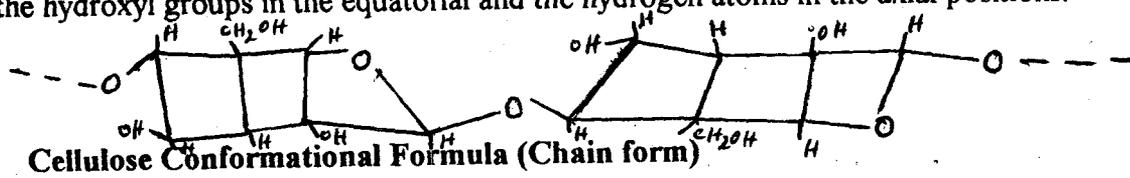
Cellulose is a high molecular weight linear polymer of  $\beta$ -D-glucopyranosyl units linked together by  $\beta$ -1-4-glucosidic bonds. Except for the  $\beta$ -D-nature of the glycosidic linked between D-glucopyranosyl units; cellulose is chemically identical with starch amylose. Cellulose molecules generally contain between about 100-3000 glucose units. The linear molecules contains regions where the structure is sufficiently regular for it to show the x-ray properties of a crystal.

Commercially, cellulose is evaluated on the basis of its  $\alpha$ -cellulose content, which is that portion of pulp insoluble in 17.5% NaOH solution.  $\beta$ -cellulose and  $\gamma$ -cellulose are all extractable from pulp by 17.5% NaOH solution.

$\beta$ -cellulose is that portion of the material; which is precipitated when the alkaline extract is acidified while  $\gamma$ -cellulose is the portion remaining in solution after acidification.



In a cellulose chain molecule, the anhydroglucose units adopt the chair configuration with the hydroxyl groups in the equatorial and the hydrogen atoms in the axial positions.



The glycosidic linkage acts as a functional group and this, along with the hydroxyl group determine the chemical properties of cellulose. All significant chemical reactions of cellulose occurs at the glycosidic linkage.

Cellulose molecules occurs mainly in form of fine fibril which is stabilized laterally by hydrogen bonding between hydroxyl groups of adjacent molecules.

The molecular arrangement of this fibrillar bundle is sufficiently regular that cellulose exhibits a crystalline x-ray diffraction pattern (Cowling *et al* , 1976).

### 2.1.3 STRUCTURE AND MORPHOLOGY OF CELLULOSE FIBRES.

Like all hydrophilic linear polymers, individual cellulose molecules are linked together to form elementary fibrils or proto fibrils, in which polymer chains are oriented in a parallel alignment and firmly bound together by hydrogen bonds. The layers so formed normally inclined at an angle to the fibre axis.

The fibrils are composed of finer microfibril or micellar strings (Rowland 1975; Cowling 1975; Cowling *et al* , 1976; Fan *et al* , 1980).

Most heterogenous reactions of cellulose occur slowly in the crystalline regions, but take place rapidly in the low-density amorphous regions where the looser packing of cellulose chain permit easier penetration of reagent molecules.

Fibrils are cemented together by polysaccharides such as hemicellulose to form microfibril. Hemicellulose is a protective membrane enclosing the micelles which it binds into fairly rigid unit and retains a good deal of flexibility.

The microfibril is surrounded by a lignin layer which protects it from degradation due to external influences.

#### 2.1.4 PHYSICAL AND CHEMICAL CONSTRAINT ON THE SUSCEPTIBILITY OF CELLULOSE TO HYDROLYSIS

There are two major processes being employed in the solubilization of cellulosic waste material - acid and enzymatic hydrolysis. Cellulose is the limiting reactant that determines the extent of hydrolysis.

Reese (1956) claimed that about 100,000 times acid compared to obtain the same degree of hydrolysis compared with the activities of enzymes catalyst. It has also been reported that enzymatic hydrolysis of cellulose causes a slower reduction of the degree of polymerization of cellulose than the acid hydrolysis (Ghose *et al* , 1971)

The relative size of the two catalyst (enzymes and mineral acid) coupled with their ability to permeate the fine structure of cellulose have been accounted for the difference in activity.

The enzymes are only able to penetrate into the large inter-crystalline spaces of the cellulose molecules while the mineral acid molecules are capable of diffusing into the smaller intercrystalline spaces and then attack glucosidic bonds which are not accessible to the enzymes.

Despite that viscous polymer (hemicellulose) and other branched polymers in hydrolyzates prevent access to enzymes attack, by restricting enzyme movement and by blocking hydrolysis sites;; enzymatic hydrolysis is capable of producing purer, undergraded products with reduced by-products.

The dominating cellulose properties such as cellulose crystallinity, lignin content, pore size, moisture content and exposed surface area have being claimed to greatly influence cellulose digestibility (Dunlap *et al* , 1976; Fan *et al* , 1980)

The lignin, hemicellulose ash, protein and fat in crystalline and non-crystalline region makes the measurement of any particular property difficult.

Lignin sheath which protects cellulose structure in another constraint to cellulolytic enzymes and even causes side reactions in acid hydrolytic where proper isolation is not effected.

## 2.2 PRETREATMENT OF CELLULOSIC MATERIALS<sup>14</sup>

Pretreatment is essential to increase the contact surface area and accessibility of reagent to cellulose molecules. The cellulose crystallinity is also reduced during pretreatment.

Cellulose is as well discovered to be protected by lignin sheath and this has to be isolated during pretreatment to increase reaction rate.

Sugar conversion from unpretreated natural feed stock is generally limited to less than 25%. Pretreatment processes are therefore necessary to convert cellulose to an accessible form for rapid hydrolysis.

Physical and chemical pretreatment have been the major processes being employed depending on their mode of attack on the substrate.

(Hatakka 1983 and Auder *et al* 1983) have shown that biological pretreatment can also be used to enhance hydrolysis rate and cellulose susceptibility.

### 2.1.1 PHYSICAL PRETREATMENT

This can be categorised as mechanical or non-mechanical. The mechanical pretreatments include ballmilling (Maiarella 1985; Mandels *et al* 1974), two roll milling (Tassinari *et al* 1980) hammer milling (Mandel *et al*, 1974, Maiorella 1986), Fitz milling (Fan *et al* 1981 b) and wet milling (Kesly *et al*, 1980). These processes utilize shearing and impacting forces to yield a fine substrate possessing a low crystallinity index.

Non-mechanical physical pretreatments include; gamma-irradiation (Dunlap *et al* 1976; Beardmore *et al*, 1980; Kumakura *et al*, 1982).

Electron-beam irradiation (Kumakura *et al*, 1978, 1982; Kaan *et al*, 1986)

Staming (Macdonald *et al* 1978, 1982; Martin *et al*, 1986) and freeze explosion (Dale *et al*, 1982)

## 2.2.2 CHEMICAL PRETREATMENTS<sup>4</sup>

Chemical pretreatments have extensively been used as a means of lignin removed, extractives removal and structural modification of lignocellulosics. They include; caustic swelling (Dunlap *et al* , 1976; Fan *et al* , 1981b). Acid pretreatment (Fan *et al* , 1981b) and chemical oxidation of lignin by an oxidizing agent e.g peracetic acid (Toyama 1976, Toyama *et al* , 1975). Some gases such as sulphur dioxide (Dunlap *et al* , 1976), high pressure hydrochloric acid (Antonopolis *et al* , 1983) and Ammonia (Detroy *et al* , 1980) have all been used for lignification.

Solvents like ethanol, butanol and acetone (Fan *et al* , 1981b), EDTA and dimethyl sulphoxide DMSO (Detry *et al* , 1981) and cadoxen (Hsu *et al* , 1980) along with suitable catalyst have been used for delignification. The possibility of solvent recovery makes this process attractive.

Generally, pretreatment is a function of quality of raw material and the characteristics of the end product. If glucose is to be produced as product or intermediate relatively pure cellulose is required. While in the production of crude single cell protein, feedstock need not be purified or restricted to cellulose composition.

The price and availability of raw materials are factors to be considered before embarking on pretreatment (Hexen, 1983).

## 2.3 METHODS OF HYDROLYSIS OF CELLULOSIC MATERIALS

Three technologies have been reported for conversion of cellulosic materials (Layokun, 1985; Harris *et al* , 1963; Nystrom *et al* , 1984). The methods are Acid hydrolysis; Enzymatic hydrolysis and Direct microbial conversion.

### 2.3.1 ACID HYDROLYSIS

Acid hydrolysis is divided into two; the rapid acid hydrolysis which involves the use of 0.5% concentrated acid at a temperature of 240°C and a pressure of 3450kPa. The hydrolysis takes place with up to 60% sugar conversion in 20 seconds. The product is flash cooled to prevent decomposition (Rugg at New York University).

Slow acid hydrolysis yields 70% fermentable sugar. Dilute acid 0.5-0.6% concentration is used and the total hydrolysis time of between 2.5 - 3.5 hours. A pressure of 1135kPa is operated at the maximum. The operating temperature is about 180°C (Harris *et al* , 1963; Millet *et al* 1976).

Sugar degradation is minimized by reacting at high temperature and pressure for very short periods (Knappet *et al* , 1980).

The use of concentrated acid requires large quantity of acid to wet the feed stock, thus acid recovery is imperative though this could be very expensive.

Advantages of acid hydrolysis are:

1. Suitability of any cellulose feedstock to acid hydrolysis
2. Lower reaction time than enzymatic hydrolysis
3. Acid is cheap and readily available
4. It can be operated on laboratory and commercial scale
5. Asepsis is not an important issue for acid hydrolysis operations.

The limitation of acid hydrolysis include:

1. Susceptibility of product to degradation due to high temperature.
2. Side reactions and possibility of by-products poisoning the main product.
3. Lower quality sugar and severe operating conditions which could lead to level corrosion.

### 2.3.2 ENZYMATIC HYDROLYSIS

This involves the use of micro-organisms in the degradation of cellulose to glucose. Fungal cellulose decompose the insoluble cellulose to  $\alpha$ -cellulose which is then broken down by endoglucanase to short-length sugars. The short-length sugars are then converted by exoglucanase to cellobiose and cellotriose which is latter converted by  $\beta$ -glucosidase to glucose.

The conversion of cellulose of glucose during enzyme hydrolysis is carried out at ambient temperature and pressure, thus reducing the energy cost.

**Advantages of enzyme hydrolysis include:**

1. Cellulase enzyme is a complex of enzymes all of which are inducible and can be formed in the presence of the substrate.
2. Cellulase is synthesized mostly by fungi and bacteria which are of course abundant in nature thereby allowing cheap production cost.
3. Neutralization and purification process are not necessary since side reaction are not feasible due to enzyme specificity.
4. The process proceeds at mild operating conditions of 4.5 to 5.0 pH; 45° to 50°c temperature and atmospheric pressure. This averts the use of expensive materials in equipment construction.
5. The sugar produced is undegraded and has high potency.

**Disadvantages of enzymes hydrolysis are:**

1. High cost of enzymes production.
2. Difficulty in enzyme recovery where appropriate immobilization technique cannot be employed due to operating conditions.
3. Possible degradation to the hydrolyzate from the microbes in the surrounding.

### 2.3.3 DIRECT MICROBIAL COVERSION

This process involves the production of a single product by growing on the cellulose-rich substrate a suitable organism. This is the basis of single cell protein production.

A development of this process involves the use of two organisms, one degrades cellulose and yields product like pentose sugars for consumption by a second organism which produces the desired product. This allows for more complete utilisation of the lignocellulose.

This affords the opportunity of conversion many industrial and agricultural waste products to protein rich feeds.

The nutritive value of the product of direct microbial conversion is of particular importance as a program supplement.

### **Advantages of direct Microbial Conversion**

- i. The product is nutritionally balanced, requiring just a minimum landscape for cultivation, shorter generation time and less capital cost of production.
- ii. It can be produced on a variety of what man considered to be waste material.
- iii. Microbes used have a shorter generation time, therefore has a rapid mass.
- iv. Microbes can be genetically manipulated to produce cells for specific purpose.

### **Problems of Direct Microbial Conversion**

- i. The taste and gastro-intestinal irritation of the feed product.
- ii. Pathogenicity of the micro-organisms which could be a source of disease or an epidemic.
- iii. Toxicity of the cell wall and high nucleic acid content of the product.

## CHAPTER THREE

### EXPERIMENTALS

#### 3.1 MATERIALS

3.1.1 **MILLET COBS:** The millet cobs were collected from a farm at the back of the Federal University of Technology, Minna mini campus. It was later sun dried.

The specie collected was Pennisetum maiwa

#### 3.1.2 CHEMICAL AND REAGENTS

- a. **Acid:** Concentrated sulphuric acid with 98% purity was collected from Stafford Chemical Industries, Agbara in Ogun state. The specific gravity being 1.834.
- b. **Diethylether:** was used for extractives removal from the grinded millet cob.
- c. **Low alkalinity copper reagent and Arsenomolybdate reagent** were for determining glucose concentration after hydrolysis.

#### 3.1.3 APPARATUS AND EQUIPMENTS

1. **Hydrolysis Reactor:** 250ml conical flasks were used as stirred reactors.
2. **Water Bath:** a product of Gallenkamp was used to ensure constant temperature.
3. **Colorimeter:** A corning colorimeter model 253 with 470mm was used to determine glucose concentration in the hydrolyzate.
4. **Others Apparatus and Equipment used were**
  - Set of sieves
  - Digital weighing balance
  - Serrated disc grinder
  - Stop watch, beakers, measuring cylinder (250ml)

## 3.2 PROCEDURE

### 3.2.1 PREPARATION OF CALIBRATION CURVE FOR THE DETERMINATION OF GLUCOSE CONCENTRATION BY SOMOGLY -NELSON METHOD<sup>16</sup>

0.1g of the standard D-glucose was dissolved in 1000ml distilled water. This was designated the standard D glucose solution 10ml each of distilled water was used to dilute 1.0ml, 10ml, 30ml, 70ml and 100ml of the standard Dglucose solution to get a concentration of  $0.9 \times 10^{-4}$ ,  $0.5 \times 10^{-4}$ ;  $0.75 \times 10^{-4}$ ;  $88 \times 10^{-4}$  and  $0.91 \times 10^{-4}$  g/ml respectively.

2.0mls of copper reagent was then added to 2.0mls of each diluted sample and boiled for ten minutes and allowed to cool. 2.0mls of arsenomolybdate reagent were then added to the cooled solutions and made up to 25mls with distilled water and shaken.

The optical density (absorbance) of the samples were then read with 9470nm colorimeter. Table 4.1 shows the result.

### 3.2.2 PRETREATMENT

#### a. Milling

Unwanted materials like paper, stone, plastics and other plant parts were separated from the millet cobs and size reduction was carried out with a serrated disc grinder. The milled sample was then sieved using vibratory sieve shaker into various particles sizes. Three different particle sizes; Pan fraction (less than  $250\mu\text{m}$ );  $250\mu\text{m}$  and  $500\mu\text{m}$  samples were collected and labelled samples A, B and c respectively. The size reduction was to effect efficient acid accessibility to the cellulose structure and increase the effective contact area for reaction.

#### b. Removal of Extractives

Waxes, starch, tannis, oil and fat resin were removed using diethy ether.

10gms of samples A, B and C were treated each with 40mls diethyl ether in 250mls beakers for three hours. The resulting residues were then washed thoroughly with distilled water, filtered, and dried. The percentage extractive was found to be 5.14% and a dark brown residue was obtained.

### c. **Lignin Isolation<sup>6</sup>**

This is the process of dissolving cellulose by concentrated acid mainly sulphuric acid or hydrochloric acid. 10gms of extractive free samples A, B and C were treated with 70mls of 6M sulphuric acid for 1 hour. The filtrate containing dissolved cellulose was further treated with 30ml of 8m sodium hydroxide which precipitates  $\alpha$ -cellulose. The precipitate were washed thoroughly with distilled water, filtered and dried. The percentage cellulose in each sample was found to be 20.24%, 16.70% and 11.72% respectively.

### 3.2.3 HYDROLYSIS STAGE

#### 1. **Temperature Variation at Constant Acid concentration of 5M**

5M solution of concentrated sulphuric acid was prepared by diluting 6.94mls of 98% concentrated (72M) sulphuric acid in distilled water and made up to 100mls

To four equal parts of the extrated cellulose were added 20mls of 5M sulphuric acid and the hydrolysis was carried out at 65°C, 70°C, 75°C and 80°C respectively for 1 hour 40 minutes. On attaining a steady temperature in each case, 2mls of the hydrolyzate was added to 2mls copper reagent and boiled for 10 minutes. After cooling, 2mls of arsenomolybdate reagent was added and the solution made up to 25mls with distilled water.

Assay for glucose was done at 20 minutes interval until 100 minutes elapsed. The same procedure was repeated for other samples at 70°C, 75°C and 80°C. The results obtained are shown in tables 4.2 to 4.5 respectively.

#### 2. **Variation of Acid Concentration at Temperature of 75°C**

2.5M and 3.5M sulphuric acid solutions were prepared and used to hydrolyse the cellulose sample. Assay for glucose was done at 20 minutes interval. The result are shown in table 4.6 abd 4.7 respectively.

## CHAPTER FOUR

## 4.0 EXPERIMENT RESULTS

Table 4.1

Calibration data for plotting the standard curve of 0.1g/ml standard D-glucose solution at 470nm.

Glucose concentration $\times 10^{-4}$ g/ml	Optical Density (Absorbance)
0.00	0.00
0.09	0.08
0.50	0.44
0.75	0.65
0.88	0.73
0.91	0.79

A plot of absorbance against glucose concentration is given in fig. 4.1. A straight line graph is obtained. Increase in concentration gives higher absorbance.

Table 4.2 Data for acid hydrolysis of Millet cob sample at 65°C using 5M solution of  $H_2SO_4$  acid for 100 minutes.

Time (mins)	Absorbance	Glucose Conc. $\times 10^{-4}$ g/ml	$\ln \frac{a_0}{a_0 - x}$	Yield %
20	0.14	0.17	$1.70 \times 10^{-3}$	1.7
40	0.18	0.21	$2.10 \times 10^{-3}$	2.1
60	0.19	0.22	$2.20 \times 10^{-3}$	2.2
80	0.22	0.26	$2.60 \times 10^{-3}$	2.6
100	0.25	0.29	$2.90 \times 10^{-3}$	2.9

**Table 4.3** Data for acid hydrolysis of Millet cob sample at 70°C using 5M solution of H<sub>2</sub>SO<sub>4</sub> acid for 100 minutes.

Time (mins)	Absorbance	Glucose Conc. X10 <sup>-4</sup> g/ml	$\ln \frac{a_0}{a_0 - x}$	Yeild %
20	0.15	0.18	1.80 x 10 <sup>-3</sup>	1.8
40	0.18	0.21	2.10 x 10 <sup>-3</sup>	2.1
60	0.19	0.22	2.20 x 10 <sup>-3</sup>	2.2
80	0.23	0.27	2.70 x 10 <sup>-3</sup>	2.7
100	0.26	0.30	3.00 x 10 <sup>-3</sup>	3.0

**Table 4.4** Data for acid hydrolysis of Millet cob sample at 75°C using 5M solution of H<sub>2</sub>SO<sub>4</sub> acid for 100 minutes.

Time (mins)	Absorbance	Glucose Conc. X10 <sup>-4</sup> g/ml	$\ln \frac{a_0}{a_0 - x}$	Yeild %
20	0.18	0.21	2.10 x 10 <sup>-3</sup>	2.1
40	0.21	0.25	2.50 x 10 <sup>-3</sup>	2.5
60	0.24	0.28	2.80 x 10 <sup>-3</sup>	2.8
80	0.27	0.31	3.10 x 10 <sup>-3</sup>	3.1
100	0.29	0.33	3.30 x 10 <sup>-3</sup>	3.3

**Table 4.5** Data for acid hydrolysis of Millet cob sample at 80°C using 5M solution of H<sub>2</sub>SO<sub>4</sub> acid for 100 minutes.

Time (mins)	Absorbance	Glucose Conc. X10 <sup>-4</sup> g/ml	$\ln \frac{a_0}{a_0 - x}$	Yield %
20	0.21	0.25	2.50 x 10 <sup>-3</sup>	2.5
40	0.24	0.28	2.80 x 10 <sup>-3</sup>	2.8
60	0.26	0.30	3.00 x 10 <sup>-3</sup>	3.0
80	0.28	0.33	3.30 x 10 <sup>-3</sup>	3.3
100	0.31	0.36	3.60 x 10 <sup>-3</sup>	3.6

**Table 4.6** Data for acid hydrolysis of Millet cob sample at 75°C using 2.5M solution of H<sub>2</sub>SO<sub>4</sub> acid for 100 minutes.

Time (mins)	Absorbance	Glucose Conc. X10 <sup>-4</sup> g/ml	$\ln \frac{a_0}{a_0 - x}$	Yield %
20	0.12	0.14	1.40 x 10 <sup>-3</sup>	1.4
40	0.14	0.17	1.70 x 10 <sup>-3</sup>	1.7
60	0.17	0.20	2.00 x 10 <sup>-3</sup>	2.0
80	0.19	0.22	2.20 x 10 <sup>-3</sup>	2.2
100	0.22	0.26	2.60 x 10 <sup>-3</sup>	2.6

**Table 4.7** Data for acid hydrolysis of Millet cob at 75°C using 3.5M solution of H<sub>2</sub>SO<sub>4</sub> acid for 100 minutes.

Time (mins)	Absorbance	Glucose Conc. X10 <sup>-4</sup> g/ml	$\frac{h a_0}{a_0 - x}$	Yield %
20	0.13	0.15	1.50 x 10 <sup>-3</sup>	1.5
40	0.14	0.17	1.70 x 10 <sup>-3</sup>	1.7
60	0.16	0.19	1.90 x 10 <sup>-3</sup>	1.9
80	0.18	0.21	2.10 x 10 <sup>-3</sup>	2.1
100	0.21	0.25	2.50 x 10 <sup>-3</sup>	2.5

**Table 4.8** Data for plotting of the curve of Ink against 1/t for various samples at 65°C; 70°C; 75°C and 80°C.

K (x 10 <sup>-5</sup> /min)	Ink	T(k)	1/T (X10 <sup>-3</sup> K <sup>-1</sup> )
1.39	-11.18	338	2.96
1.25	-11.29	343	2.92
1.79	-10.93	348	2.87
1.56	-11.07	353	2.83

FIG. 4.2, PLOT OF GLUCOSE CONCENTRATION VS TIME FOR VARYING TEMPERATURE

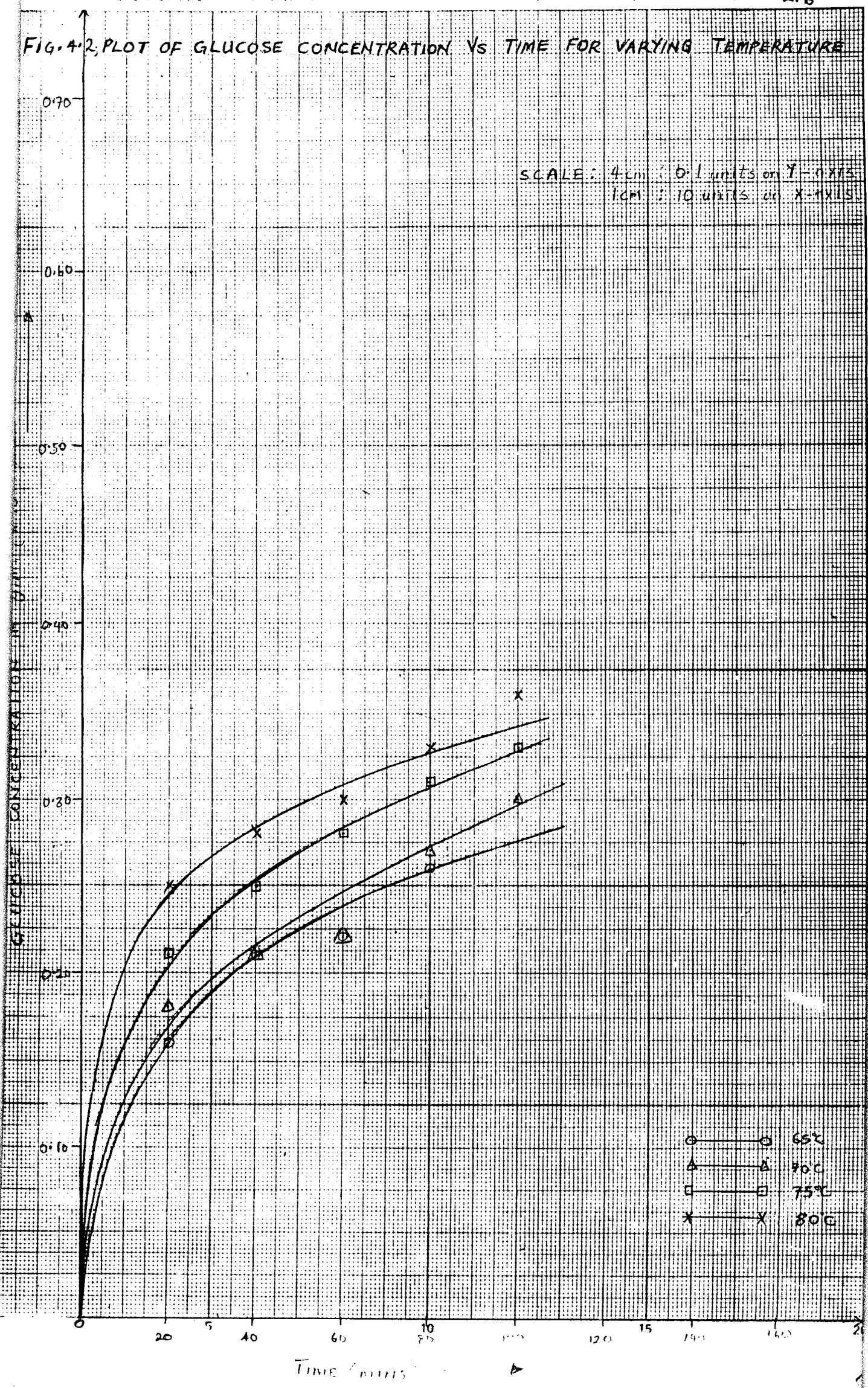
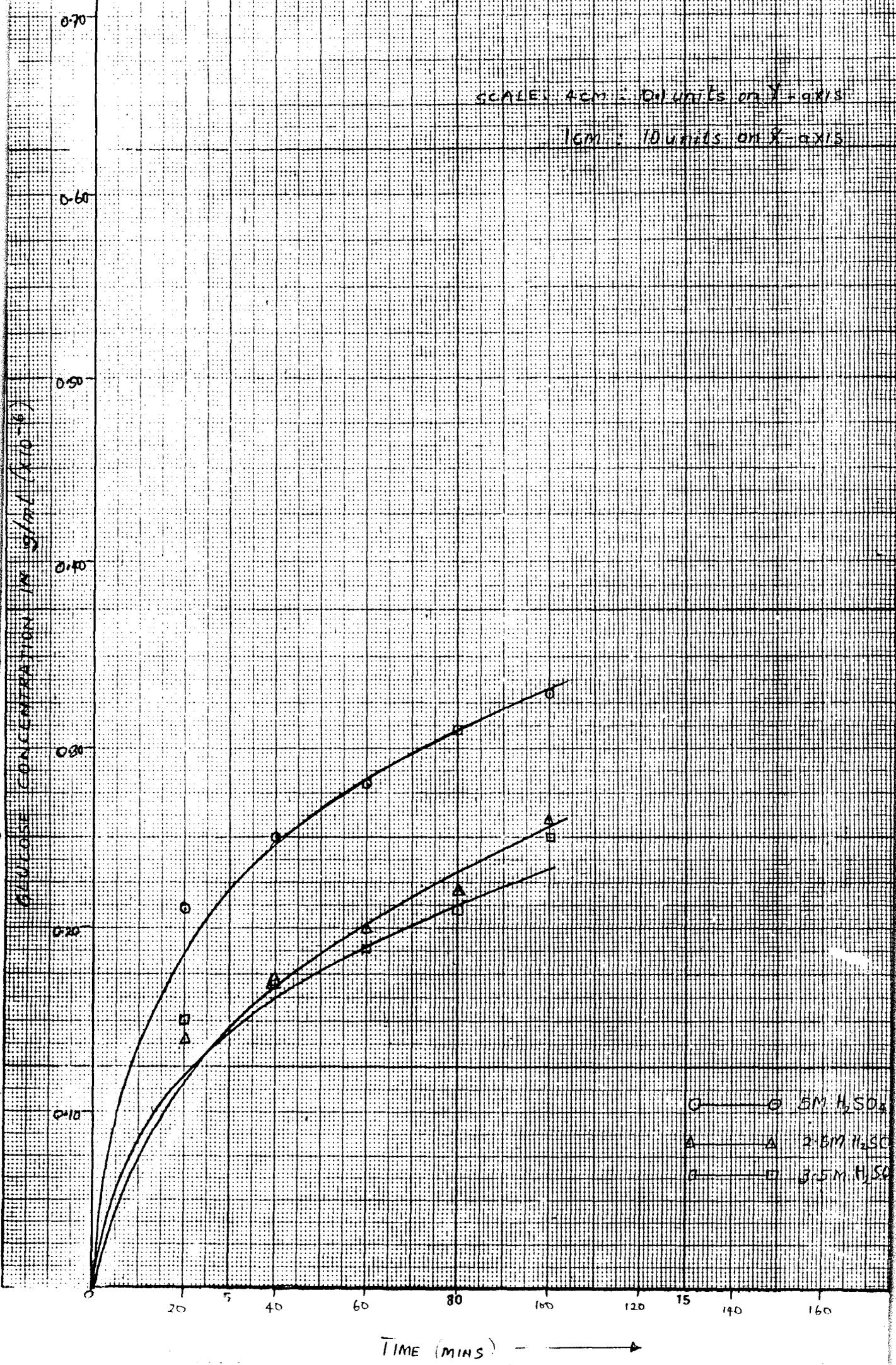


FIG. 4-3; PLOT OF GLUCOSE CONCENTRATION VS TIME FOR VARYING  $H_2SO_4$  CONCENTRATION AT  $75^\circ C$

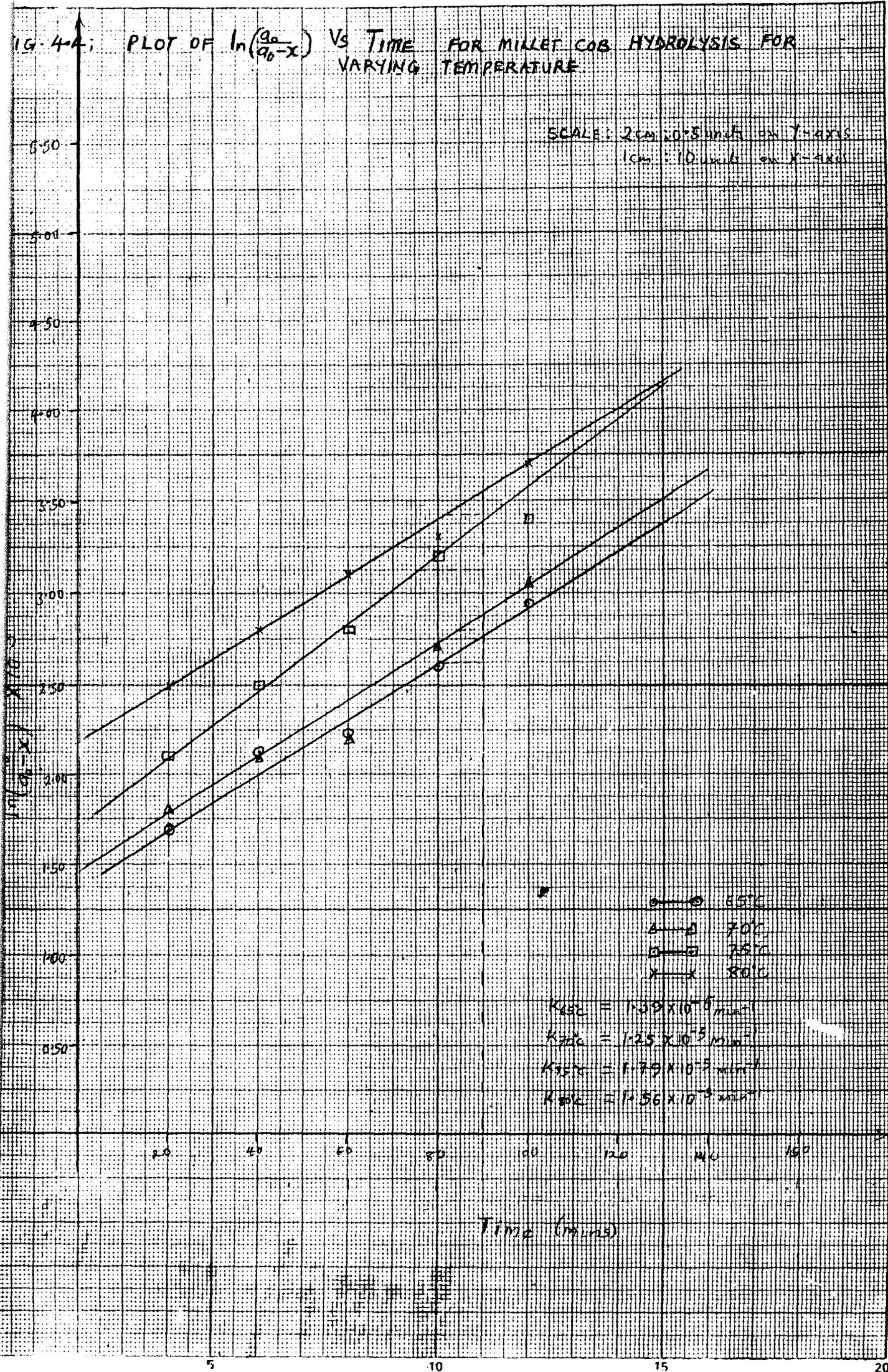


○ — ○ 5M  $H_2SO_4$   
 ▲ — ▲ 2.5M  $H_2SO_4$   
 □ — □ 3.5M  $H_2SO_4$

TIME (MINS) —————>

IG-4-A; PLOT OF  $\ln\left(\frac{q_0}{q_0-x}\right)$  VS TIME FOR MILLET COB HYDROLYSIS FOR VARYING TEMPERATURE.

SCALE: 2cm : 0.5 units on Y-axis  
1cm : 10 units on X-axis



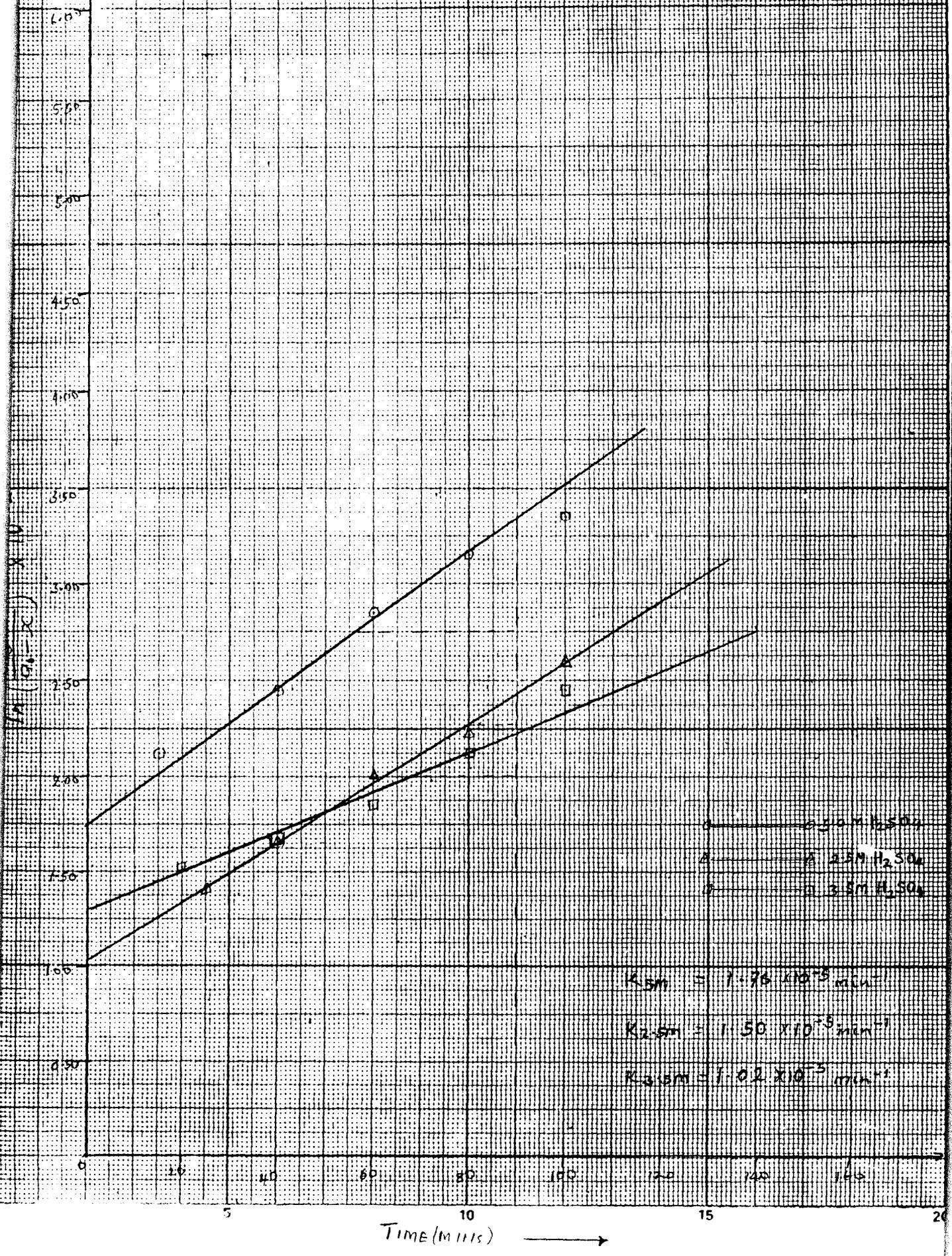
○—○ 65°C  
 △—△ 70°C  
 □—□ 75°C  
 ×—× 80°C

$k_{65°C} = 1.39 \times 10^{-5} \text{ min}^{-1}$   
 $k_{70°C} = 1.25 \times 10^{-5} \text{ min}^{-1}$   
 $k_{75°C} = 1.79 \times 10^{-5} \text{ min}^{-1}$   
 $k_{80°C} = 1.56 \times 10^{-5} \text{ min}^{-1}$

Time (mins)

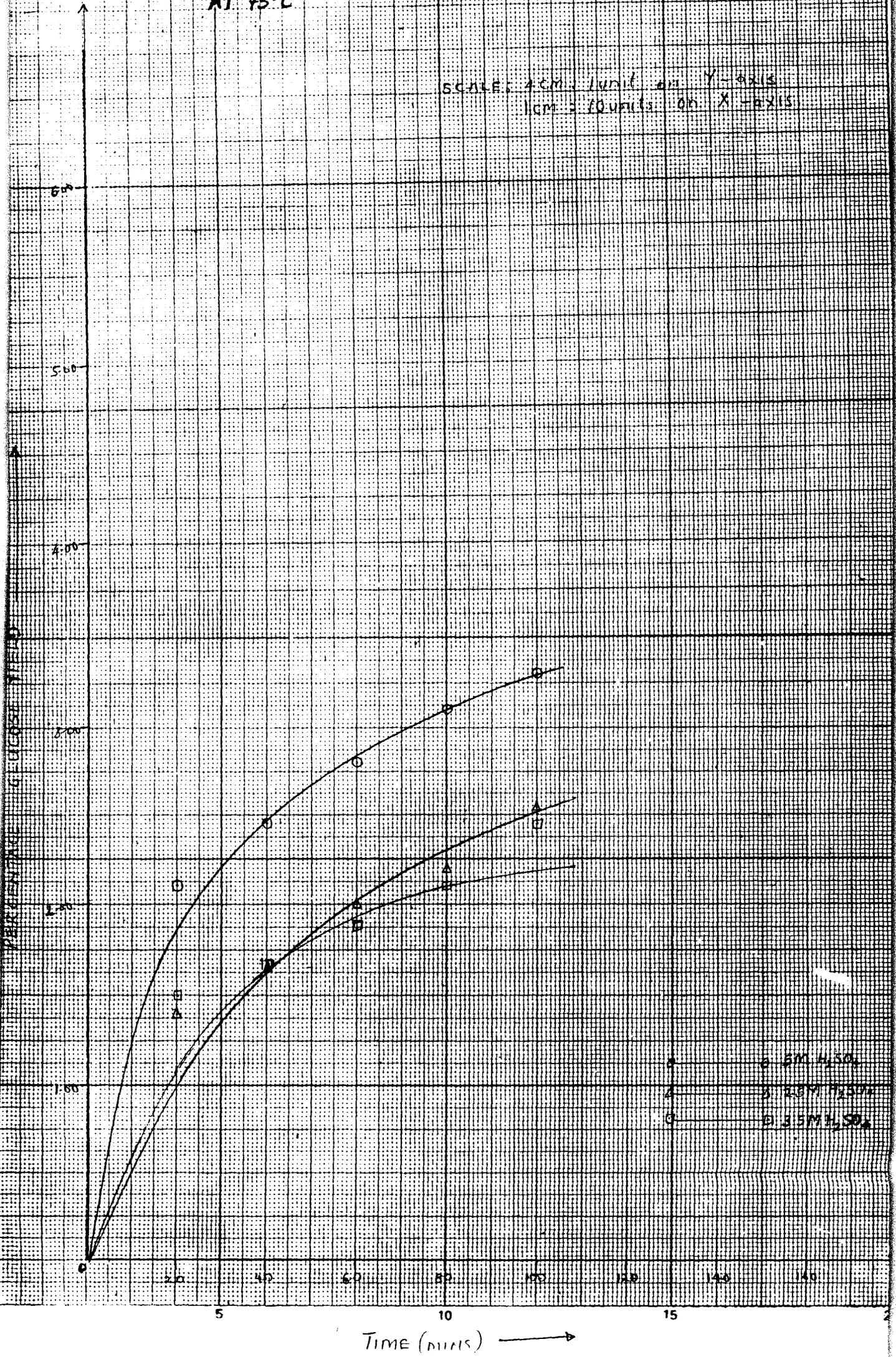
Q. 4.5, PLOT OF  $\ln\left(\frac{a_0}{a_0-x}\right)$  VS TIME FOR VARYING  $H_2SO_4$  CONCENTRATION AT  $75^\circ C$

SCALE: 2cm: 0.5 UNIT ON Y-AXIS  
1cm: 10 UNIT ON X-AXIS



19.4.6. PLOT OF PERCENTAGE GLUCOSE YIELD VS TIME FOR VARYING  $H_2SO_4$  CONCENTRATION AT  $75^\circ C$

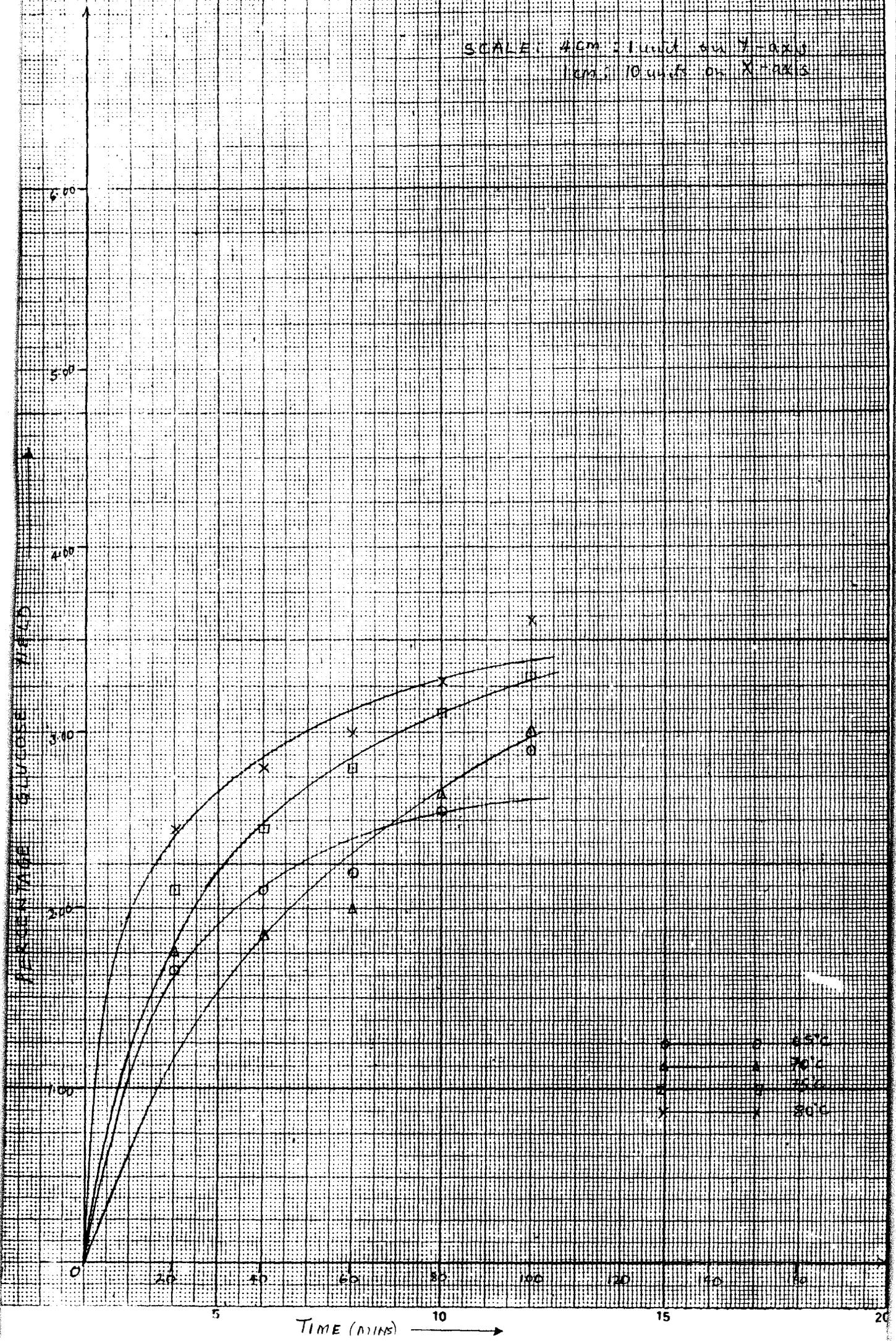
SCALE: 1cm. unit on Y-axis  
1cm = 10 units on X-axis



TIME (MINS) →

9.4-7; PLOT OF PERCENTAGE GLUCOSE YIELD VS TIME FOR VARYING TEMPERATURE

SCALE: 4cm : 1 unit on Y-axis  
1cm : 10 units on X-axis



g: 4.8;

GRAPH OF  $\ln k$  Vs  $\frac{1}{T}$

SCALE: 2cm: 0.1 unit on Y-axis  
 2cm: 0.02 unit on X-axis

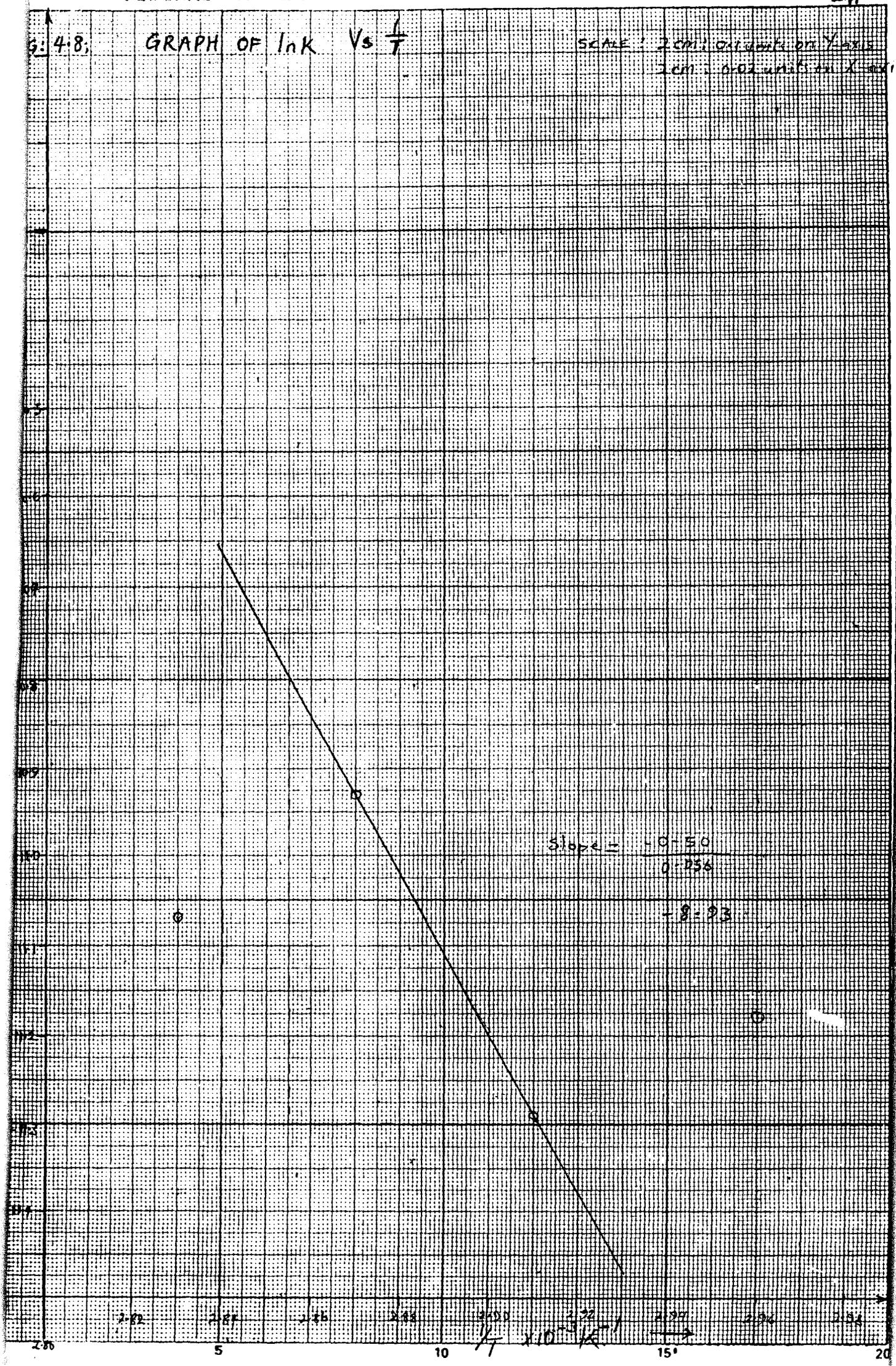
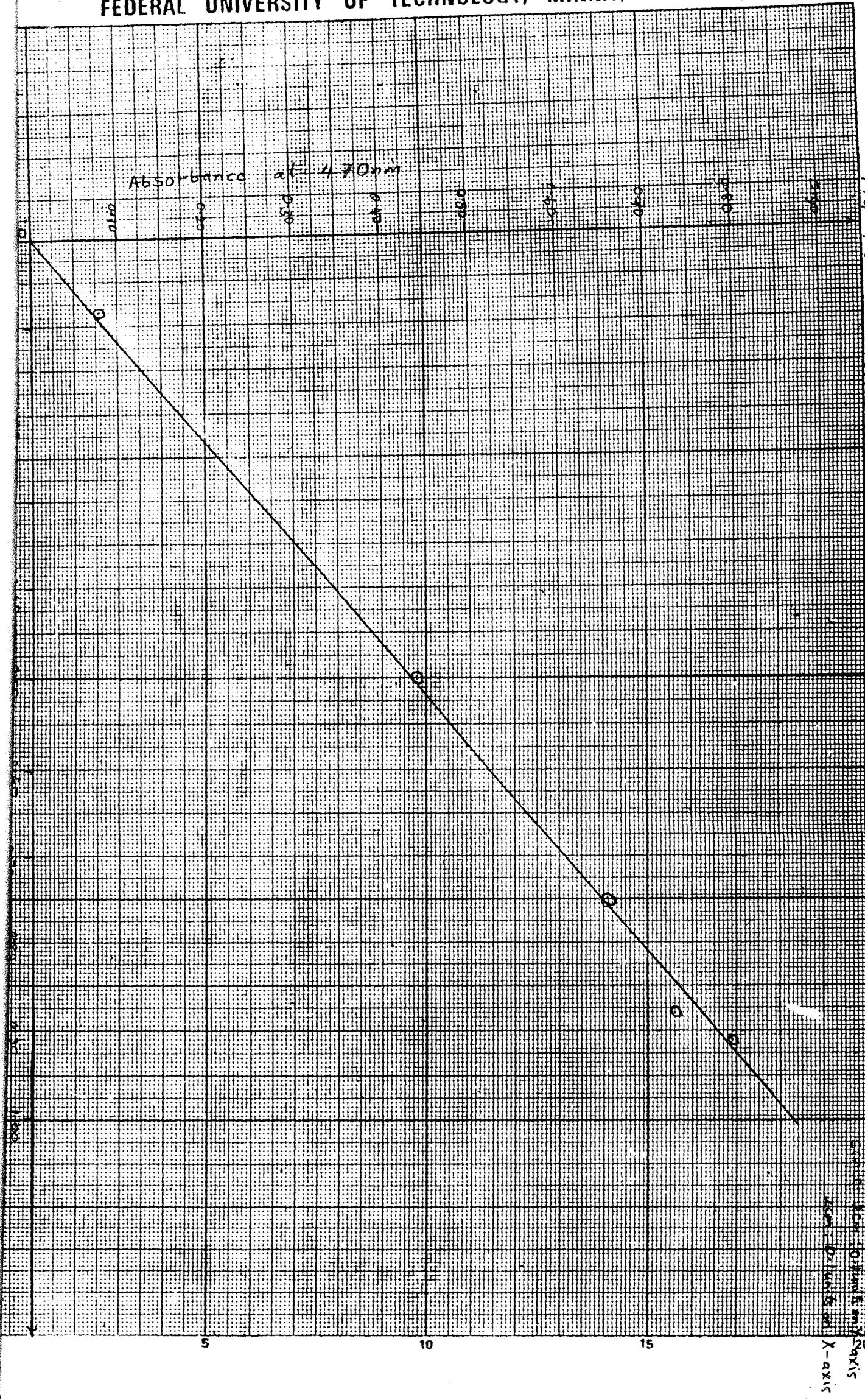


Fig. 4.1 CALIBRATION CURVE FOR D-GLUCOSE STANDARDS SOLUTION



Y-axis  
Absorbance at 470nm  
X-axis  
D-glucose concentration (mg/ml)

## CHAPTER FIVE

### 5.0 DESIGN PROJECT

#### 5.1 INTRODUCTION

Design being the most important and rewarding aspect of Chemical Engineering affords the opportunity of knowing the exact operation of a process. The quantity of materials needed and the amount of product obtainable, the suitable material for equipment construction process operating conditions, equipment specification, safety and the economy of the process can adequately be determined during design.

This work designs a process for the acid hydrolysis of cellulosic material (Millet cob) based on the results obtained experimentally.

Five basic equipment are involved in this process. They are

- i. Ball mill Pulverizer for size reduction
- ii. Leaching tank for extractive removal
- iii. Filter for filtration
- iv. Reactor - hydrolysis tank
- v. Counter current washer for product recovery.

The auxillary equipments required are:

- i. Centrifugal pumps
- ii. Storage tanks for holding water and Acid

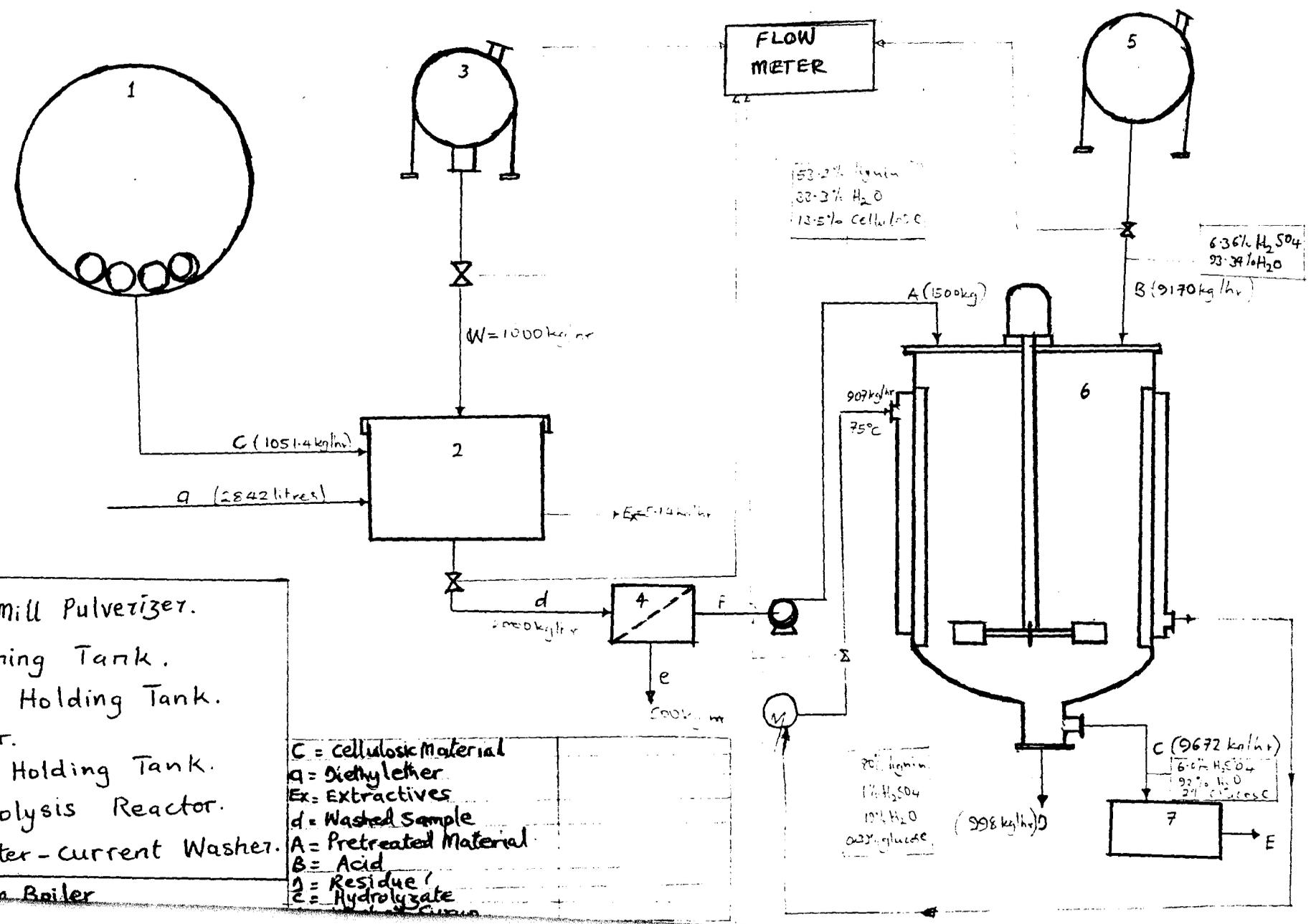
The detail design of the hydrolysis reactor was carried out.

A batch reactor is recommended for this process considering the pretreatment stages involved before the feed stock is passed into the reactor. The number of hours involved in the pretreatment could not have made the process proceed continuously.

A steam jacketed vessel is recommended considering the suspension of the particulate in the liquid medium.

#### 5.1.2 DESIGN PROBLEM STATEMENT

This work is to design a batch reactor with steam jacket to process 1000kg/hr of cellulose material using 5M sulphuric acid at a constant temperature of 75°C.



1. Ball Mill Pulverizer.
2. Leaching Tank.
3. Water Holding Tank.
4. Filter.
5. Acid Holding Tank.
6. Hydrolysis Reactor.
7. Counter-current Washer.
8. Steam Boiler

C = cellulosic material  
 a = Diethyl ether  
 Ex = Extractives  
 d = Washed Sample  
 A = Pretreated Material  
 B = Acid  
 g = Residue  
 e = Hydrolyzate  
 C = Hydrolyzate

15.2% lignin  
 32.3% H<sub>2</sub>O  
 13.5% Cellulose

6.36% H<sub>2</sub>SO<sub>4</sub>  
 93.39% H<sub>2</sub>O

20% lignin  
 1% H<sub>2</sub>SO<sub>4</sub>  
 10% H<sub>2</sub>O  
 69% glucose

6.0% H<sub>2</sub>SO<sub>4</sub>  
 92% H<sub>2</sub>O  
 2% Cellulose

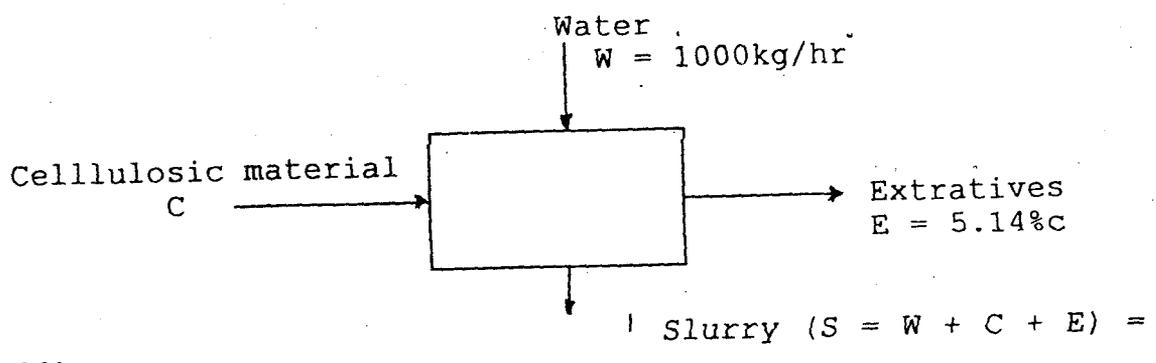
5.2 MATERIAL BALANCE

Basis: 1000kg/hr of cellulosic material to be hydrolyzed per batch.

Balance around the Leaching Tank.

All the solvent used for Leaching vapourized before washing with water.

5.14% of cellulosic material fed to the leaching tank is composed of extractives.



2000kg  
 $C + W = S + E$

$C = S + E - W = 2000 + 51.1 - 1000 = 1051.4 \text{ kg/hr}$

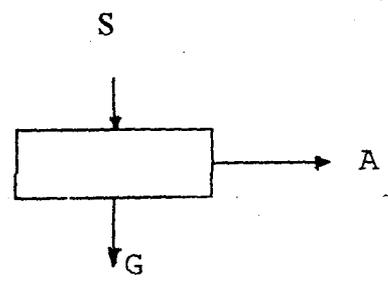
Volume of solvent used for Leaching.

100ml diethylether was used for pretreating 37g of sample i.e

for 1051.4kg  $\frac{0.1 \text{ lit} \times 1051.4 \text{ kg}}{0.037 \text{ kg}} = 2842 \text{ litres}$

Balance around the Filter

50% dewatering



$S = G + A \quad (G = 0.255)$

$A = S - 0.255$

$A = S(1 - 0.25) = S(0.75) = 2000(0.75) = 1500 \text{ kg}$

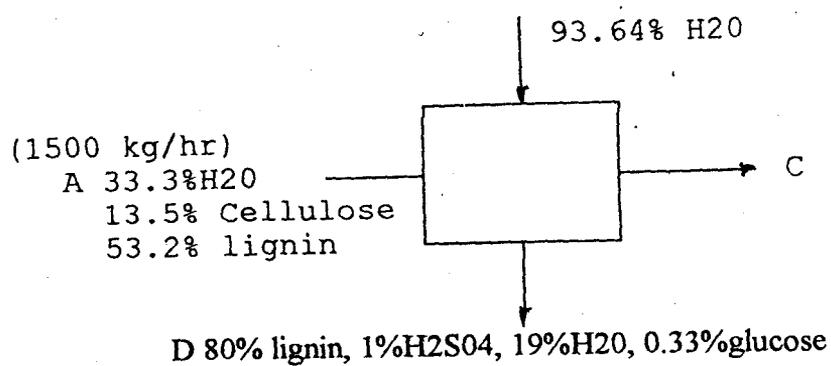
Balance Around the Hydrolysis Reactor.

50ml Acid hydrolysed 10g of cellulosic material

for 1000kg cellulosic material

$$\frac{0.05 \times 1000}{0.01} = 5000 \text{ litres (9170 kg/hr)}$$

(9170kg/hr) B 6.36% H<sub>2</sub>SO<sub>4</sub>



Overall Material balance

$$A + B = C + D$$

$$1500 + 9170 = C + D$$

$$10670 - D = C$$

Balance on lignin

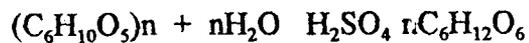
$$0.532 A = 0.8 D$$

$$D = \frac{0.532 \times 1500}{0.8} = 998 \text{ kg/hr}$$

$$C = 10670 - D$$

$$= 10670 - 998 = 9672 \text{ kg/hr}$$

from Reaction Stoichiometry



$$202.4 \text{ kg} \quad 24.42 \text{ kg} \quad 224.83 \text{ kg}$$

$$\text{i.e. } \frac{224.89}{1000} \times 100$$

$$1000 \quad 1 \quad = \quad 22.5\% \text{ glucose was produced}$$

Balance on acid

$$0.0636B = 0.001D + X_A C$$

$$X_A = \frac{(0.636 \times 9170) - (0.001 \times 998)}{9672} = 0.06$$

i.e 6.0%  $H_2SO_4$  is in stream C.

Balance on  $H_2O$

$$0.33A + 0.9364B = 0.19D + X_H C$$

$$X_H = \frac{(0.33 \times 1500) + (0.9364 \times 9170) - (0.19 \times 998)}{9672}$$

$$= 0.92$$

i.e 92%  $H_2O$  is in C

### 5.3 ENERGY BALANCE

Since there is no heat supplied to any other part of the process but the hydrolysis stage, energy balance is carried out only around the hydrolysis reactor.

Heat gain (loss) by a system =  $mcpdT$

$$Q_A = M_A C_p dT \quad M_A = 1500 \text{ kg} \quad C_p = \text{mean cp of A constituent} \quad dT = 25^\circ \text{C}$$

$$\text{i.e } Q_A = 1500[(0.135 \times 1340) + (0.532 \times 1465) + (0.333 \times 4180)]25 = 8.82 \times 10^7 \text{ KJ/hr.}$$

$$Q_B = 9170[(0.0636 \times 9449) + (0.9364 \times 4180)]25 = 9.03 \times 10^8 \text{ KJ/hr.}$$

$$Q_C = 9672[(0.06 \times 9449) + (0.92 \times 4180) + (0.02 \times 1151)]75 = 3.22 \times 10^9 \text{ KJ/hr.}$$

$$Q_D = 998[(0.01 \times 9449) + (0.8 \times 1464) + (0.19 \times 4180) + (3.3 \times 10^{-3} \times 1151)]75 = 1.55 \times 10^8 \text{ KJ/hr.}$$

$$Q_S = Q_D + Q_C - Q_A - Q_B = 3.38 \times 10^8 - 9.91 \times 10^8$$

$$= 2.39 \times 10^6 \text{ kJ/HR} = 663.9 \text{ kW}$$

Since the heat is supplied by steam

$$\text{Steam required} = \frac{\text{Quantity of Heat}}{\text{Latent Heat of Steam}}$$

$$\text{Latent heat of steam at } 75^{\circ}\text{C} = 2635\text{KJ/Kg}$$

$$\text{i.e steam required} = \frac{2.39 \times 10^6}{2635} = 907\text{kg/hr}$$

### REACTION TIME<sup>2</sup>

$$t = 1/K \text{ LNa}_0 / a_0 - x \text{ for 1st order reaction}$$

from experimental data;  $K = 1.79 \times 10^{-5}\text{min}^{-1}$

$$\text{In } a_0 / a_0 - x = 3.25 \times 10^{-2} \text{ (at } 75^{\circ}\text{C)}$$

$$\begin{aligned} \text{i.e } t &= \frac{1}{1.79} \times \frac{3.30 \times 10^{-3}}{10^{-5}} \\ &= 184\text{mins} = 3.06\text{hrs} \end{aligned}$$

### 5.4 EQUIPMENT SIZING

#### REACTOR VOLUME

$$\text{Weight of reactants} = 10670\text{kg}$$

$$\text{Average density of reactant} = 1114\text{kg}^{\text{m}^{-3}}$$

$$\text{From Density} = \text{Mass/Volume}$$

$$\text{Volume} = \text{Mass/Density} = 10670/1114 = 9.58\text{m}^3$$

Giving a 20% safety factor

$$\text{Reactor Volume} = 9.58 + 1.92 = 11.5\text{m}^3$$

For a cylindrical vessel with ellipsoidal base

$$V = \frac{11\pi D_T^3}{48} \quad D_T = \text{tank diameter}$$

$$\text{i.e } 11.5 = \frac{11\pi D_T^3}{48}$$

$$D_T^3 = 15.97$$

$$D_T = \sqrt[3]{15.97} = 2.52\text{m}$$

$$\text{Total Vessel height} = 1.3D_T = 3.28\text{m}$$

$$\text{Thickness of the baffle, J} = D_T/10 = 0.252\text{m}$$

$$\text{Height of baffle} = D_T = 2.52\text{m}$$

Height of impeller above tank base  $D_i = D_T/3 = 2.52\text{m}/3 = 0.84\text{m}$

Agitator Diameter  $D_a = D_T/3 = 2.52/3 = 0.84\text{m}$

Width of impeller blade  $W = D_a/5 = 0.84/5 = 0.168$

Length of impeller blade  $L_a = D_a/4 = 0.84/4 = 0.21\text{m}$

### 5.5 Agitator Power Consumption for Suspended Solid - Liquid Medium.

Using Buurman et al" correlation for differences in physical properties and solid concentration in agitated vessel, the agitator power consumption can be calculated.

Change in critical rotation speed  $n_c: (\Delta D_p)^{0.2} (\Delta \rho)^{0.45} (\Delta B)^{0.13}$

$D_p$  = particle size;  $\rho$  = particle density,  $B = \frac{100 \times \text{weight of solid}}{\text{weight of liquid}}$

$D_p$  of sand = 200cm;  $\rho = 1.59$  and  $B = 11.1$

$D_p$  of sample = 250cm;  $\rho = 0.81$  and  $B = 10.3$

$$\Delta n_c : \left(\frac{250}{200}\right)^{0.2} \left(\frac{0.81}{1.59}\right)^{0.45} \left(\frac{10.3}{11.1}\right)^{0.13} = 0.769$$

$$\Delta p_c = \Delta_c n^3 = (0.769)^3 = 0.455$$

From text  $P/V = 2.1\text{hp}/1000\text{gal}$  for sand

$$V = 3038\text{gal}; P/V = 2.1 \times 0.455 = 0.956 \text{ hp/gal for sample}$$

$$P = \frac{0.956 \times 3038}{1000} = 2.9\text{hp} \quad 2.18\text{Kw}$$

$$\text{Rotation Speed : } n^3 = P_{gc}/N_p D_a^5$$

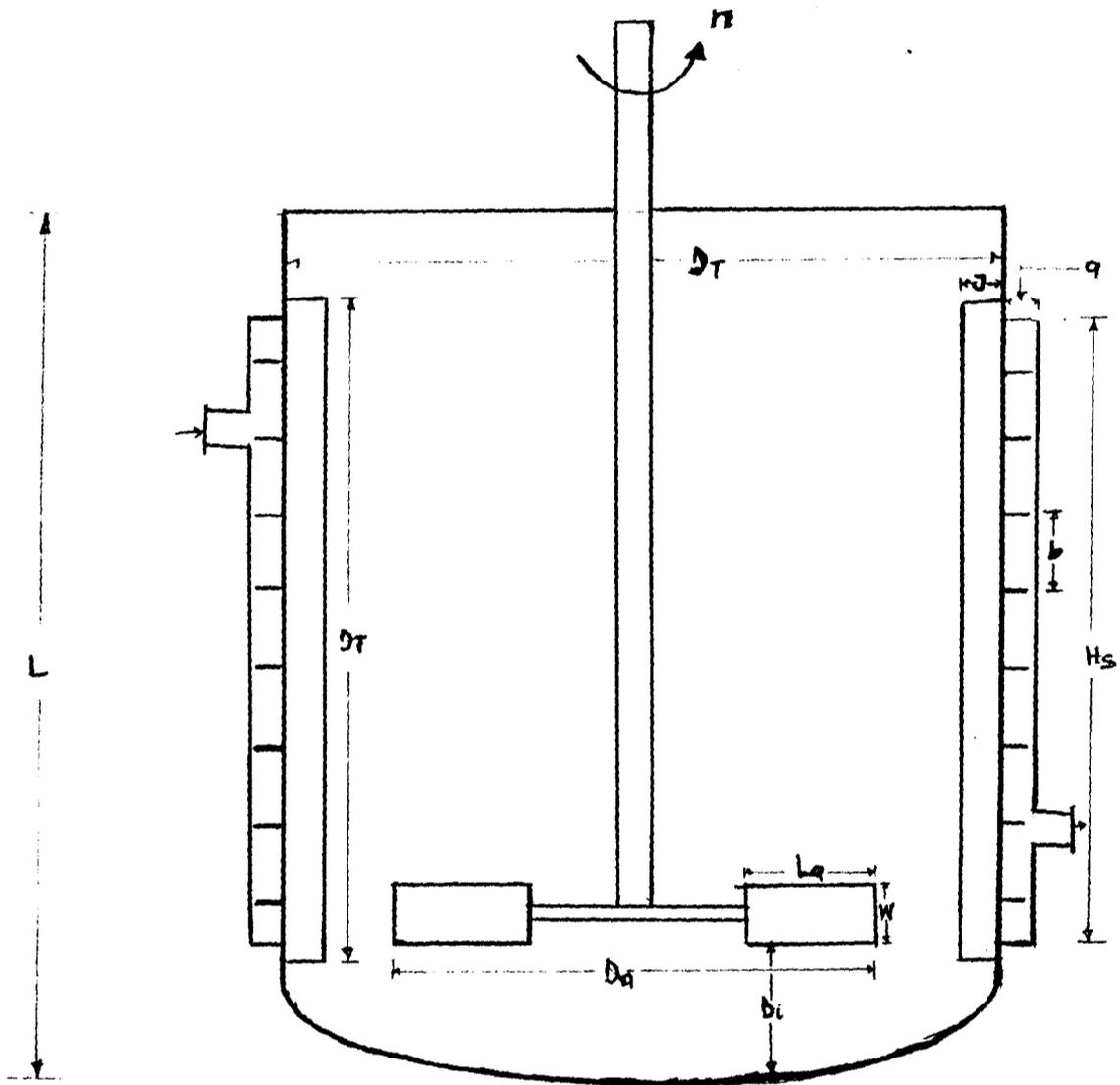
For four blade turbine impeller  $N_p = 1.27$

slurry density  $\rho_s =$

$$\frac{1}{\frac{0.094}{0.81} + \frac{0.056}{1.834} + 0.85} = 1.003\text{g/cm}^3 = 62.61\text{b/ft}^3$$

$$n^3 = \frac{2.9 \times 550 \times 32.17}{1.27 \times 62.6 \times (2.76)^5} = 4.03$$

5.2: SIZING OF HYDROLYSIS REACTOR



$D_T = 2.52m$   
 $J = 0.252m$   
 $L = 3.28m$   
 $D_i = 0.84m$   
 $D_a = 0.84m$   
 $W = 0.168m$   
 $L_a = 0.21m$

$H_s = 1.5m$   
 $q = 0.075m$   
 $b = 0.2m$   
 $n = 1.59 rps$

$$n = 3\sqrt{4.03} = 1.59 \text{ rps}$$

$$n = 1.59 \text{ rps}$$

## 5.6 HEAT EXCHANGE

$$N_{Re} = \frac{\rho ND^2}{\mu} = \frac{1114 \times 1.59 \times (0.84)^2}{1.49 \times 10^{-3}} = 838792.71$$

$$N_{Pr} = \frac{C_p \rho}{k} = \frac{6854.8 \times 1.49 \times 10^3}{0.56} = 18.24$$

$$\text{Nusselt (Nu)} = 1.10 \text{Re}^{0.62} \text{Pr}^{0.33} \left(\frac{\mu}{\mu_w}\right)^{0.14} \text{ for } N_{Re} >$$

Neglecting viscosity correction term

$$\text{Nu} = 1.10(838792.7)^{0.62} (18.24)^{0.33} = 13495.74$$

$$\text{Nu} = \frac{h_v D}{k_f} = 13495.74$$

$$h_v = \frac{k_f \times \text{Nu}}{D} = \frac{0.668 \times 13495.74}{0.84} = 10732.33 \text{ w m}^{-2} \text{ } ^\circ\text{C}^{-1}$$

$$1/U = 1/h_j + 1/h_v + \frac{\text{vessel thickness}}{k \text{ of vessel material}}$$

$$h_j = 3815 \text{ w m}^{-2} \text{ } ^\circ\text{C}^{-1}; \text{ vessel thickness} = 10 \text{ mm}$$

$$k \text{ of vessel material (stainless steel)} = 16 \text{ w m}^{-2} \text{ } ^\circ\text{C}^{-1}$$

$$\text{i.e. } \frac{1}{U} = \frac{1}{30815} + \frac{1}{107320.33} + \frac{1.0 \times 10^{-3}}{16} = 9.80 \times 10^{-4}$$

$$U = 1/80 \times 10^{-4} = 1020 \text{ w m}^{-2} \text{ } ^\circ\text{C}^{-1}$$

Steam jacket is fitted to cylindrical section of the vessel only and it is 1.5m high.

Space between jacket and vessel wall is 0.075

$$\text{Pitch between spirals in jacket} = (\text{height of jacket})/\text{pitch}$$

$$= 1.5/0.2 = 7.5 =$$

$$\text{Length of channel} = 8 \times \pi \times 2.52 = 63.3 \text{ m}$$

$$\text{Cross section area of the channel} = 0.075 \times 0.2 = 1.5 \times 10^{-2} \text{ m}^2$$

Hydraulic mean diameter =  $\frac{4 \times \text{cross sectional Area}}{\text{Wetted perimeter}}$

$$= \frac{4(0.075 \times 0.2)}{2(0.075 \times 0.2)} = 2M$$

$$\text{velocity through channel, it} = \frac{907}{3600} \times \frac{1}{973.7} \times \frac{1}{1.5 \times 10^{-2}}$$

$$= 0.017 \text{m/s}$$

## 5.7 PIPING AND PUMPING

For stream A, carbon steel pipe could be used since the fluid passing through it is not corrosive. For carbon steel pipe:

$$\text{Pipe diameter } dp = 293 G^{0.53} \rho^{-0.37}$$

$$G \text{ mass flowrate of stream A} = 1500 \text{kg/hr} ; \rho = \text{density (kgm}^{-3}\text{)}$$

$$\text{i.e } dp = \frac{293 \times (1500)^{0.53} (678.74)^{-0.37}}{3600} = 16.51 \text{mm}$$

Since stream B contains Acid, stainless steel pipe is suitable pipe diameter for stainless steel

$$dp = 260 G^{0.53} \rho^{-0.37}$$

$$\text{i.e } dp = \frac{260 \times (9170)^{0.52} (1053)^{-0.37}}{3600} = 32.2 \text{mm}$$

For stream C; using stainless steel pipe:

$$\text{Pipe diameter } dp = \frac{260 \times (9672)^{0.52} (1061)^{-0.37}}{3600} = 33.0 \text{mm}$$

## 5.8 PUMP POWER REQUIREMENT

Centrifugal pump is recommended for transporting the fluids. The pumps power requirements  $P_B$ , is calculated thus:

$$P_B = \frac{m \Delta H}{N} ; \quad m = \text{mass of flow rate in kg per s} \\ \Delta H = \text{change in head; } N = \text{Pump efficiency}$$

For stream A;  $m = 1500 \text{kg/hr}$ ;  $\Delta H = 10 \text{m}$ ,  $N = 85\%$

$$P_B = \frac{1500}{3600} \times \frac{10}{0.85} = 4.9 \text{kw}$$

For stream C;  $m = 9672 \text{kg/hr}$ ;  $\Delta H = 3.5 \text{m}$ ,  $N = 85\%$

$$P_B = \frac{9672}{3600} \times \frac{3.5}{0.85} = 11.1 \text{kw}$$

## 5.9 MATERIAL OF CONSTRUCTION<sup>12</sup>

Generally, numerous materials are available for fabrication of chemical process equipments. The suitability of these materials depend on their properties and the properties of the materials they will be in contact with coupled with the areas of application.

For this process in which acidic medium and high temperatures are involved, stainless steel is chosen as the construction material; the stainless steel being able to resist acidic corrosion.

To impact this corrosion resistance, stainless steel of chromium content above 12% should be used. The higher the chromium content the more resistant the alloy is to corrosion in oxidising conditions. Addition of Nickel improves the corrosion resistance in non-oxidising environments.

The particular type of stainless steel recommended is the Austenitic 304 type. This has a composition of 18 - 20% chromium and less than 7% Nickel. It is also known as 18/8 stainless steel.

**Mechanical Properties:** Austenitic stainless steels have greater strength than plain carbon steels, particularly at high temperatures. At 300°C and 600°C, the design stress are 108 and 62N/mm<sup>2</sup> respectively as compared to 77N/mm<sup>2</sup> and zero of mildsteel. Thermal conductivity of (304) 18/8 stainless steel is 16w/m°C.

## 5.10 SAFETY CONSIDERATION<sup>12</sup>

To ensure the safety of the acid hydrolysis process, the optimum temperature for the process is kept constant. This is achieved by supplying steam at constant temperature and at a steady flow. This will avert the possibility of side reactions which could be hazardous.

The valves controlling the flow of fluids are ensured to be in good working condition to avoid leakages.

Acid holding tanks and piping are constructed of stainless steel to prevent corrosion.

## 5.11 COST ANALYSIS OF THE REACTOR<sup>12</sup>

### Variable Costs

#### 1. Raw materials

9170kg 6.36% H <sub>2</sub> SO <sub>4</sub> at N650.70 per ton	N5,967.00
500kg of Demineralised water at N20.25 per ton	N10.13
907kg of steam at N810 per ton	N734.67
65.45MJ/batch Electricity at N1.62 per MJ	N106.03

SHIPPING OF RAW MATERIALS @ N1000/ton N5000.00

### FIXED COSTS

Reactor (Jacketed)	N2,868,817.13
Agitator (Turbine)	N70,871.15
Pumps (Centrifugal)	N620,297.11
Fixed Capital	N3559985.40
Maintenance 5% of fixed capital	N177999.27
Insurance 1% of fixed capital	N35599.854
Local taxes 2% of fixed capital	N71199.854
Royalties 1% of fixed capital	N35599.854
<b>Total Fixed costs</b>	<b>N3880384.1</b>

Sales expenses and general overhead 20%

direct production cost = N71436.07

Production cost by batch = N71436.07 + N3559985.40 + N11817.83

= N3643239.3

Production cost per kg =  $\frac{N3643239.30}{12 \times 0.02 \times 9672}$

= N1569.50

## 5.12 PROJECT EVALUATION <sup>12</sup>

But for the cost of reactor fabrication, all other cost associated with this design is economically viable. The cost of the reactor can be minimized by locally fabricating it which will reduce the effect of exchange rate. With this the process will be profitable going by the present demand for glucose which will continuously have a high market demand and reduce cost of importation of glucose in Nigeria.

## CHAPTER SIX

### 6.1 DISCUSSION OF RESULTS

The glucose concentration obtained after hydrolyzing with 5M sulphuric acid at temperatures of 65°C, 70°C and 80°C was found to increase with rising temperature. This is visible from Fig . The glucose concentrations at temperatures 65°C and 70°C were very close with an average difference of about  $0.1 \times 10^{-4}$ g/ml.

At 75°C, the glucose concentration was further increased with better yield as compared to those obtained at lower temperatures. This high glucose concentration was as well noticed at 80°C.

Fig 4.7 also shows that there is an increase in glucose yield at higher temperatures. This suggests that at lower temperature below 75°C the increase in glucose yield is very negligible. But at temperature above 75°C the increase in yield is very pronounced. That is, very high yield could be achieved at very high temperature if there will be no alteration in the reaction pathway which could lead to decomposition of the product.

A first order kinetics can be used to describe the acid hydrolysis reaction as evident from the temperatures investigated.

The reaction rate constants estimated from fig. Are  $K_{65^{\circ}\text{C}} = 1.39 \times 10^{-5} \text{ min}^{-1}$ ;  $K_{70^{\circ}\text{C}} = 1.25 \times 10^{-5} \text{ min}^{-1}$ ;  $K_{75^{\circ}\text{C}} = 1.79 \times 10^{-5} \text{ min}^{-1}$ ;  $K_{80^{\circ}\text{C}} = 1.56 \times 10^{-5} \text{ min}^{-1}$ .

The dependence of reaction rate on temperature was evaluated using Arrhenius law  
i.e  $\ln K = \ln k_0 + \frac{(-E_a)}{(RT)}$

The plot of the natural logarithm of the reaction rate constants against the inverse of temperatures yielded a straight line from the Arrhenius plot, the activation energy of the reaction was found to be 74.25kJ/gmol. This was arrived at by determining the slope of the plot. Though the activation energy was higher than that reported at 60°C(25.7KJ/gmol) for saw dust, it was very close to that obtained (72.3KJ/gmol) using maize cobs.

The plot of percentage glucose yield against time for varying acid concentration Fig. Indicates higher yields at 5M acid concentration. At 2.5M and 3.5M acid concentration the yields were very close but lower than that at 5M acid concentration. For this work, the optimum acid concentration was 5M. At much higher concentration, side reactions and products degradation may be expected.

In the design of the reactor for hydrolysis a vessel of 11.5m<sup>3</sup> capacity is needed to produce 193.4kg glucose. Steam of 907kg/hr is needed for the process. Jacketed, agitated vessel is designed for the hydrolysis process considering the nature of the reacting medium (suspending solid - liquid medium).

The power requirement of the agitator is 2.18kw with a rotation speed of 1-59 rps.

The number of auxiliary equipment needed in the process is minimized to reduce cost.

Five major stages are involved in the process. These include

- i Size reduction with a Ball mill pulverizer
- ii Pretreatment in a leaching tank to ease hydrolysis
- iii Filtration
- iv Acid hydrolysis reactor
- v The counter-current washer for product recovery.

Stainless steel is recommended as the material of construction to prevent corrosion and leakages which are part of the safety measures involved in the process.

The costing of the reactor reveals that about ₦1569.50 will be needed to produce a kilogram of the product. This may not be the actual cost of production since the costing is over the reactor only and not the whole plant.

Considering the relative abundance of the main raw material (cellulosic material) the process will surely be cost effective.

## 6.2 CONCLUSION AND RECOMMENDATION

It is evident from this research work that a reasonable quantity of D-glucose is contained in millet cobs which is an agricultural waste product, combined with other agricultural waste material, glucose can be produced on a commercial scale.

The yield of the process is found to be a function of the acid concentration and the operating temperatures. At higher acid concentration and temperature higher yield is expected though a shift in reaction course which may lead to product degradation is probable.

A first - order kinetic is discovered for the hydrolysis reaction of millet cobs as experienced with other cellulosic material.

The economical analysis of the reactor after design proves this process to be economically viable. Millet cobs combined with ether cellulosic materials can be hydrolysed on a large commercial scale for glucose production.

It is being recommended that works on this area should be extended to product recovery and attempts could be made on designing other parts of the process involved in the hydrolysis.

## REFERENCES

1. Comprehensive Biotechnology Murray Moo - Young Vol 3 (869 - 873)
2. Encyclopedia of Science and Technology M. C. Grawhill 2 (749)
3. Advances in Enzymatic hydrolysis of cellulose and related materials; Mandela Marry and Resse E. T.
4. Structure, Pretreatment and Hydrolysis of cellulose and lignocellulose materials, Chang M. M., Chou T. V. And Tsao G. T. 1981.
5. Cellulose as a novel energy source in advances in Biochemical Engineering Vol. 2 Resse E. T. *et al*
6. Kinetics of Acid Hydrolysis of saw dust for Glucose production. Oyeyemi O. S. Thesis F. U. T. Minna (1997).
7. Principle of Biochemistry Abraham White *et al* sixth edition.
8. The Recycling and Disposal of solid waste; Micheal E. Henstock (15 - 45)
9. Chemistry of Explosive Vol. 2 T. Urban Ski (215 - 231)
10. An Introduction to Fungal Biotechnology, Wainwright (10 - 11)
11. Unit Operations in Chemical Engineering; McCabe and Smith ; *McGraw - Hill*
12. Chemical Engineering Vol. 6. Richardson and Coulson. Second Edition
13. Chemical Engineering Handbook; Perry and Green
14. Treatment process to increase cellulose microbial Digestibility, AICHE symposium series New York No. 158, 72 Dunlo C. E.; Thomason J and Chiang L. C. (1976)
15. Practical Acid Hydrolysis of poplar wood as a pretreatment for enzymatic Hydrolysis. Biotechnology and Bioengineering symposium series. New York II(1981) Knappert D, Grethlein and Converse A.
16. A photometric Adaptation of the Somogyi - Nelson method for determination of glucose, Journal of Biological Chemistry Baltimore 153.
17. Preliminary studies on the Biochemical conversion of saw dust to alcohol via Glucose. Proceeding of Nigeria society of chemical Engineers, Tenth annual conference. Loyukun S. K.
18. Mixing - Biochemical Industries; J. R. Butters (25 - 34)

## APPENDIX

### 1. DETERMINATION OF CELLULOSE CONTENT IN 10 GRAMS OF MILLET COBS.

Millet cobs contain 20.24% cellulose

10g of sample contains 2.024g of cellulose

1g contains  $2.024/10 = 0.2024\text{g}$

0.2024g of cellulose dissolved in 20ml  $\text{H}_2\text{SO}_4$  will give a glucose concentration of

0.2024

$$20 = 0.01\text{g/ml}$$

Initial glucose concentration  $a_0 = 0.01\text{g/ml}$

For a first order reaction

$$Kt = \ln \left( \frac{a_0}{a_0 - x} \right)$$

$x =$  Concentration of D-glucose from hydrolysis of millet cob

$k =$  reaction rate constant

$t =$  time

e.g for  $x = 0.330 \times 10^{-4}\text{g/ml}$

$$\ln \left( \frac{a_0}{a_0 - x} \right) = \frac{0.01}{(0.01 - 0.330 \times 10^{-4})}$$

$$= 3.30 \times 10^{-3}$$

### 2. DETERMINATION OF ACTIVATION ENERGY OF THE HYDROLYSIS REACTION OF MILLET COB SAMPLE

This can be determined by plotting  $\log k$  against  $1/T$  using Arrhenius law

$$\ln k = \ln k_0 - (E/RT)$$

Slope =  $-E/R$  ;  $R =$  Gas constant

From the graph

$$\text{Slope} = -7.2 \times 10^3$$

$$\text{i.e } -E = -8.23 \times 10^3 \times \frac{8.3143}{1000}$$

$$= -74.25\text{KJ/gmol}$$

$$E = 74.25\text{KJ/gmol}$$

### 3. THE SOMOGLY - NELSON PROCEDURE FOR QUANTITATIVE DETERMINATION OF REDUCING SUGARS

In the Somogyl-Nelson procedure (Somogyl 1945; Nelson 1944) for quantitative determination of reducing sugars, the basic chemical principle is the ability of reducing saccharides to reduce copper(II) ion to copper (I) ion in alkaline medium. The heating of sugar with a free keto or aldehyde group in an alkaline solution will result to the break down of sugar into a number of small molecules with reducing properties.

This alteration thus increases the reducing ability of the sugars. The copper (II) ion is reduced to red-coloured cuprous oxide. The cuprous oxide is in turn used to reduce molybdate reagent to a blue coloured compound. Colorimeter is then used to measure the color intensity and therefore the extent of reaction.

### 4. REAGENT PREPARATION

#### 1. Low Ability of Copper reagent

Twelve grams of Rochelle salt/potassium sodium Tartrate and twenty four grams of anhydrous sodium carbonate were dissolved in 250ml distilled water.

Sixteen grams of sodium hydrogen carbonate was added to the solution. A solution of 144grams anhydrous sodium sulphate in 500ml water was boiled to expel air. The two solutions were combined and made up to 800ml. This was labelled solution 'A'.

A solution of 4grams of cupric sulphate pentahydrate in 400ml water was prepared. A solution of 36grams anhydrous sodium sulphate in 150ml of water was boiled to expel air. The two solutions were mixed and made up to 200ml. This was labelled 'B'.

The two solution ('A' and 'B') were allowed to stand for one week and a supernatant of solutions A and B were used in ration 4:1.

#### 2. Aysenomolybdate Reagent

Twenty one ml of 98% sulphuric acid was added to 25grams of ammonium molybdate in 450ml of water.

This was followed by 3grams of disodium hydrogen aysenate heptahydrate ( $\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$ ) dissolved in 25ml of water.

The resulting solutions were mixed for 24 hours at 37°C and stored in a glass stoppered brown bottle.

## PHYSICAL PROPERTIES OF MATERIALS

Materials	Specific Gravity	Cp(J/kgk)	Thermal Conductivities (w/m°C)
H <sub>2</sub> SO <sub>4</sub>	1.834	9449	0.014
Lignin	0.32	1465.4	
Cellulose	1.3-1.4	1339.8	0.19
Glucose	1.544	1151.4	
H <sub>2</sub> O	1.0	4180	0.624