PROCESS DEVELOPMENT AND EQUIPMENT DESIGN FOR DEXTRIN MANUFACTURE FROM STARCH

A THESIS

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CERTIFICATION

This thesis entitled "Process Development and Equipment Design for dextrin Manufacture form starch" by AGBH, E. A., meets the regulations governing the award of the degree of Master of Science in Chemical Engineering of the Ahmadu Bello University Zaria, and is approved for its contribution to the knowledge of literacy presentation.

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DECLARATION

I hereby declare that this thesis has been composed by myself and that it is a record of my own research work. It has not been accepted in any previous application for a higher degree.

All sources of information are specifically acknowledged by means of references.

AGEH, E. A.

DEDICATION

TO

The body of Christ, all who earnestly await the second advent of the Lord and Master JESUS CHRIST.

ACKNOWLEDGEMENT

I wish to express my sincere thanks to my supervisors, Prof. R.O. Ebewele and Dr. J.O. Oludipe for their stimulating guidance and constructive criticism throughout the various stages of the project.

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To Bukola my fiancee I say THANK YOU for the support, patience and love. Darling, I do not know how I found you but the Lord is good. You are a great blessing to me.

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AGEH, E.A.

ABSTRACT

In a bid to develop local substitute for imported adhesives, seeing that the local consumption is high, an attempt was made to study the process of dextrin manufacture from starch and to design a converter vessel (Dextrinator) for the process.

An experimental study was carried out to examine the effect of the various process variables on the product auality. White dextrin was prepared from cassava starch by adding 2M HC1 as catalyst to 200g of the starch at a conversion temperature of 120c. For a conversion period of 5 hours, the product had cold water solubility of 90%, high fluidity and is useful as a paper adhesive.

A model for the dextrinization process was developed. From the model, the temperature of the starch material in the dextrinator is related to the temperature of the heating fluid (oil) by the equation;

The oil temperature varies with time according to the equation

$$T_o = \frac{W - W'}{H_b} t + T_i$$

From this two equation a nomograph was obtained from which the prediction of the eventual temperature of the heating oil could be made for a specified operating temperature (temperature of starch material).

At steady state the equation governing the system is given by;

$$\frac{W}{m_s} t = X_a C_{pa}(T_v - T_o) + (X_a - X_b) L$$

Kinetic model test revealed that the process can be considered as a first order reaction.

The design and fabrication of a dextrinator capable of processing 4kg of starch into dextrin was carried out.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

TABLES

FIGURES

PLATES

LIST OF SYMBOLS AND ABBREVIATIONS

Symbol/Abbreviation	Description	Unit
C	Concentration	g/mol
C_p	Specific heat capacity	J/kg/K
H	Heat Capacity	J/kg
h	Height	m
k_1, k_2, K	rate constants	
L	Latent heat of vapourization	J/kg
m	Mass	kg
MS	Mild steel	
Q	Quantity of heat	J
r	Radius	m
S	Surface area	m^2
T	Temperature	^oC
t	time	sec
V	Volume	m^3
W	Watt	J/sec
X	Conversion, moisture content	
x	thickness	
ϕ	diameter	
ρ	density	
Δ	timed change	

Subscripts

o - oil
j - jacket
j - jacket
c - catalyst
s - starch
R - reactor
d - dextrinator
v - reactor vessel
m - moisture

a - initial condition
b - final condition
s - starch
R - reactor

CHAPTER ONE

INTRODUCTION

1.1 Dextrin

The term dextrin has been used to describe a large number of starch products. Generally speaking it covers the range of compounds produced when starch is subjected to heat treatment, alone or in the presence of catalysts. "Pyro"dexrins is a better name and more exact description[1]. This process, though sometimes considered among the many methods of chemical modification of starch, is more of a thermal modification process which from an experimental point of view, is relatively less harmful.

Dry roasting causes both depolymerization and condensation of starch fragments. The result is more highly branched molecules with greater solution stability than the parent starch. Dextrin are commonly placed in three categories; White dextrin, Yellow/Canary dextrin and British gums.

Dextrins are the outstanding starch derivatives made for adhesive purposes. The capacity to formulate adhesives of higher solid level generally accounts for the greater use of dextrin over starches. Dextrin give faster tack development, more rapid drying and increased production rates[5].

1.2 Economics

Adhesives are essential components needed to make hundreds of products, among them aircraft, automobiles, corrugated cartons, plywood, envelopes, stamps, pressure-sensitive and remoistenable tapes, laminates, labels, abrasive wheels, shoes, tires, and non -woven fabrics. As at 1960, statistics of the United States consumption of Adhesives reveals that starch and dextrin are the largest-volume adhesives having 26.8% of the total volume consumed.[3] In the present day Starch/Dextrin based adhesives are still very much in use principally for bonding of paper products. Poly(vinyl acetate) and other synthetic adhesives bases, which give superior bond occurring, tack or other properties, are growing competitors for the paper bonding market. The availability and low cost of the natural products makes them highly competitive.

1.3 Project Aim

The main objective of this work is to study the dextrinization process, develop, design and fabricate a reaction vessel (Dextrinator) for the conversion of starch to dextrin. Much work has been carried out on equipment design for dextrinization of starch; most of these are patented and designed for specific product requirements. Moreover, the procedures or processes employed are proprietary in nature and not free from patent restrictions. Rowe and Hagen[5] Patented an improved steam jacketed cooker containing a vertical agitator, Philip[7] developed a continuous process of conversion in which a moving belt carries a thin layer of acidified starch. In the patented process of Starkle and Meier[8], starch is dextrinized in a non-oxidizing environment to avoid discoloration. Fredrickson[9] recommends converting starch to dextrin in a fluidized bed. However, the design and construction of a jacketed oil heated agitated dextrinizer is carried out in this work. Rate study would be carried out on a laboratory scale to establish the optimum operating conditions and the system advanced to pilot scale.

1.4 Project Rationale and Significance.

The rapid growth of the adhesive industry has resulted from its many advantages over other methods of joining materials. Adhesives are pervasive in our industrial society, indispensable in the clothes we wear, shoes, our books, in the office, our homes, etc. Adhesives are being consumed by the packaging industries for corrugated cardboard manufacture, carton sealing, bottle labelling, metal can sealing, envelope, paper cup and the non-packaging industries such as construction, textile, automotive, electrical, etc.

Local consumption of adhesives in the country has risen tremendously as revealed by figures obtained from a survey on the subject. Investigation reveals that a greater percentage of the demand is met by importation. For instance, the Nigerian Breweries Limited (NBL) alone imports over 200 tonnes of adhesive for bottle labelling, the cost of which is above ₦48.3 million naira. (1995 figures)

A survey carried out in 1994/95[10] records a value of 445 tonnes as the total adhesive consumption for the period and the analysis covered only a few states in the country. The 1991 records from the office of statistics[11] (ref. Appendix A1) show that in that year alone the country imported 2,254 tonnes of dextrin and starch-based adhesives at a cost of ₦29,407,653.

From the foregoing, and given the current economic recession that has plagued the nation, there's a dire need for local development of adhesives as potential substitute for imported adhesives in the various industries. This would cut down greatly the foreign exchange expended on importation of these materials. The local industries should adopt policies that will enhance import substitution and local sourcing of raw materials. It is imperative to explore avenues by which our abundant natural and human resources can be harnessed and developed for technological self reliance. It is in line with this objective that this project was motivated.

1.5 Benefits and Economic Implications

Various challenging technological lessons can be derived from this project, and more importantly, a lot of foreign exchange savings and earnings are envisaged on completion of project as it is hoped to produce an equipment that will service the current requirement in our local industry. The market potential of dextrin or of dextrin based adhesives in Nigeria is great and the raw material sourcing is cheap, the process is relatively inexpensive and the equipment for the manufacture can be fabricated locally. Thus the profitability in engaging in its manufacture is enormous.

CHAPTER TWO

LITERATURE REVIEW

2.1 Starch

Starch is one of the most widely distributed substances in nature, occurring in most plants. It is formed in the leaves and green parts of the plant from atmospheric water and carbon dioxide, through the agency of chlorophyll and sunlight. During the hours of darkness, the starch is broken down into sugars which are transported by means of the cell juice to other parts of the plant. Some of the sugars are reconverted into starch and it is by this means that starch is built up in the fruits, bulb and tubers of the various plants. It is from these sources of concentrated material that the commercial starch is obtained by a variety of methods used to separate the starch from the protein and fibers which are also present[1].

Pure isolated starch is a white, amorphous, relatively tasteless solid which possesses no odor and which is insoluble in cold water. Under the microscope starch is seen to consist of tiny spherule or granules, the size and shape of which are specific for each variety of starch. Starch granules are made up of amylose and amylopectin. Amylose is a linear glucose polymer and amylopectin is a branched glucose polymer.

Starch as a raw material is abundant, cheap, renewable and very pure. Its use in making derivatives with characteristics similar to those of water-soluble natural products (like saccharose, animal glue and natural gums) has been considered seriously for over two centuries. Since the discovery of starch sugars by Kirchoff in 1811 and the practical applications of the so-called dextrins in 1821, a starch industry has developed all over the world where each country processes its locally produced starches[2].

2.1.1 Starch Modification

Although very large amounts of unmodified starches are used, the biggest proportion of starch manufactured is further processed into one modification or another. This is particularly true for the countries with the highest standards of living. No longer are operators in various industries prepared to adapt their processing to the properties of raw starch in spite of its cheapness and abundance; starch products have now to be tailored to meet the requirements of each industry and this involves a great deal of technically controlled processing.

In the natural state starch exists in the form of discrete microscopic granules that are held together by an extended micellar network of associated molecules. As a result of this structural arrangement starch is insoluble in cold water despite the fact that the starch molecule is highly hydroxylated and therefore very hydrophylic. Starch modifications are therefore aimed at increasing the cold water solubility of the product. For adhesive applications, the modification, which could either be chemical, enzymic or thermal in nature, are aimed at building in specific physical properties. In the main, these chemical treatments are controlled carefully so that the physical integrity of the starch granule will be undamaged. Modifications results in increase dispersibility in water, increase in solid content, reduced viscosity and products giving a continuous film when spread.

The chemical modifications of starch are nowadays under constant investigation from an environmental point of view. Some of the compounds currently used in these modifications are toxic and/or carcinogenic. Since starch production process is very dependent on the availability of water, it also leads to waste water production and subsequent water pollution. A more environmentally friendly way of achieving the desired modification is therefore needed[2].

2.2 Adhesives

An adhesive is a substance capable of holding materials together by surface attachment[3]. Most solid surfaces or substrates are very irregular on a microscopic scale and if two such surfaces are brought together there is very little contact. The total force of attraction between the surfaces is therefore small and surfaces are easily separated. The purpose of an adhesive is to fill at least some of the irregularities of the surfaces and thus achieve a much higher degree of molecular contact with both surfaces. In effect, the adhesive acts as a bridge between the surfaces. An adhesive must initially be sufficiently fluid to permit it to fill the irregularities of the surfaces, it then must solidify so that it has a sufficiently high cohesive strength to withstand applied forces. 'Permanently tacky' adhesives which are used, eg, in self adhesive tapes are an exception. Adhesives offer many advantages over other methods of joining materials; these include:

1. Thin films and small particles that could not be joined by other techniques are readily bonded with adhesives. Typical of such products are labels, abrasive wheels, particle board etc.
2. Stresses are distributed over wider areas, making possible assemblies lighter than could be achieved by mechanical fastening.
3. Dimensional stability of anisotropic materials can be improved by cross bonding as in plywood and random wed non-woven fabrics.
4. The layer of glue acts also as an insulator in electrical equipment; a moisture barrier in laminates and sealants and a corrosion inhibiting barrier when two dissimilar metals are bonded together.

5. Using an adhesive to make an assembly increases fatigue resistance which is a most important factor of its application in the aircraft industry.
6. Most important of all in many application is the lower processing cost.

However there are some limitations in using adhesives to form assemblies. The major limitation is that the adhesive joint is formed by means of surface attachment and is therefore sensitive to the substrate surface condition. Another limitation of adhesive bonding is the lack of a non-destructive quality control procedure. When a rivet or any mechanical fastener has not been properly installed, it is obvious. However, an adhesive which is totally enclosed by the adherent is very difficult to inspect.

2.2.1 Classification of Adhesives

Adhesives may be classified according to composition, properties or uses. Classifications based on composition are often useful in certain limited considerations but are difficult to use over a broad field of application because of the complexity of modern adhesive formulations. One possible broad classification of adhesives based on composition, may be indicated as follows:

- Naturally occurring materials
  - Starch and dextrin (from vegetable source)

- Proteins (from both vegetable and animal sources)
- Other materials (asphalt, sodium silicate, shellac, natural rubber)

- Synthetic materials
  - Thermoplastic resins (cellulose, esters, polyamides, polyvinyl alcohol and derivatives, etc)
  - Thermosetting resins (urea, melamine phenol resorcinol, epoxy resins etc).

Often, modern adhesive formulations will contain a number of different components from two or more of the above groups.

2.2.2 Starch Based Adhesives

There are two types of adhesives which are made of starches, modified starches and dextrins; the roll dried adhesives and liquid adhesives.

Principal commercial sources of starch are corn, potato, tapioca and wheat. Starch can be degraded inexpensively in a number of ways; by enzymes, oxidizing agents,acids, and heat into adhesives having a wide range of aqueous viscosity and solid concentrations. The industrial degradation products of starch may be classified into three main groups viz[1];

(i) Thin boiling starches

(ii) Oxidized starches

(iii) Dextrin

Thin boiling starches are produced by wet-processing of starch in acid slurries. Oxidized starch often called chlorinated starch is produced by wet treatment with sodium hypochlorite while dextrins are the product of dry roasting of starch.

2.3 Pyrodextrin

When starch is heated dry with or without acid as catalyst, pyrodextrin of various grades are formed. The extensive commercial utilization of pyrodextrins is said to date back from their serendipitous discovery in 1821 when fire engulfed a textile factory in Dublin, Ireland, and the starch stored were burnt producing brown, sticky starch powder which dissolved in water[12]. It was later discovered that dextrin having a wide range of solution properties could be made by dry-roasting starch alone or in the presence of an acidic or alkaline catalyst. In the immediate past, the production of dextrin has been an art rather than a science, each operator having his own special technique and each factory having its own special range of products. This attitude is disappearing and the methods of manufacture are being placed on a scientific basis. Starches and dextrin are used in numerous adhesive applications such as tube winding, laminating, case and carton sealing, bottle labeling, flat gumming, envelope sealing and gummed tape manufacture[5]. Dextrins are so versatile and adaptable that they find a wide variety of other applications. Because of the diversity of dextrins, it is possible to indicate only the class of each found most suitable for each application and to show how properties can be modified in manufacturing or by the addition of various adjuncts

2.4 Production of Pyrodextrin

The manufacture of pyrodextrin in the dry state is practised to obtain products which are partially or entirely cold water soluble and which have lower viscosities than the native starch. During dextrinization, not only are the solubility and fluidity increased, but also, the tendency for the dextrin to gel, setback or retrograde is reduced, thereby improving the utility of the product for adhesive formulations.

Pyrodextrins are divided into three primary groups. Those formed by heating starch alone usually to temperatures in the range 180°C - 210°C are termed British gums. They differ in a number of respects from the pyrodextrins produced from starch to which a small proportion of mineral acid has been added before heating. The acid converted pyrodextrins are more extensively used commercially than the British gums; those converted at relatively low temperatures (80^0C-120^0C) are known as white dextrin, while those converted at a higher temperature are termed yellow dextrin or canary dextrin.

2.4.1 Raw Material

Dextrins can be produced from all commercial grain and tuber starches. Although the conversion methods are mainly the same for all starches, the ease of conversion and the usefulness of the starch dextrins vary appreciably depending on the nature and quality of starch.

Potato starch is generally regarded as the easiest to convert, potato dextrins have excellent adhesiveness, clarity and solution stability. However their application has been limited by an objectionable cucumber like odour that is characteristic of the parent starch.

Tapioca (cassava) and Sago starches convert nearly as easily as does potato starch. Dispersions of these tapioca dextrins also have excellent clarity and stability and have the added advantage of being virtually tasteless.

Corn and wheat starches require longer processing and higher temperature for conversion to dextrin than does potato starch. Corn dextrins have good adhesive properties, but their pastes do not have the clarity of those from potato or tapioca dextrins and the paste tends to retrograde or thicken rapidly during storage.

Table 2.1 gives a summary of the manufacturing conditions and physical properties of the various categories of pyrodextrins.

2.4.2 Production Variables

There are many variables affecting the production of pyrodextrins, which include the following:

- Type or source of starch
- Kind and concentration of Catalyst
- Moisture content of the starch
- Period of storage before roasting
- Rate of heating
- Duration of the heating
- The air flow during roasting (whether or not draft is used in the heating process)
- Type of reaction vessel.

Small variations in any of these factors may give a product with different characteristics.

Table 2.1 Manufacturing Conditions for dextrins

	Dextrin Type		
	White	Canary	British Gum
Roasting Temperature (^{0}C)	80 - 130	135 - 220	150 - 220 (180 - 190 critical)
Roasting Period (hrs)	3 - 8	6 - 18	10 - 24
Amount of Catalyst	Large proportion	Small proportion	Nil
Solubility	Low - high	High	High
Viscosity	Low - high	Low	Low - high
Colour	White or cream	Buff to dark tan	Light to dark tan

2.4.3 Production Steps

There are four major steps in the production of pyrodextrins. These are dehydration, acidification, converting and cooling[5,12].

A. Size reduction and Acidification

The starch is ground, sieved through fine silk and then acidified. The acidification is accomplished by mixing the starch with dilute solution of the acid. The primary concern in acidification is to avoid non-uniform distribution. Sufficient mixing time ensures uniform distribution. Hydrochloric acid is the preferred catalyst because it disperses easily and uniformly through the starch and it tends to volatize during the last stages of dextrinization.

B. Drying

The next step is usually a rapid drying process to reduce the moisture content. The drying process can be carried out in the same vessel in which the conversion will be done .

C. Conversion step

Conversion is usually carried out in a dextrinator heated either by steam, oil jackets or by direct heating. The rate of temperature increase and the residual moisture content during the heating cycle are critical for proper conversion. High moisture coupled with a slow rise in temperature results in low-viscosity products with high sugar levels. Heating rate is limited by the maximum temperature differential that can be tolerated without charring the starch near to the walls of the heating elements. Dextrinator must have means of controlling temperature and removal of volatile products.

D. Cooling and Blending

After specified levels of viscosity, soluble material and colour have been achieved conversion is stopped by cooling. This can be done by transferring the dextrin to a cold water jacketed drum in which agitation is provided. After cooling the dextrin may be blended, if necessary, with other dextrins to bring it to within the required specification and remoistened with added water to bring it back to a moisture level near that of the parent starch.

This is done for technical reasons as well as purely commercial ones. When dextrin is remoistened to about 10% moisture, it disperses more easily in water than the dry dextrin and forms fewer lumps. Acidic dextrin may be neutralized by addition of ammonia. Acidity decreases the stability of the product but may also be advantageous to the user if further modification is desirable. The flow chart for the dextrinization process is shown below in **Fig** 2.1.

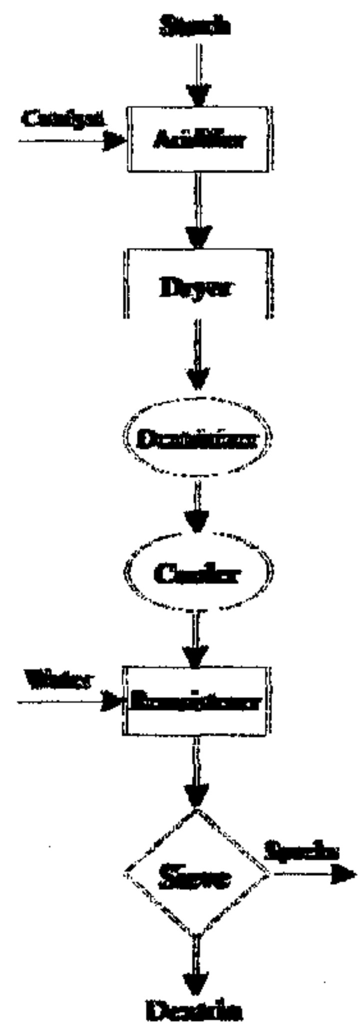


Fig. 2.1 Flow chart for dextrinization process

2.5 Chemical Structure and Reaction Mechanism.

Although superficially simple, dextrinization produces fundamental changes in molecular structure that leads to complex mixtures of products. The primary reactions appear to be:

1. hydrolytic cleavage of the starch molecule resulting in the formation of lower molecular weight and more water soluble compounds.
2. transglucosylation leading to the formation of more-highly branched molecules with little net change in molecular weight.
3. some repolymerization or condensation of the smaller molecules, particularly during manufacture of highly converted products.

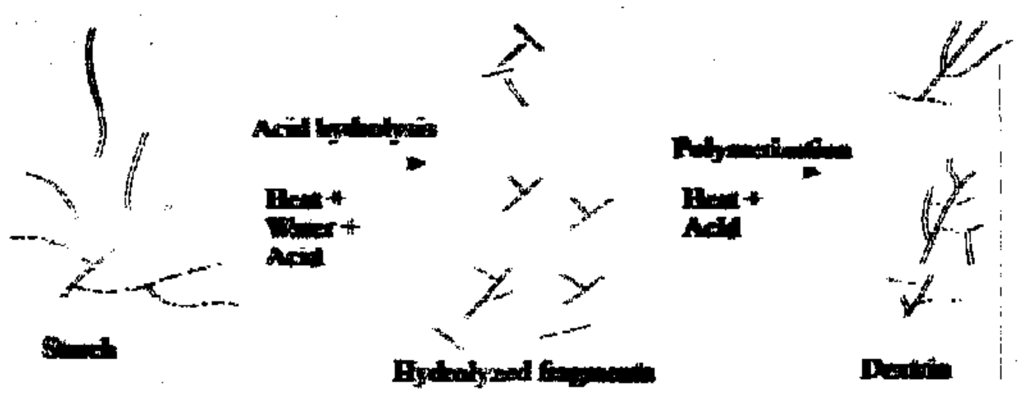


Fig 2.2. Hydrolysis and repolymerization during dextrinization of starch[5]

In addition, some carbon dioxide and other gaseous products may be formed. Transglucosylation is an important reaction in pyrodextrinization. It probably is an intermolecular exchange in which some predominant α-D-$(1 \rightarrow 4)$ glucosidic linkages of native starch are changed to α-D-(1 → 6) linkages[5].

Geerdes and co-workers[13,15] suggest that the extent of transglucosylation can be estimated from the percentage of D-glucose units resistant to periodate oxidation, for the reaction makes both the linear and the branched polysaccharides of starch progressively more branched. As this occurs, the dextrins disperse more readily and form clearer, less viscous and more stable solutions than did the original starch.

White dextrin formation.

The formation of a typical white dextrin is essentially a hydrolytic reaction that leads to a steady increase in water solubility and reducing values and a corresponding decrease in viscosity. Sparingly soluble white dextrins retain the retrogradative characteristics of the original starch.

Canary dextrin formation.

Conditions for the preparation of the yellow or canary dextrin favours more extensive structural changes. At first, hydrolysis predominates, however, as the temperature increases, the mixture becomes drier and conditions become more favourable for transglucosylation and polymerization reactions. Thus, there is initially an increase in the alkali lability followed by a decrease indicating a decrease and then an increase in the average molecular size. Examination of the structures of several highly converted Canary dextrin has shown that they contain greater proportion of branches than does the original starch. Their formation can be ascribed to tranglucosylation.

British Gums.

For British gum formation the viscosity and alkali lability do not change as rapidly with time of conversion as in the manufacture of White dextrins, only moderate increases in reducing values are observed[12]. Significantly, British gums have relatively high molecular weights, are dispersible and still retain the properties of imparting high viscosity. Some hydrolysis probably occurs in the absence of added catalyst, particularly during the early stages of the process, Hydrolysis is caused by residual water in the starch and traces of acidic materials present or formed during heating, the action of which is prevented by alkaline buffers which can also promote atmospheric oxidation at the high temperatures used. The major reaction appears to be transglucosylation with resultant formation of highly branched molecules.

2.5.1 Mechanism of formation of acid converted pyrodextrins

The mechanism of conversion is complex and involve a series of processes of which the principal ones are hydrolytic scission, rearrangement of molecules and repolymerization.

Several possible mechanisms for the chain-branching process have been proposed[12]. (Fig 2.3) as follows;

(a) Rupture of the α-D-(1→4) links with the formation of 1,6-anhydro-end groups, which subsequently react with hydroxyl group at other positions to give the branch points.

(b) A synchronous type of transglycosylation process involving attack of a hydroxyl group at C-2, C-3, or C-6 on the glycosidic link of an adjacent α-D-(1→4) linked chain.

(c) Hydrolysis of the α-D-(1→4) links followed by a reversion process with formation of links at other positions.

Of the alternative mechanisms proposed for pyrodextrin formation, the route involving simultaneous hydrolysis and reversion mechanism (mechanism (c)) provides the most rational agreement with the observed facts of pyrodextrin formation under acid catalysis. It has been shown that at the initial phase of thermal conversion, the curves for alkali lability, reducing value, periodate uptake, and formic acid release, show a rise, which may be interpreted as involving hydrolytic scission of the chains together with some degree of reversion to give a more highly branched structure (D. Horton; Starch: Chem & Tech 1965). At higher degrees of thermal conversion, the properties show a progressive decrease in value and it may be considered that reversion is the principal reaction. Since the reversion process is reversible, the distribution of the linkages in the product, if equilibrium is reached, may be expected to be determined according to their relative thermodynamic stabilities. It is a known that (1→6) links are thermodynamically more stable than (1→4) links and that isomaltose is hydrolysed more slowly than other disaccharides of D-glucose.

The failure of any investigation to reveal definitive evidence for anhydro intermediates in the acid catalyzed dextrinization process and the fact that conversion takes place at considerably lower temperature than does conversion to British gum, would suggest that the anhydro end-group mechanism (a) is not significant in the acid catalyzed process, except perhaps during conversion in the higher temperature ranges. The transglycosylation mechanism (b) cannot be excluded as a possible simultaneous process. It would be difficult to reconcile this as the sole mechanism with the development of a maximum in reducing value during conversion.

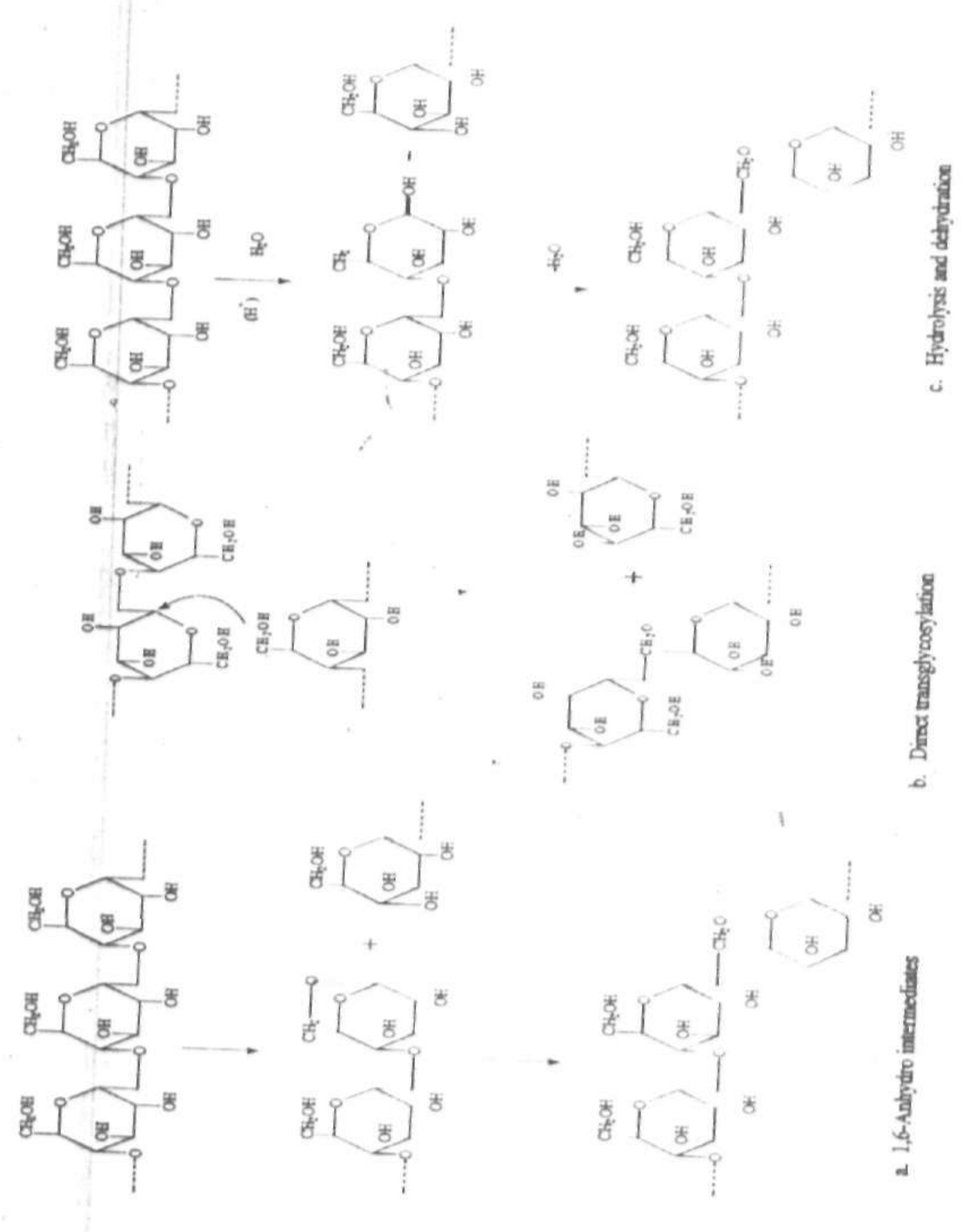


Fig 2.3 Possible Mechanisms for the chain branching reaction.

2.6 Industrial applications of pyrodextrin

Pyrodextrins are widely used in the industries. The greatest amount of dextrin is used as a base component for adhesives in the paper industry.

The following are some of the important applications of these products[11]:

1. **Corrugated cardboard manufacture**: One of the large users of these property is the corrugated board industry which includes the making of cartons, boxes and containers.
2. **Remoistening gums**: these are adhesives which are coated on to surfaces and dried and which are moistened by the user before applying to the second surface, such as postage stamps and envelops flaps. Cassava dextrin in aqueous solution are well suited for this purpose as they give a high solids solution with clean machining properties.
3. **Wallpaper and home use**; various types of starch products are the basis of general home adhesives such as wallpaper and other uses, and which are usually packed in small containers.
4. **Foundry industry**: Starch is used as an adhesive, coating the sand grains and binding them together in making cores which are placed in moulds in the manufacture of castings for metals.

5. Well drilling: Starches and modified starches mixed with clay are used to give the correct viscosity and water holding capacity in bores that are drilled for the establishment of oil wells or water wells. These starch products are substituting such products as aquagel and impermex as a mud indispensable in drilling wells. For this purpose a cold water soluble pre-gelatinized starch is desired, which can be made up to paste of the required concentration on the spot.
6. Paper industry: In the paper and board industries, starch is used in large quantities at three points during the process:
   - at the wet end where the basic cellulose fibre is beaten to a suitable pulp in order to increase the strength of the finished paper and to impart body and resistance to scuffing and folding;
   - at the size press at which stage the paper sheet or board has been formed and partially dried. The starch is usually added to one or both sides of the paper sheet or board which has been partially dried to improve the finish, appearance, occurring and the printing properties of the paper. Oxidized and modified starches are usually used for this purpose.
   - coating operation - when a pigment coating is required for the paper, starch acts as a coating agent and as an adhesive.

Other large dextrin consumers include textile, pharmaceutical, food and other industries. A list of dextrin uses are presented in Table 1[13] in Appendix A2

CHAPTER THREE

EXPERIMENTAL

3.1 Introduction

It is obvious that because of the nature of dextrinization process and the molecular complexity of starch, an almost unlimited number of dextrin structures is possible. Complications are however considerably reduced by the fact that all the variations in structure lead to only two major characteristic changes: molecular size of the dextrin molecule, and the other essentially a change in the degree of linearity. Each of these changes has a specific effect on the physical and chemical characteristics of the dextrin. Variation in the average molecular weight influences the viscosity of the dextrin, while the change in linearity greatly influences the solution stability characteristics and solubility.

3.2 Process Study and Optimization

The parameters which are used to characterize a dextrin were studied while monitoring the progress of the reaction.

3.2.1 Investigation on the effect of moisture content

100g of cassava (tapioca) starch containing 20% moisture and to which 10ml of 3% Hydrochloric acid (HCl) has been added was heated to a temperature of 115°C. A thick black mass resulted after about 10 min and the reaction was quickly terminated by cooling.

The moisture content was then reduced to 12% by drying the bulk cassava in an oven at 40 - 50°C. On heating to 120°C for 1 hour, the product obtained contained lots of black specks and black aggregates. Given the above; 100g of the starch was spread thinly on a flat glass plate and heated to dryness in an oven at 50°C.

Five batches of 20g dried starch each were taken in four separate 200ml beakers and the starches were moisturized with distilled water at different moisture levels of 7%, 6%, 5%, 4% and 3%. The content were well stirred to ensure proper mixing. Each of the five moisturized starches were acidified with 4% dilute HCl. Sufficient mixing time was employed to ensure that the catalyst was evenly distributed throughout the starch. The starch samples were placed in an oven for dextrinization to proceed. A roasting temperature of 120°C was maintained and the residence time in the oven was 180 min (3hrs). Samples were taken at intervals of 30min for analysis.

3.2.2 Effect of varying acid strength.

Four batches of 20g dried starch all having a moisture content of 5% were taken in separate 200ml beaker. HCl with acid strength of 3%,4%,5% and 6% were respectively added to the four batches of starch samples. The samples were mixed thoroughly and then heated at 120°C for 3 hours. Samples were withdrawn at intervals of 30min for analysis.

3.2.3 Acid to Starch ratio.

To determine the quantity of acid to be added for the formation of white dextrin, the following experiment was carried out.

9g of starch was dissolved in 18ml of water, and the pH of the starch suspension was taken. Hydrochloric acid was added dropwise, while monitoring the pH of the suspension, until the pH dropped to about 2.6. The quantity of acid added was then calculated to establish the acid-starch ratio on w/v basis

3.2.4 White dextrin formation.

Farbest Starch (cassava), a product of Farbest Industries Nigeria Limited Ibadan, was employed in this experiment. The starch (moisture content 7%) was acidified before heating by addition of 2M HCl or 6%HCl. To reduce the black spec formation due to local acid concentration, a perfume sprayer was improvised to produce very small droplets and uniform spray. The amount of acid added corresponded to that needed to raise the pH of the sample to 2.6, as was predetermined in a preliminary experiment above. For 200g of the starch sample, an acid - starch ratio of 1:50 v/w basis was established. The acidified starch was then heated slowly for about 40 min. raising the temperature from ambient (25^{0}C) to 67.5^{0}C at a heating rate of 2^{0}C/min for 20 minutes and maintaining the temperature at 67.5^{0}C for a further 20 minutes. The temperature of the sample was finally raised to 120°C (average) and kept at that level for 6 hours. The heat treatment was carried out in a vessel immersed in an oil bath equipped with a thermostatic heater. Samples were withdrawn at intervals of 1 hr and cooled to room temperature. The pH, solubility and viscosity of the samples were determined. Photometric analysis was also carried out on the samples by measuring the absorbance of a 50% solid concentration of the sample with the set wave length at 375nm using a spectrophotometer.

CHAPTER FOUR

PROCESS MODELLING AND SIMULATION

4.1 Introduction

It is well known fact that small scale experiments are not always a reliable guide to large scale results, sometimes a process which is satisfactory in the pilot scale gives trouble on the large scale and occasionally the reverse is found to be true. It is significant to note however that while in recent years there has been some tendency to curtail or even to omit the pilot stage in developing new processes, an opposite trend is seen in relation to established processes, namely, the use of models to predict the effects of changes of design and operating conditions in existing large scale plants. The aim of model theory is to predict these scale effects and determine the condition under which the performance of a model gives a reliable forecast of prototype performance.

In modelling the dextrinization process the focus would be at balancing between product quality and energy requirement, this translates to a balance between the design variables (the working temperature, amount of catalyst and residence time of the product in the reaction vessel. Model construction and parameter estimation would eliminate the rather expensive and hectic experimental process of generating results, it also presents a more rational way of tackling the problem at hand which involves the possibility of having countless number of products.

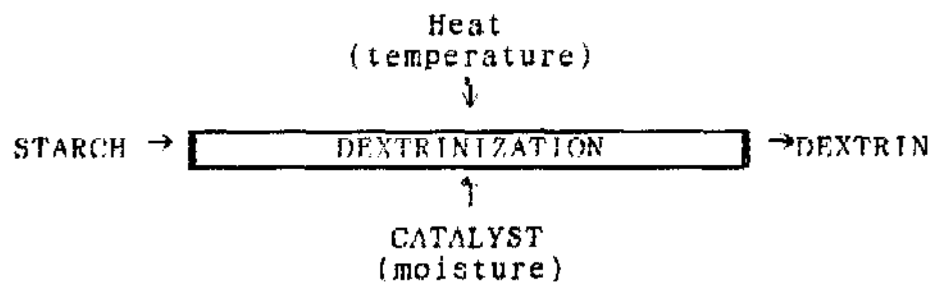
4.2 Model structure

From literature it was ascertained that repolymerization is responsible for cold water dispersibility and for excellent cook stability. This is influenced by high temperature reaction conditions. Temperature increase favours more extensive structural changes as the mixture becomes drier. Structural changes leads to high molecular weight products implying the dominance of condensation reaction. Suppressed repolymerization or greater linearity results in partial cold water dispersibility and *retrogradation or congealing of cooked paste.*

From process study we see that conversion is a function of the added catalyst. Rate of conversion increases with large amount of acid. The amount of acid required for conversion is a function of the specific physical properties required. If large amount of acid is used, the hydrolytic fission reaction at the initial stage is *accelerated* and a consequence of this is the low solubility of the product in cold water. The product also will retain varying degrees of the set-back tendencies from the original starch. Hence to obtain a better quality of product at much less processing time one has to optimize the acidification rate and the reaction temperature.

The model structure would be based on white dextrin formation where reaction is essentially hydrolytic in nature.

The process can be analyzed using a black box representation as shown below.



The production variables would be reduced to two; the temperature and quantity of catalyst (starch-acid ratio) for ease of computation. The moisture content factor and *acid strength are lumped as one variable.*

Since the design of an oil heated, jacketed reactor is to be carried out, two options may be considered in constructing the model structure.

OPTION A: An operation scheme which involves heating the fluid (oil) in the jacket to a constant temperature before inserting the converter vessel or

OPTION B: *Heat energy supply to both the heating fluid and* the starch material simultaneously (a form of indirect heating of the starch material).

Considering the second option, an energy balance across the system yields;

for the **transient** state

rate of heat input	=	rate of heat gain by oil	+	rate of heat gain by vessel	+	rate of heat gain by reactor content

$$\frac{\partial Q}{\partial t} = m_o C_{po} \frac{\partial T_o}{\partial t} + m_v C_{pv} \frac{\partial T_v}{\partial t} + m_s C_{ps} \frac{\partial T_s}{\partial t} \qquad (4.1)$$

If we assume that the vessel and the oil gains heat at the same rate, we can lump the variables so that

$$\frac{\partial Q}{\partial t} = H_o \frac{\partial T_o}{\partial t} + H_s \frac{\partial T_s}{\partial t} \qquad (4.2)$$

where H_o = lumped heat capacity of the oil and vessel

H_s = heat capacity of the starch.

If we also assume that the thermal response of the starch material is slow such that the oil would have gained heat to raise its temperature to T' at time t' before an observable temperature rise of the starch, then on integration;

where Ti = initial temperature

$$\int_0^{t'} \frac{\partial Q}{\partial t} = \int_{Ti}^{T'} H_0 \frac{\partial T_0}{\partial t} \tag{4.3}$$

$$\Rightarrow \int_0^{t'} \frac{1}{H_0} \frac{\partial Q}{\partial t} \partial t = \int_{Ti}^{T'} \partial T_0$$

$$\Rightarrow \frac{W}{H_0} t' = (T_0' \quad Ti) \tag{4.4}$$

equation 4.4 can be rewritten as

$$T_0' = \frac{W}{H_0} t' + T_i \tag{4.5}$$

It is assumed that the heat capacities are constant over this temperature range.

from equation (5.2)

$$\int_0^{t} \frac{\partial Q}{\partial t} \partial t = \int_{Ti}^{T} (H_0 \partial T_0 + H_S \partial T_S) \tag{4.6}$$

$$\Rightarrow \int_0^{t'} \frac{\partial Q}{\partial t} \partial t + \int_{t'}^{t} \frac{\partial Q}{\partial t} \partial t = \int_{Ti}^{T'} H_0 \partial T_0 + \int_{Ti}^{T'} H_S \partial T_S + \int_{T'}^{T} (H_0 \partial T_0 + H_S \partial T_S)$$

$$\int_0^{t'} W \partial t + \int_{t'}^{t} W \partial t = H_0 \int_{Ti}^{T'} \partial T_0 + \int_{T'}^{T} (H_0 \partial T_0 + H_S \partial T_S)$$

$$\Rightarrow Wt' + W(t - t') = Wt' + H_0(T_0 - T_0') + H_S(T_S - T_S') \tag{4.7}$$

substituting for T_0' from equation (4.5)

$$Wt = Wt' + H_0T_0 - Wt' - H_0T_i + H_ST_S - H_ST_S' \tag{4.8}$$

$$= H_0(T_0 - T_i) + H_S(T_S - T_S')$$

but $T_S' = T_{Si} = T_i$

$$\therefore Wt = H_0(T_0 - T_i) + H_S(T_S - T_i) \tag{4.9}$$

$$(T_S - T_i) = [Wt - H_0(T_0 - T_i)]/ H_S$$

$$\Rightarrow \quad \Delta T_s = \frac{W}{H_s} t \quad \frac{H_0}{H_s} \Delta T_0 \qquad (4.10)$$

this equation can be simulated to determine the values of T_s (Temperature of starch) at corresponding values of T_0 and t.

To determine the variation of T_0 with time t for the rest of the period after t'., the heat taken by the starch in this period would be evaluated;

$$\int_{t'}^{t} \frac{dQ}{dt} = \int_{T'}^{T} H_s \frac{dT_s}{dt} \qquad (4.11)$$

$$\int_{t'}^{t} \frac{1}{H_s} \frac{dQ}{dt} dt = \int_{T'}^{T} dT_s \qquad (4.12)$$

$$\Rightarrow \quad \frac{W'}{H_s} (t \quad t') = (T_s \quad T_s') \qquad (4.13)$$

$$\therefore \quad W' = \frac{H_s (T_s \quad T_s')}{(t \quad t')} \qquad (4.14)$$

From equation (4.5)

$$T_0 = \frac{W \quad W'}{H_0} t + T_i \qquad (4.15)$$

for t = (t - t')

A computer program to carry out the simulation and the simulation results are given in appendix B.

At steady state, the operating temperature is known i.e T_s hence ΔT_s will be a constant and from equation (4.10)

$$T_p = \frac{W}{H_0} t \quad \frac{H_s}{H_0} C + T_i \qquad (4.16)$$

also

Heat input = Heat taken by moisture (water + volatiles)

$$\frac{dQ}{dt} = m_{ca} \; C_{pc} \; (T_r \quad T_s) + (m_{ca} \quad m_{cb}) \; L \qquad (4.17)$$

if m_s is the mass of starch to be dried per unit time and X_a and X_b are the initial and final liquid/moisture content in mass of liquid per unit mass of starch then

$$\frac{1}{m_s} \frac{dQ}{dt} = X_a \; C_{pc} \; (T_r \quad T_s) + (X_a \quad X_b) \; L \qquad (18)$$

$$\Rightarrow \frac{W}{m_s} t = X_a \; C_{pc} \; (T_r \quad T_s) + (X_a \quad X_b) \; L \qquad (4.18)$$

Hence the residence time t of the starch material in the reactor (dextrinator) is a function of the acid starch ratio

Kinetic model

$$\text{Starch} \xrightarrow[\text{heat}]{k_1} \text{Dextrin} \qquad \text{- Uncatalysed reaction}$$

$$\text{Starch} \xrightarrow[\text{acid + heat}]{k_2} \text{Dextrin} \qquad \text{- Catalysed reaction}$$

the rate equation will be

$$\frac{dC_s}{dt} = (k_1 + k_2 C_c)\, C_s \qquad (4.19)$$

$$-\frac{dX_s}{d(1 - X_s)} = (k_1 + k_2 C_c)\, dt \qquad (4.20)$$

Integrating

$$-\ln(1 - X_s) = K_{obs}\, t \qquad (5.21)$$

where $K_{obs} = k_1 + k_2 C_c$ observed rate constant

Hence a plot of $-\ln(1 - X_s)$ against t is expected to yield a straight line passing through the origin for the model to be true.

A plot to verify the rate law as predicted by the kinetic model is given in Appendix B.

The regression analysis gives a value of 70.4% as the regression coefficient. This value is not high enough to justify the model, this implies that the reaction is more complex. However we can consider the reaction as a pseudo first order reaction.

General Assumptions

In deriving all the above equations the following general assumptions were made:

- Heat loses are negligible
- The process is entirely a thermal process hence no complications arising from diffusion
- Over the temperature ranges considered the specific heat capacities and the heat of vapourization are constant
- All vapourization occur at a constant temperature
- Heat absorbed by moisture and volatiles at the transient state is negligible
- The conversion process has a first order kinetics.

CHAPTER FIVE

EQUIPMENT DESIGN AND FABRICATION

5.1 Introduction

One very important variable in the manufacture of dextrin from starch is the type and design of the converter vessel. In the case of the acid converted pyrodextrin production, it is essential that the converter vessel be provided with proper agitation, as thorough mixing to ensure effective acidification of the starch is needed. It is also necessary that the vessel be equipped with temperature control mechanism since temperature is a key variable in determining product quality. The equipment must also provide for removal of volatile products.

In summary, the requirements for a dextrin converter (dextrinator) includes the following:

a) Proper agitation, either by mechanical means or forced convection.

b) Heat control mechanism

c) Means of removal of volatile products.

5.2 Design Options

The choice of type of equipment to be employed in a dextrinization process depends on the method to be adopted, whether batch or continuous production. For batch processes, vessels can vary in capacity from 100 to 10,000lbs (about 45 - 4500kg) and can be vertical or horizontal. Because dry powdered starch is highly combustible direct heating is not encouraged and indirect heating of the cooker is preferred. Another serious disadvantage of direct firing is that it does not permit good surface temperature control and may cause scorching of the material in the vessel wall.

In the work of Rowe and Hagen (C.A.1944) use is made of an inner metal sheet to contain the material treated, an outer shell forming with the inner shell a steam jacket divided to form plurality of circular steam ducts, an inlet and a condensate outlet for each of the ducts. A partition is provided extending across each duct which forms a steam barrier between its inlet and outlet, the inlet and outlet being arranged in proximity to the partition so that steam entering the ducts is compelled to flow continuously through a substantial length of the ducts. A means such as a mechanical agitator for agitating the material under treatment is also provided. The main object in dividing the jacket into zones is to achieve uniform transfer of heat to the starch.

This design is a rather complex and energy inefficient, as the steam is under-utilized. It is also capital intensive - a steam generator will be required together with other accessories, making it unattractive for the small scale industrialist. The temperature control mechanism for such an equipment will be an onerous task to design. Hence for a small scale production the design is unacceptable.

For the continuous conversion process developed by Philips[7], in which a moving belt carries a thin layer of acidified starch through a heated oven, the gains accruable from increased production capacities and process intensification may be sapped by the high fixed cost and maintenance cost resulting from the large sized equipment that will be involved. A possible setup of the equipment is shown in Figure 6.1. The oven would have to be large to allow for enough residence time since it has been established (Chapter four) that an optimum residence time of 5 hours may be required for conversion into white dextrin. Running cost involved would appreciate over and above that of the Hagen cooker and might not appeal to the small scale investor.

Analyzing the fluidized bed option as suggested by Frederickson., the dextrinization process can be considerably accelerated since the material surface area is greater compared to its mass. By fluidization the aim is to suspend the starch particles in a vertical hot air stream thus exposing as much surface area of the particle as possible to a forced convection effect of the air. This way the requirements for proper agitation and removal of volatiles will be achieved. A possible design is as shown in Figure 6.2. The heater battery could employ a steam coil, electric heater or even a heat pump for heating. A major setback in this design is the fact that temperature control might be difficult and also that it might not be economically justifiable.

Given these setbacks, a much simpler design similar to that of "Hagen cooker" and which meets all the design requirements is considered. It should be much more economical vis-a-vis other options appraised and also easier to operate.

5.3 The converter design

Design Data

The most important parameters in the design of the converter vessel include:

- Operating temperature: the amount of heat to be added to the system is a function of the operating temperature and the amount of starch to be processed
- Amount of starch to be processed: this determines the capacity of the vessel
- Available material of construction

5.3.1 Material of construction

In the selection of construction materials, besides the availability factor and cost, care had to be taken with regards to the corrosive nature of hydrochloric acid (HCl). HCl is one of the most corrosive chemicals known, however even at slightly elevated temperatures, completely dry hydrogen chloride gas has very little corrosive action and is easily handled in iron equipments. Aluminium or stainless steel would have been the appropriate materials but considering the cost and availability of the materials, a cheaper option, mild steel, had to be chosen.

Since the starch - white dextrin transformation takes place with dilute HCl as catalyst and at low temperatures, a mild steel container suffices. Also fuel oil has very little or no effect on mild steel in terms of corrosion thus the choice of mild steel as the construction material is justified.

5.3.2 Component Designs

Reactor Vessel

Mild steel(MS) of thickness varying from 0.2mm to 3mm are available in the market. MS of high thickness will not be easily shaped except with the use of machines, it also might hamper the flow of heat energy to the starch material causing a temperature gradient. On the other hand MS of say 0.2mm thickness might not be strong enough to withstand the agitation within the vessel hence it is only logical to employ MS of thickness 0.75mm. The reactor vessel is therefore constructed with MS of thickness 0.75mm, shaped as a cylindrical vessel with a hemispherical bottom. It is fitted with a handle to enable removal from the heater jacket into another medium for cooling.

The volume of reactor required can be calculated knowing the quantity of starch to be processed, also the optimum dimension (in cm) of material required is computed as 20 in diameter and 12.1 in height (see Appendix), as shown in Figure 6.3.

Reactor Jacket

The jacket to contain the heating fluid is made of same material as the reactor vessel and is fitted with a 1.5KW electric heater. The jacket, which is lagged with appropriate material to prevent heat loss to the surroundings, is cylindrical in shape with a curvature at the bottom. The dimensions (in cm) of the jacket is estimated as 28.5 in diameter and 38.97 total height (see Appendix) as shown in Figure 6.4. The choice of 1500W Watt rating was influenced by the thermal response of the heating fluid employed. Available in the market are variations from 500W to 2500W. For a unit mass of the fluid the response time required for a degree rise in temperature was computed (Appendix). For higher Watt ratings, temperature control becomes difficult as the thermal gain would be large, whereas for lower values, longer time would be required resulting in higher residence time of the material in the reactor.

Agitator(Impeller)

The impeller is very critical to the design since proper agitation would be required at the acidification and dextrinization stages of the process which will be carried out in the converter vessel. The agitator is designed with two sets of blades, one arranged at 60^{o} to the horizontal and the other at 75^{o} to the horizontal. This arrangement of the blades is to facilitate thorough mixing of the starch material. At the bottom of the agitator rod is fitted a blade shaped in line with the bottom of the converter vessel to scrape the bottom of the vessel so that dead zones are eliminated. The impeller is mechanically driven by a motor of variable speed. Figure 6.5 shows the dimensions of the impeller and it's assembly.

Temperature Control

For temperature measurement and control a wide range of equipments are applicable. These include; thermocouples, thermistors, resistance thermometers, radiation pyrometers. The suitability of each one of them depends on the temperature range. For the system under copnsideration (T < 150^{o}C) a resistance thermometer will be suitable. A contact thermometer which functions as a resistance thermometer is employed and it is assumed that it is capable of remote electrical transmission without appreciable transmission loss and with consequential accuracy.

The temperature control system adopted consists of the contact thermometer (mounted on the reactor jacket) connected to an electronic relay system such that the supply of electric current to the heater is switched off when the temperature of the oil reaches the set temperature fixed on the contact thermometer, and switches on the heater when the temperature falls below the set temperature so that the heat energy is supplied to the system to raise its temperature.

The total set up is shown in Plate 6.1 and its components in Plate 6.2.

A test run was carried out with the fabricated equipment, the temperature of the starch was raised to 120^{o}C, the heat loss from the equipment was, however, enormous which could be attributed to poor lagging.

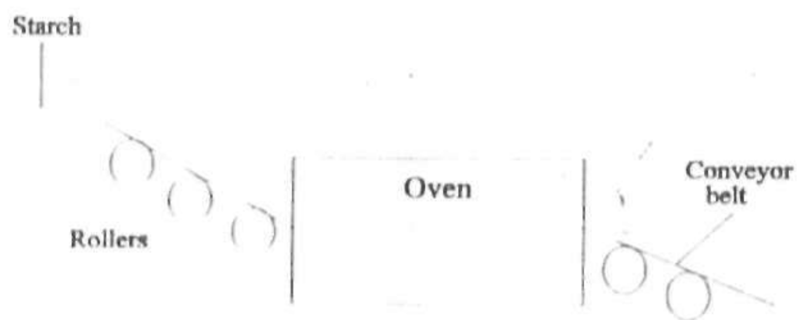


Fig 5.1: Schematic illustration of the setup for continuous production of dextrin

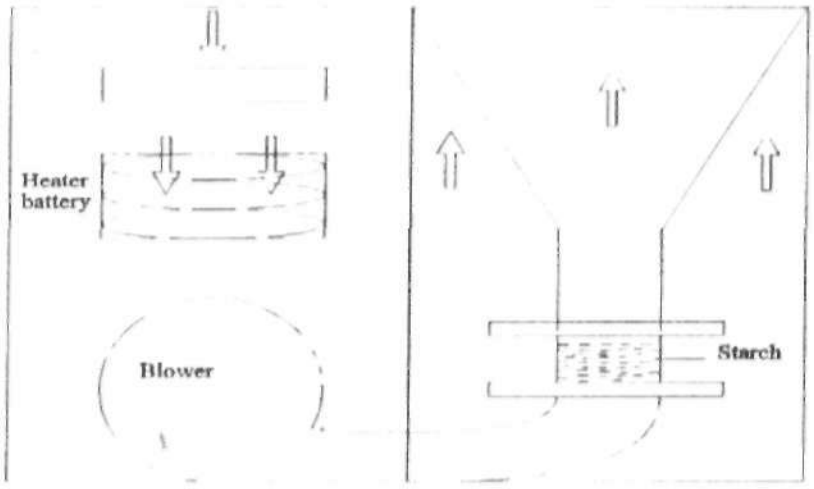


Fig 5.2: Schematic illustration of a fluidized bed dextrin converter.

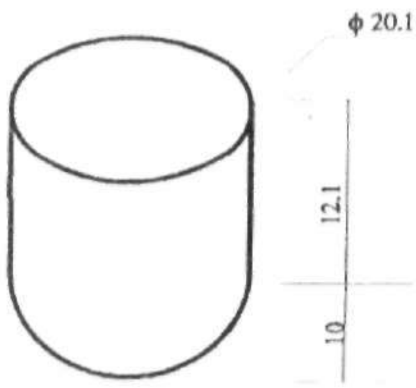


Fig 5.3. Reactor (converter) vessel showing dimensions

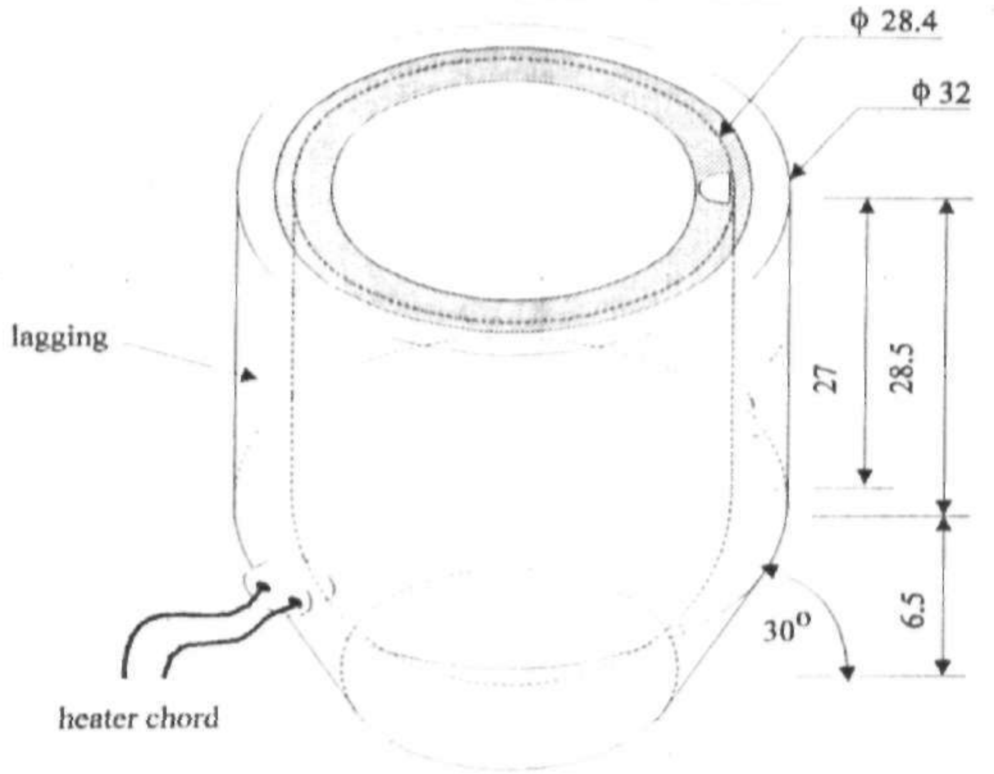


Fig. 5.4: Reactor jacket showing dimensions

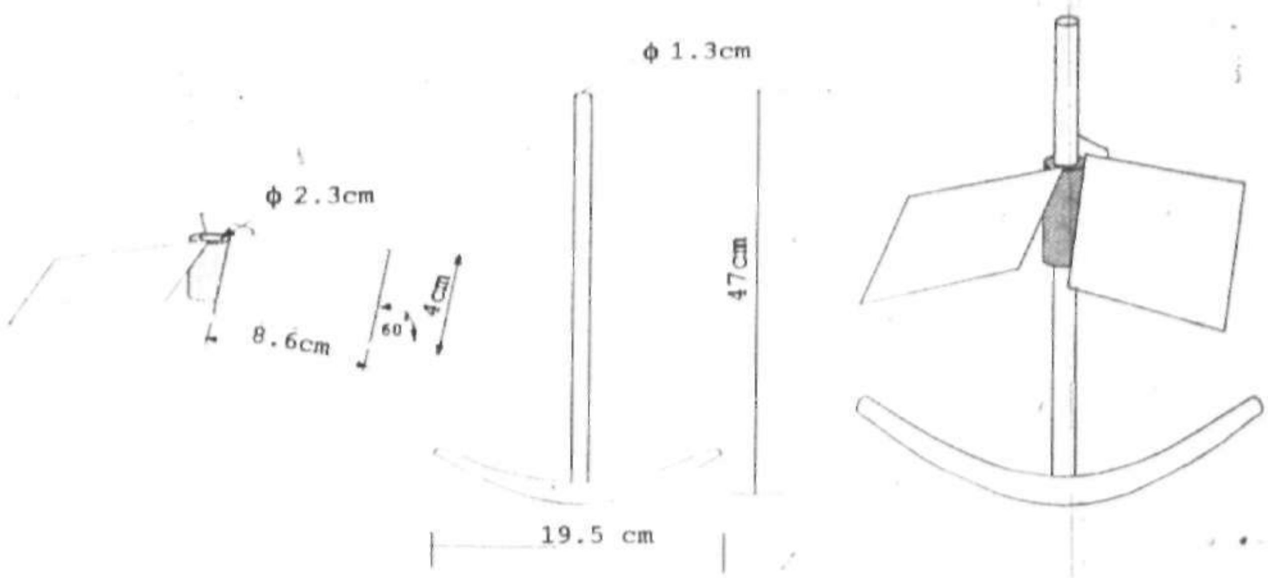


Fig. 5.5. Impeller components and assembly

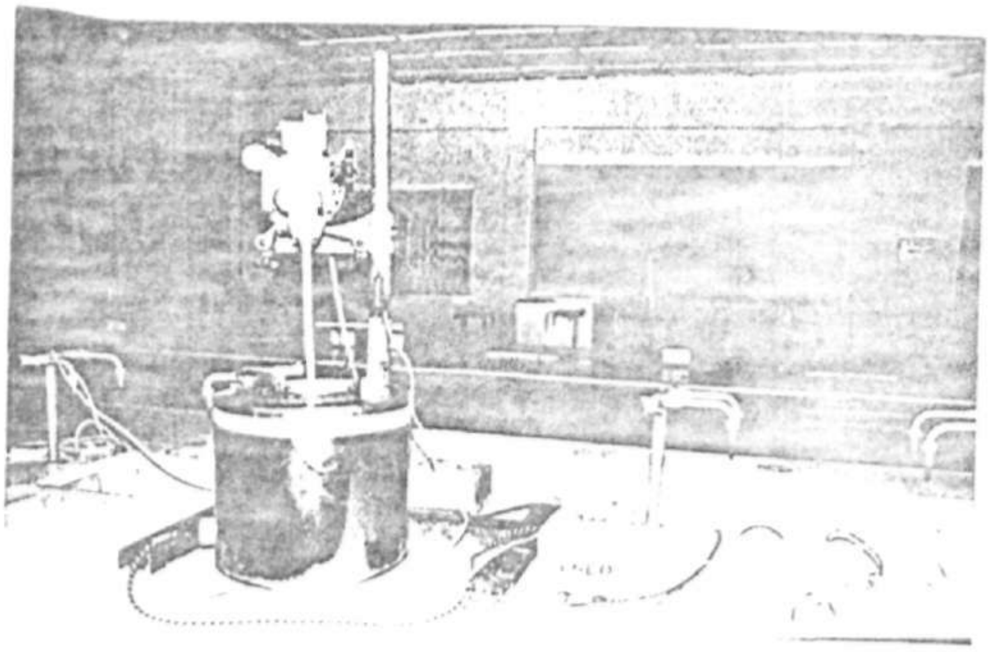


Plate 5a. Total Setup of the Detrinator design

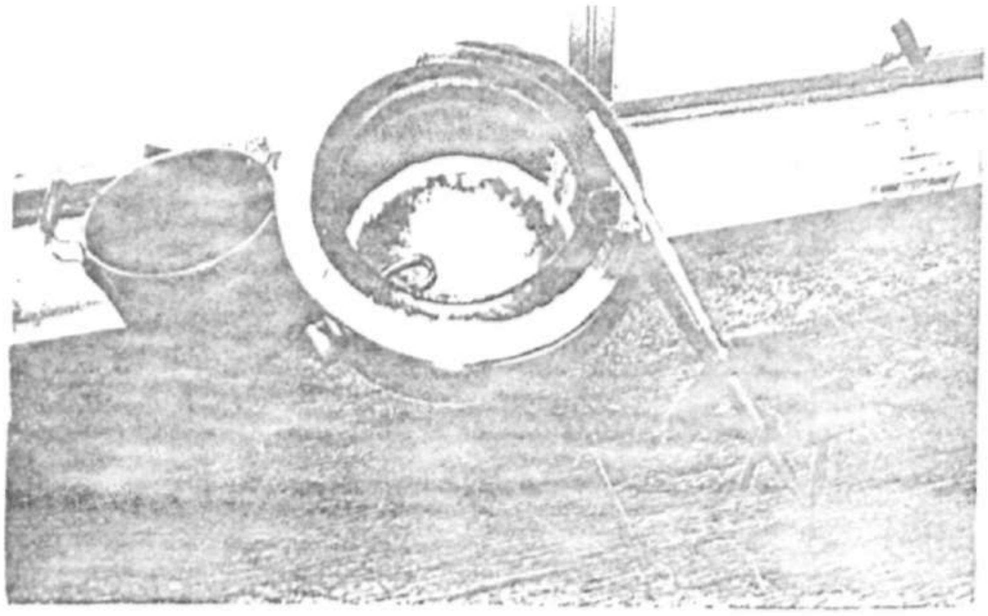


Plate 5b. Components of the Dextrinator.

CHAPTER SIX

RESULTS AND DISCUSSION

6.1 Moisture Content

Fig 6.1 Shows the variation of the solubilities of dextrin (Product) with moisture content levels for different roasting periods. From the figure it is observed that optimum moisture levels lies between 5% and 7%: at these points the curves attain a plateau. Dextrinization carried out with moisture content level of 7% however, gave a product containing negligible black spec formation. Tests for higher moisture content levels yielded unsatisfactory results. A thick black mass resulted from a moisture content of 20%, high black speck formation for 12%. Hence it can be concluded that higher percentages of moisture content in the starting material for dextrinization are undesirable. It is known that high moisture content promotes starch hydrolysis and suppresses condensation (repolymerization) reaction. Consequently the product yield and solubility is affected.

6.2 Effect of Acid strength

Fig 6.2 shows the variation of solubilities of the dextrin product with acid strength for different roasting periods. At higher roasting periods the curve almost flattens out, thus revealing that the effect of the acid concentrations is only significant at the early stages of dextrinization. The solubilities for a particular roasting time increases with increasing acid strength. One other change noticed was the darkening of the product progressively as the acid strength was increased (Table 6.1).

The amount of acid needed for a particular preparation will be a function of the specific physical properties required. If a large amount of acid is used, the hydrolytic scission reaction at the initial stage is accelerated and a consequence of this is the low solubility of the product in cold water. The product also retains varying degree of the setback tendencies from the original starch paste.

6.3 Optimum reaction parameters for dextrin formation.

The following gives the result of the analysis carried out to determine the optimum reaction parameters for white dextrin formation from starch as spelt out in section 3.2.4.

Catalyst depletion with reaction.

Variation of the pH with time is illustrated in Fig 6.3. The upward trend of the curve indicates that the acid catalyst gets depleted by evaporation as the reaction progresses.

Solubility

Fig 6.4. shows the solubility plot for the samples for various conversion periods. The solubility was highest for a conversion period of 5hrs (90%) and then decreased to 80% at t=6hrs. A possible explanation for the observed behaviour could be due to the fact that hydrolysis and repolymerization reaction occur simultaneously during the dextrinization process and since repolymerization favours increased solubility it appears to be dominating at t=5hrs, and at t=6hrs, hydrolysis could be the main reaction. Fig 6.5. shows the plot of absorbance of the samples versus time. Notice the resemblance between Fig 6.4. and Fig 6.5., Since absorbance is a function of concentration of the solution, it directly relates to solubility and can be used as an index for measuring the conversion.

Viscosity

Fig 6.6. shows the viscosity profile for the cold water solution of the samples. It shows an increase in viscosity at the initial stage (up to t=2hrs) and then a sharp decrease. The decline in viscosity may be due to hydrolytic scission of the molecules. A rising tendency in the value of the viscosity was observed at a conversion period of 6hrs. This could be as a result of formation of the reversion products. Fig 6.7. compares the viscosity values of cold water solutions of dextrins after 2 months of preparation, to the initial viscosities. A high degree of set back tendencies are shown by products obtained for conversion periods t=1hr to t=3hrs. Values obtained for conversion times t=4hrs to t=6hrs are essentially the same indicating that conversion products at those periods are more soluble. Products obtained for shorter conversion periods are prone to retrogradation as indicated by their enhanced viscosities.

Property change with storage

Table 6.1 gives the different physical properties of the dextrin samples compared with those of the parent starch. Observations were made after 8 months of production. The product with highly converted materials have more stable properties as exemplified in the table and by Fig. 4.7. for which comparison was made after two months of production. The physical changes are produced by chemical changes induced in the molecular structure of the parent starch by the dextrinization process. An increase in the proportion of lower - molecular weight materials enhances water solubility and produces a darkening of color.

Table 6.1: Product properties for different conversion periods

Sample	Conversion Period (hr)	Nature of Conc. solution (50%)	Solution colour	Powder colour
Starch		Insoluble	White (Suspension)	White
A	1	Slightly soluble	Gold Yellow	Creamish White
B	2	Thick cloud of ppts	Brown	Cream (light)
C	3	Colloidal	Brown	Middle grey cream
D	4	Increased fluidity	Dark Brown	Cream
E	5	More fluid	Yellowish Brown	Yellowish Cream
F	6	More fluid	Dark Brown	Buff

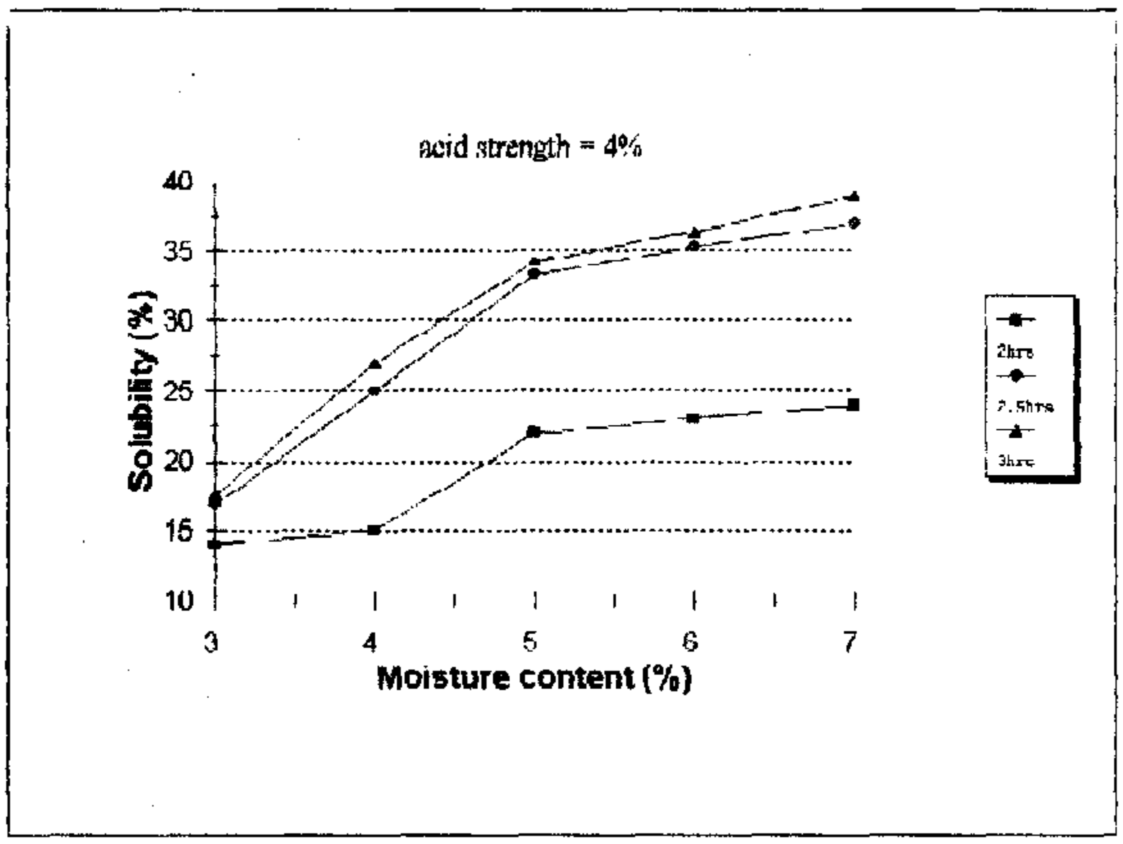


Fig. 6.1. Effect of Moisture Content on Conversion

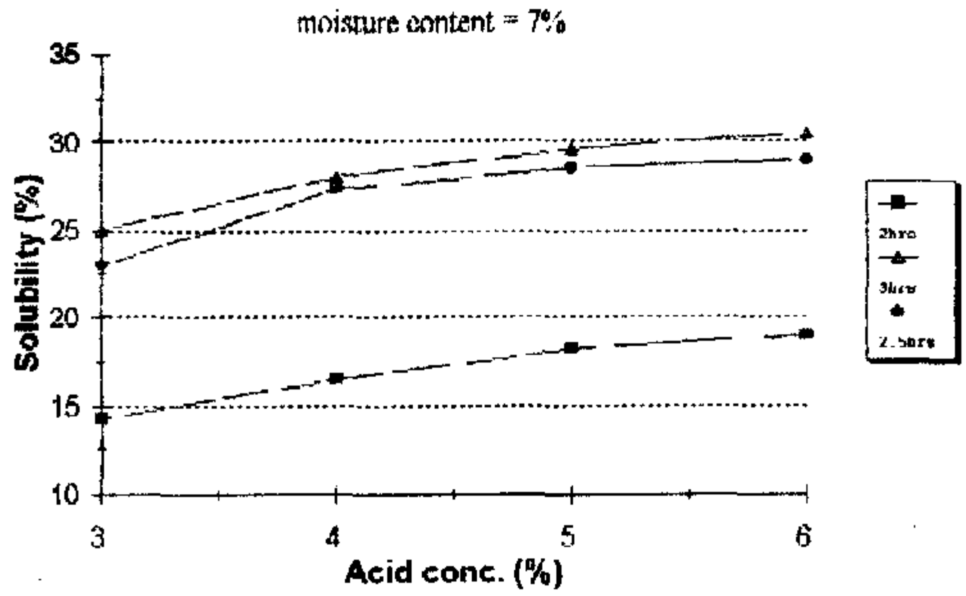


Fig. 6.2. Effect of Acid strength on Conversion

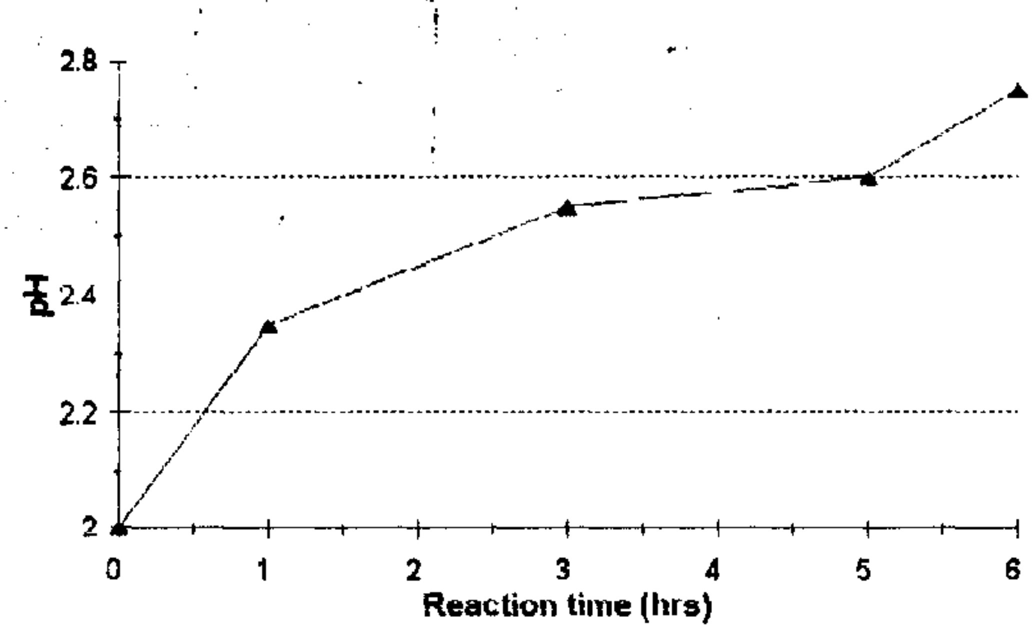


Fig. 6.3. Catalyst depletion with reaction time

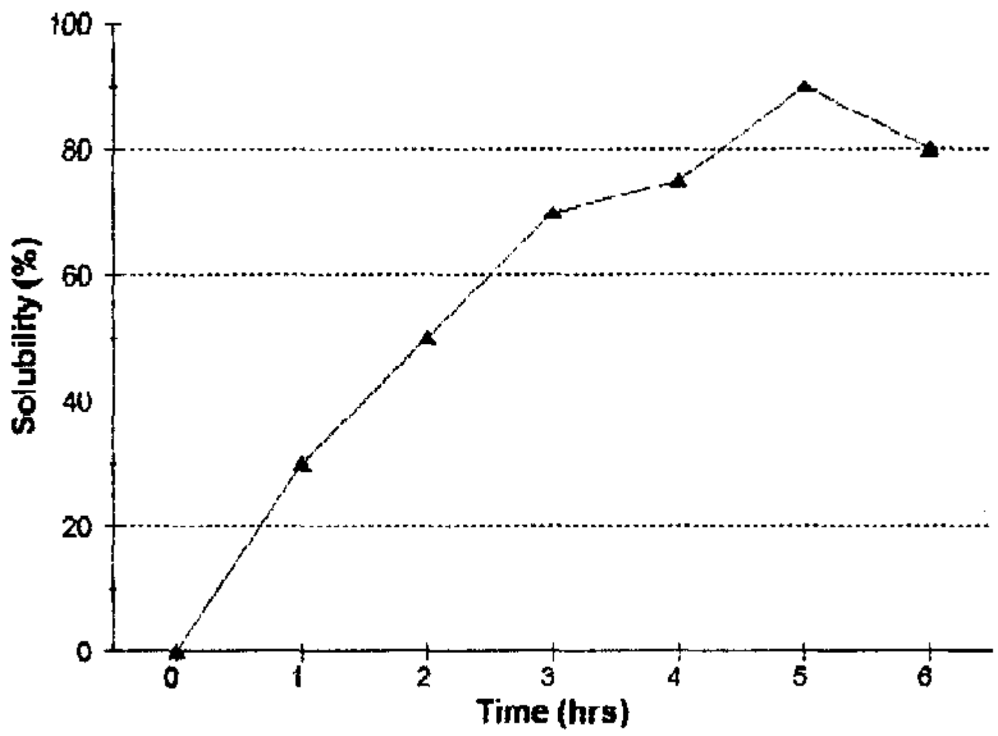


Fig. 6.4. Solubility plot for white dextrin production.

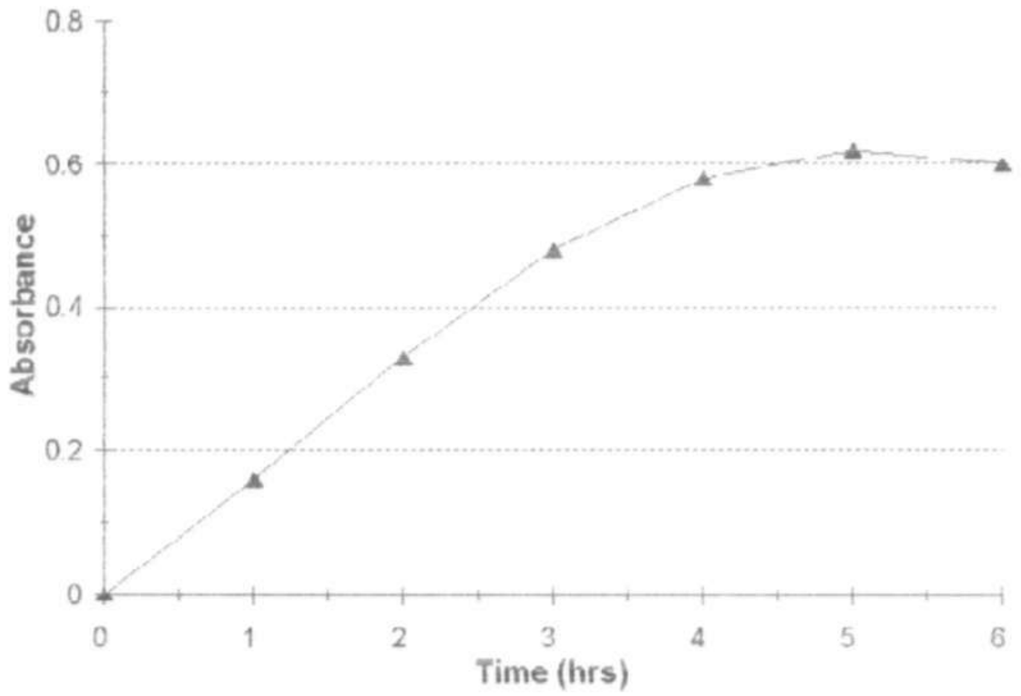


Fig. 6.5. Absorbance curve for white dextrin production.

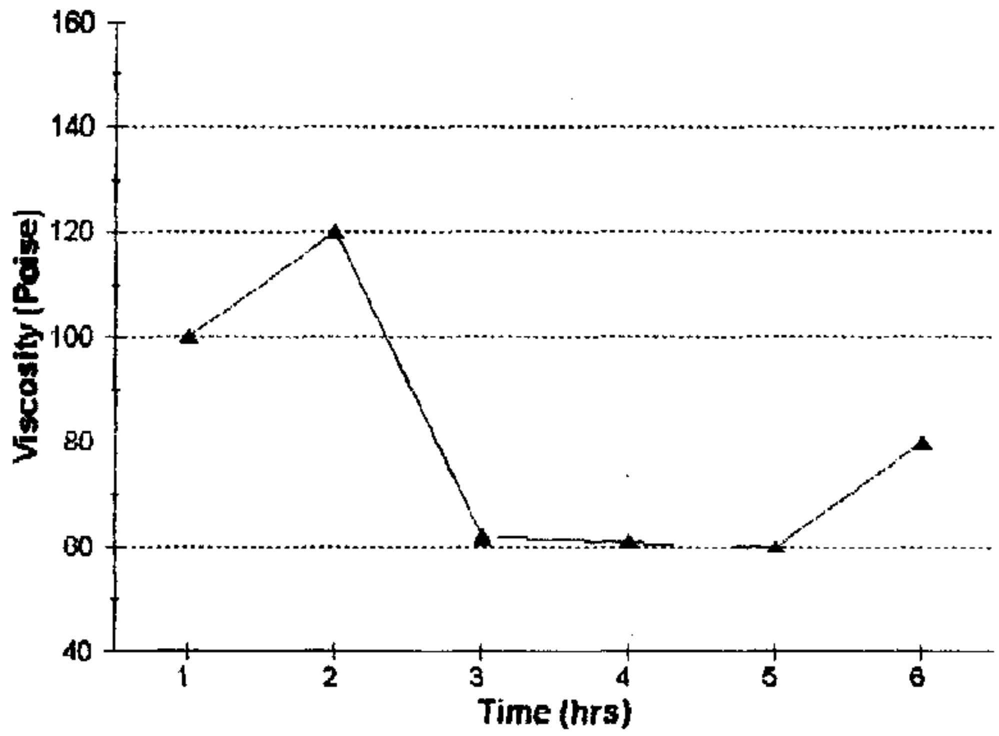


Fig. 6.6. Viscosity profile for white dextrin product.

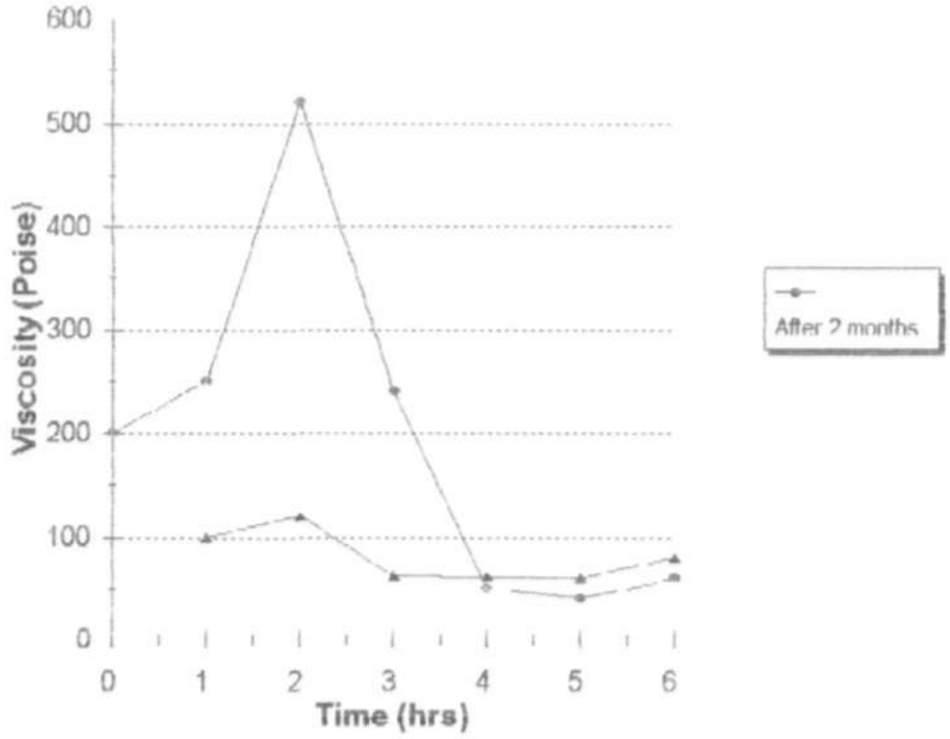


Fig. 6.7. Viscosity profile for product after 2 months.

CHAPTER SEVEN

CONCLUSION AND RECOMMENDATION

From the process study carried out, the following inferences can be drawn

- Higher percentages of moisture content in the starting material for dextrinization are undesirable.
- Effect of the acid (catalyst) concentration is only significant at the early stages of dextrinization.
- The concentration of the added acid catalyst influences the qualities of the resulting product.
- Spraying during acidification of the starting material promotes even distribution of the acid, reduces black speck formation and hence increases product yield and quality.
- The degree of conversion can be monitored by measuring the absorbance of the product.
- For white dextrin manufacture, optimum conversion period lies between 4 - 6 hours and the resulting products have stable viscosities.

Mathematical modelling of the process for white dextrin manufacture from starch reveals that the temperature of the starch material in the dextrinator is related to the temperature of the heating fluid (oil) by the equation:

$$-\ \Delta T_S = \frac{W}{H_S}\, t \quad \frac{H_O}{H_S}\, \Delta T_O \qquad (5.10)$$

The variation of the heating oil temperature with time is for the transient state is given by the equation

$$T_O = \frac{W \quad W^{\#}}{H_O}\, t + T_i \qquad (5.15)$$

- At steady state when the temperature is maintained constant the equation governing the system is given by

$$-\ \frac{W}{m_S}\, t = X_a\, C_{pc}\, (T_V \quad T_S) + (X_a \quad X_b)\, L \qquad (5.18)$$

- From the above equation it is evident that the residence time t of the starch material in the reactor is a function of the acid:starch ratio.
- The regression result obtained for the kinetic model indicates that the process is can be considered as a first order reaction.

Test run result of the fabricated dextrinator, shows that the equipment is capable of processing 4kg of starch, converting it into dextrin. The equipment would however need to be appropriately lagged for better performance.

RECOMMENDATION

Starch derived products go into almost every industry and because the application area is so large, the starch industry is vulnerable to attack from more specialised synthetic products. In the textile, foundry, paper-coating industries, synthetic polymers are presenting serious threat to starch products but those produced are still expensive. Much work is therefore, needed to be carried out to form products combining starch and synthetic polymers so that the best of both materials can be obtained. The future of the starch utilization in such industries can be bright if technical efforts continue to make use of the new synthetic materials.

Another area of further study would be to investigate the kinetics of the dextrinization process. To the best of my knowledge no data have been published on the rate constants of the acid converted pyrodextrin reactions. Hence it will be worthwhile to carry out a research on the subject.

Testing and optimization of the fabricated dextrinator in relation to the model developed should be carried out. Also an investigation into the continuous production process option, adopting the fluidized bed, should be carried out.

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APPENDICES

APPENDIX A1

Dextrin, starch glues importation for the year 1991.*

Country	Quantity (kg)	Value (₦)
Canada	762	15,250
U.S	18,819	135,374
China	2,786	20,312
India	100	6,353
Japan	39,772	596,588
S. Korea	9,778	160,000
Singapore	36,898	442,780
Taiwan	685,781	9,221,996
Belgium	153,474	3,454,657
Denmark	130,481	2,036,065
France	212,125	5,272,316
Germany	194,404	1,941,253
Ireland	375,000	445,709
Italy	74,423	877,967
Netherlands	40,966	273,938
Switzerland	780	32,064
U.K	273,913	4,094,047
Other Europe	3,150	377,984
Total	2,253,412	29,407,653

* Courtesy: Federal Office of Statistics, Kaduna.

APPENDIX A2

DEXTRIN APPLICATIONS*

Application	Suitable Dextrin		
	White	Canary	British Gum
Adhesives			
Bag bottom	x		x
Bag seam	x		
Bill posting	x		
Carton sealing	x	x	x
Cigarrette seam	x		
Container sealing	x	x	
Envelop gum		x	
Envelop seal		x	
Gummed tape		x	
Laminating paste	x	x	x
Library paste	x		
Lining paste	x		
Linoleum cement		x	
Paper tube and cone winding	x	x	
Postage stamp		x	
Ceramics			
Pottery and tile glazes	x		
Cord Polishing	x		
Crayons	x	x	
Detergents	x		
Dyes	x	x	
Feed blocks		x	
Flares and fireworks		x	
Food uses	x	x	
Foundaries			
Sand binders		x	
Core paste		x	
core wash		x	
Fuel briquettes		x	
Insecticides		x	

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Application	Suitable Dextrin		
	White	Canary	British Gum
Leather			
Adhesives	x		
Shoe Counter pastes	x		
Shoe polishes	x		
Linoleum		x	
Paints			
Cold water	x		
poster	x		
Paper			
Calender sizing	x		
Coatings	x		
Tub sizing	x		
Wall paper	x		
Patching plaster	x		
Plaster board	x		
Printing			
Ink vehicle			x
Textile	x		x
Protective colloids	x	x	
Textiles			
Cloth printing	x		x
Dyeing	x		x
Glass fibre sizing	x		
Felt sizing	x		
Finishing	x		x
Rug sizing			x
Stiffining	x		
Warp sizing	x		x
Welding rods		x	
Window shades	x		

* Adapted

APPENDIX B1

COMPUTER PROGRAM AND SIMULATION RESULT

Computer program (written in Clipper package) for the simulation of the model equation is given below and the output is plotted in Figure B1.

```
Program k:
        const   ti      =       25;
                        w       =       1500;


Procedure Heat
        local  i, ti = 25, w = 1500, ho = 11574, hs = 5024.4, tp = 25*60
        use data new
        for     i = 0 to 7200
                if(i < 1500, to = w/ho*i + ti, (wp = hs*(ts - ti)/(i - tp), to = (w -
                wp)*i/ho + ti))
                ts = ti+ w*i - ho*(to - ti)
                if mod(i,600) = 0
                        ? i/60, to, ts
                        append blank
                        time = i/60
                        data->f_to = to
                        data->f_ts = ts
                endif
        next    i
        return
```

APPENDIX B2

Figure B1 below is a plot of $-\ln(1-X_s)$ *against time to* verify the pertinence of the proposed rate law for the dextrinization process. The data ploted were obtained from the experiment carried out to produce white dextrin from cassava starch (Chapter three). It is assumed that Solubility values can be taken as an index of conversion.

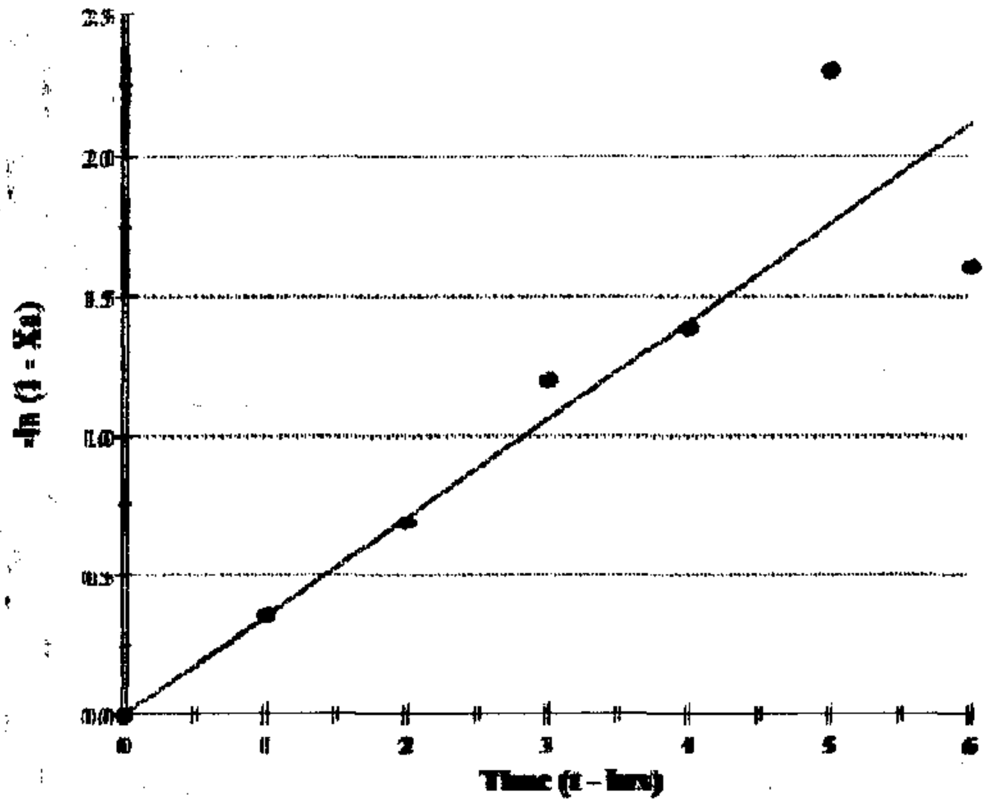

Fig B2: Plot of -ln(1-Xs) against time.

The regression analysis, also shown below, gives a value of 84% as the regression coefficient. This value is high enough to justify the model, this implies that the reaction can be considered as a first order reaction.

Regression Output:

Constant	0
Std Err of Y Est	0.3068429
R Squared	0.8480056
No. of Observations	7
Degrees of Freedom	6
X Coefficient(s)	0.3523077
Std Err of Coef.	0.0321659

R^2 = regression coeffient = 84%

APPENDIX C

DESIGN CALCULATIONS

Reactor Vessel

To calculate the minimum surface area of MS required for the fabrication:

$S = 2\pi rh + 3\pi r^2$ (1)

$V_R = \pi r^2 h + 2/3(\pi r^3)$ (2)

eliminate h

$$h = \frac{1}{\pi r^2}(V \quad \frac{2}{3}\pi r^3) \tag{3}$$

substituting for h in (1)

$$S = \frac{2}{r}(V \quad \frac{2}{3}\pi r^3) + 3\pi r^2 \tag{4}$$

differentiating

$$\frac{\partial S}{\partial r} = \frac{2V}{r^2} \quad \frac{8}{3}\pi r + 6\pi r \tag{5}$$

$$\frac{\partial S}{\partial r} = 0 \rightarrow \quad 2V \quad \frac{8}{3}\pi r^3 + 6\pi r^3 = 0$$

$$\therefore \quad r = (\frac{3V}{5\pi})^{\frac{1}{3}} \tag{6}$$

$$\frac{\partial^2 S}{\partial r^2} = \frac{4V}{r^3}\pi r^3 \quad \frac{8}{3}\pi r^2 + 6\pi = +ve \tag{7}$$

hence r has a minimum.

Volume = mass/density (8)

For a 4kg mass of starch

V = 4/1538

= $2.6 * 10^{-3} m^3$

substituting for V in eqn. (6)

$$r = \left(\frac{3 * 2.6*10^{3}}{5\pi}\right)^{\frac{1}{3}}$$

= 0.07918m = 7.92cm

Φ = 2r = 0.1584m =15.84cm

substituting for r in eqn. (3)

h = 0.07922m = 7.92cm

To allow for a tolerance factor of 26.5% for the diameter and 53% *for the height (this values are arbitrarilly chosen)*

Φ = 1.265 * 15.84 = 20.04cm

h = 1.53 * 7.92 = 12.1cm

Reactor Jacket

To determine the dimension of the reactor jacket the quantity of the heating fluid required must be known. This can be calculated if the heat duty is known.

Heat duty:

The quantity of heat required to heat the material (starch + *moisture) in the reactor vessel to a temperature of* 120°C (operating temperature) can be computed from the equation below

it is assumed that starch with 7% moisture content will be

$$Q = m_V C_{pV} \Delta T_V + m_S C_{pS} \Delta T_S + 0.07 m_S C_{pm} \Delta T_m + 0.07 m_S L \qquad (9)$$

used.

To determine the mass of the vessel material

$m_V = \rho_V V_V$

V_V = surface area * thickness

$= (2\pi rh + 3\pi r^2) * x$

$= 1.277*10^{-4} m^3$

$\therefore m_V = 7833 * 1.277*10^{-4}$

$= 1kg.$

From equation 9

$Q = 1*502.42*95 + 4*1256.1*95 + 0.07*4*4195.5*75 + 0.07*4*1.738*10^6$

$= 1.0997*10^6 J$

but this quantity of heat will also be supplied to the heating oil

$Q = m_o C_{po} \Delta T_o$

$m_o = Q/(C_{po} \Delta T_o) = 1.0997*10^6/(2.1355*10^3 * 95)$

$= 5.42kg$

from eqn. (8)

$V_o = 5.42/852 = 6.36*10^{-3} m^3.$

since the reactor will be inserted into the jacket, the volume of the jacket,

$V_j = V_R + V_o$

$= 1.23*10^{-2} m^3$

from eqn. (6) $r_j = 0.1329m$

$\Rightarrow \Phi_j = 0.2658m$

also from eqn.(3)

$h_j = 0.026m$

allowing for 7% tolerance to accommodate the contact *thermometer (about 3cm in diameter) that will be placed in the* annular space between the jacket and the reactor vessel

$\Phi_j = 1.07 * 0.2658$

$= 0.0285m \Rightarrow 28.5cm$

The total height of the vessel

$= r_j + h_j = 16.85cm.$

to accommodate the heater at the bottom of the reactor vessel this value will be increased by a factor of 100%

$\Rightarrow h_T = 2 * 16.85 = 33.7cm$

with this alteration the volume of oil that will now be required can be calculated from eqn. (2)

$V_j = \pi(0.1425)^2(0.1955) + 2/3\pi(0.1425)^3$

$= 0.01853m^3$

since the oil will occupy the annular space

$V_o = V_j - V_R$

$= 0.01853 - 0.00594$

$= 0.012596m^3 \Rightarrow 12.6litres.$

<u>Thermal Responce of Heating fluid</u>

From literature the average value of C_p of the oil for a temperature range 40-120°C is 2.1355kJ/kgK, this implies that for for a unit mass of the oil, 2.1355kJ would effect a degree rise in temperature .

Thermal energy supplied = Energy gained

$V I t = m C_p \Delta T$

$t = C_p / V\ I \quad \div m,\ \Delta T$ = unit increase

computing for the respective heater ratings:

for 2500W, $t = 2.1355/2.5 = 0.85$sec

for 2000W, $t = 2.1355/2 = 1.07$sec

for 1500W, $t = 2.1355/1.5 = 1.42$sec

for 1000W, $t = 2.1355/1 = 2.14$sec

for 500W, $t = 2.1355/0.5 = 4.27$sec.