An- Najah National University
Faculty of Graduate Studies

Production of Bio-Ethanol from Olive Pulp

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Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry, Faculty of Graduate Studies, An –Najah National University, Palestine.
2011

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DEDICATION

Admiration is dedicated to my beloved parents for endless supports and hopes, their great love and care are unforgettable, and to my husband and my son Mahmoud for their inspiration and understanding during difficult times.

Acknowledgement

Praise and thanks to Almighty Allah , the most merciful for assisting and directing me to the right path, without his help my effort would have gone astray. It would have been impossible to make this thesis without the help and support of several persons: First of all I would like to express my sincere gratitude to my supervisors Dr. Othman Hamed and Dr. Shehdeh Jodeh for their excellent guidance throughout this work and they gave me always time for discussions, full of encouragement and patience. I would like to thank, Mr. Maher Kharoof the director of Quality Control Manager in Jerusalem pharmaceuticals Co.Ltd, who was always concerned about my project and his support was very reviving. I really appreciate and thank Dr. Mohammed Al-Nuri for his consistent help me and support during my research. Finally, many thank to Mr .Omair Nabulsi, and Nafez Dweekat and Mohammad Asa’ad and Khaled Abu Nasser and Najwah Sobuh for their help during this work.

الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان:

Production of Bio-Ethanol from Olive Pulp

استخلاص الايثانول الحيوي من جفت الزيتون

أقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، و أن هذه الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل أي درجة علمية أو بحث علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

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Abstract

Jeft is a side product of oil industry. It consists of wood components: cellulose, hemicelluloses, lignin, and extracts. We succeeded in extracting about 40-45% cellulose from Jeft. The extracted cellulose was subjected to analysis by IR, Sugar contents, Intrinsic Viscosity, and Scanning Electronic Microscope. Results of these analyses indicate that cellulose present in Jeft has a microcrystalline structure with low IV (Intrinsic Viscosity). This property makes it ideal for drug and food applications. In this study, Jeft and extracted cellulose were subjected to hydrolysis to sugar by acids such as HCl and H_2SO_4. The purpose of the hydrolysis was to convert produced sugar to ethanol which could be used as auto fuel. Highest yield of 64% sugar was obtained using acid alone (concentrated HCl). The yield of sugar was enhanced to about 49.89% using diluted HCl (10%) with Lewis acid $ZnCl_2$ (20%) . These results indicate that cellulose obtained from Jeft has a microcrystalline structure. These results are consistent with the results obtained from Intrinsic Viscosity (IV), Scanning Electron Microscope (SEM), and Infrared spectroscopy (IR) studies which all showed that cellulose has a microcrystalline structure. Medium rate of hydrolysis could be attributed to the high crystallinity of cellulose which reduces the accessibility of hydrolyzing agent to cellulose structure.

CHAPTER ONE
INTRODUCTION

1.1 Background

The world is becoming highly dependent on fossil resources (fuel) such as petroleum derivatives, natural gas, and coal to fulfill its energy needs. Furthermore, a wide range of industrial polymers like synthetic resins, textiles, lubricants, fertilizers, etc. are also derived from petroleum resources. The consumption rate of fossil fuel in the world has increased by 50% in the period 1980–2004, and the consumption of fossil fuel is expected to increase to 600 X 10^{15} MT/annually by 2030.[1]

The availability of fossil fuel is continuously decreasing since they are not-renewable and the demand on it is continuously increasing. As a result of that, the prices of fossil fuel is also continuously increasing. Another major issue in increase of using fossil fuel are that more CO_2 is emitted to the atmosphere which enhances the possibility of global warming. Several evidences are available that this will have a major impact on our global climate.[2]These issues have stimulated the development of alternative renewable resources for fuels. Biomass is a prime candidate because it is the only renewable resource for the production of conventional fuel and petrochemicals products.[3-10]

1.2 Biomass

Biomass is a term used to define organic matters that are renewable and biodegradable. The definition includes crops and trees, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes and other waste materials such as olive industry waste (Jeft).[11] The annual production of biomass is about 1.7–2.0×10^{11} tons however, only 6×10^{9} tons are currently used for food and non-food applications.[12] Food applications are by far the most important (96.5−97%). The remainder is used in non-food applications, for example as a feedstock for the production of chemicals.

Biomass compositions depend strongly on its source. Generally, biomass consists of the following three components: [13]

1. Cellulose (38–50%).
2. Hemicelluloses (23–32%).
3. Lignin (15–25%).

1.2.1 Cellulose

Cellulose is a linear water-insoluble polymer consisting of several hundred up to tens of thousands of glucose units as shown in Figure 1.1 Cellulose is the most abundant biopolymer, it is produced in nature at approximately 2×10^{9} tons/year.[14]

Cellulose has no taste, odorless, hydrophilic, chiral and biodegradable. Upon acid hydrolysis , it breaks down into its glucose monomers. Usually hydrolysis is performed by treatment with diluted or concentrated acids at low or high temperature.

Cellulose is derived from D-glucose units, which condense through β (1→4) glycosidic bonds.[15-16] This linkage pattern contrasts with that for α (1→4)-glycosidic bonds present in starch, glycogen, and other carbohydrates. Cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues.

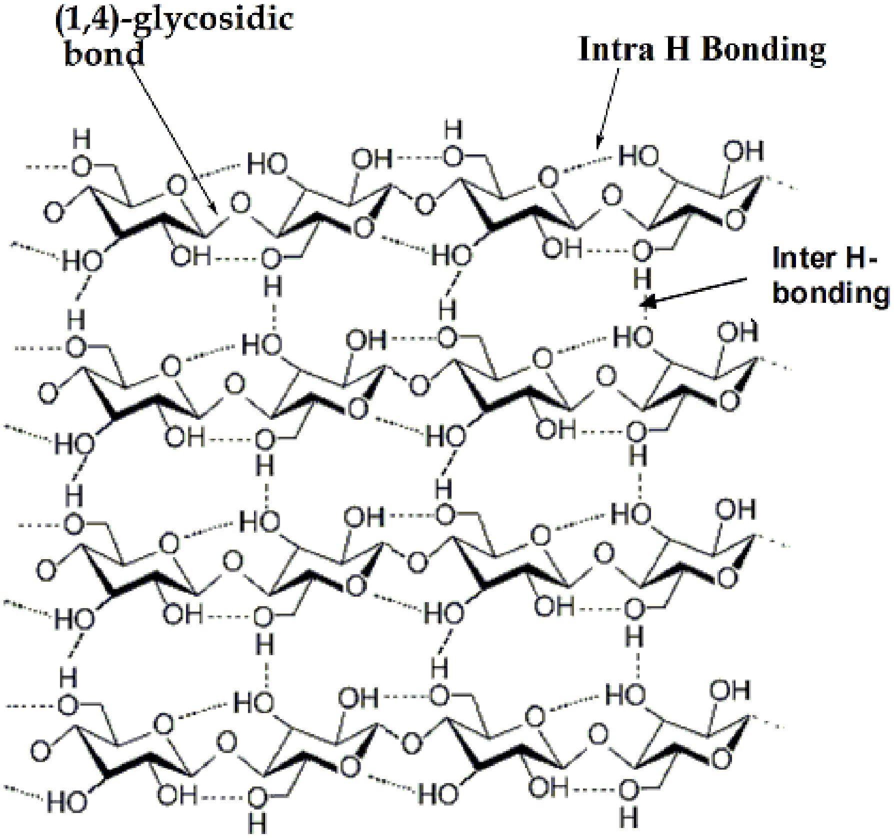


Fig (1.1): 3-D Structure of Cellulose Shows Intra- and Inter-H Bonding

The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen molecules on the same or on a neighbor chain, holding the chains firmly together side-by-side and forming microfibrils with high tensile strength.[15-17] This strength is important in cell walls, where the microfibrils are meshed into a carbohydrate matrix**,** conferring rigidity to plant cells.

1.2.1.1 Cellulose Applications

Cellulose and its derivatives have unlimited number of commercial applications among which the manufacture of paper and feedstock for unlimited number of commercial products.

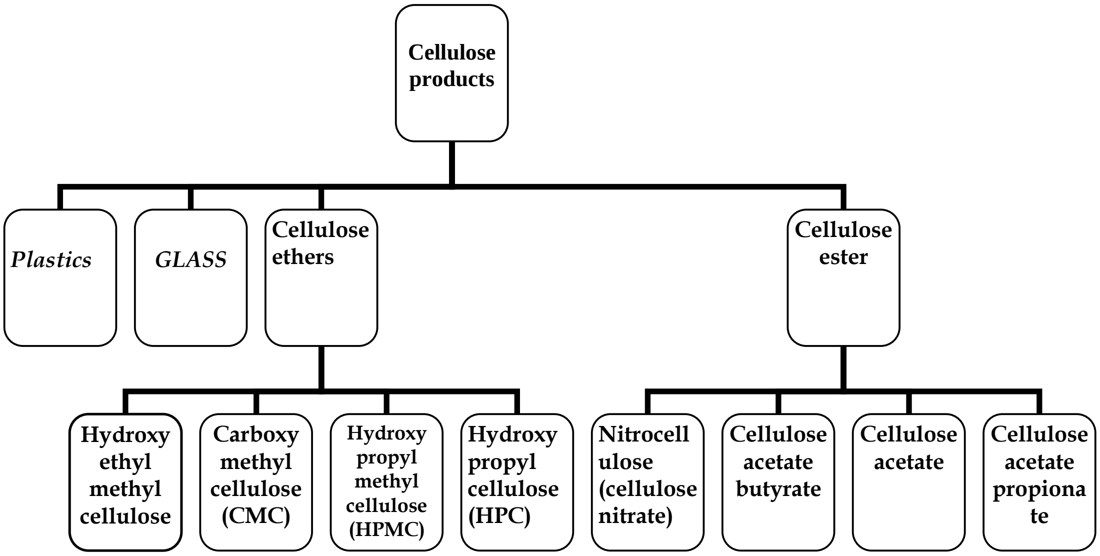


Fig (1.2): A Summary of Some of the Cellulose Derivatives

Cellulose also represents a very cheap and readily available substrate for the preparation of sugars, which may be used alone or microbially fermented to produce alcohols and other industrial chemicals. Other applications for cellulose is in laboratory as the stationary phase for thin layer chromatography.[18]

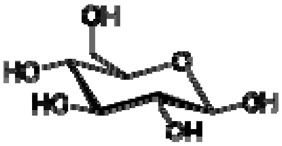
Cellulose fibers are also used in liquid filtration, sometimes in combination with diatomaceous earth or other filtration media, to create a filter bed of inert material.[19]

Another important application of cellulose is in making super absorbent sponges, water soluble adhesives, and binders which are usually made from cellulose derivatives such as methyl cellulose and carboxymethyl cellulose.[20]

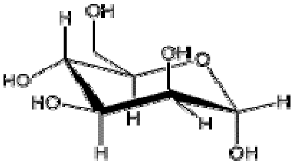
Cellulose also is the raw material in the manufacturing of nitrocellulose (cellulose nitrate) usually used in smokeless gunpowder and as the base material for celluloid used for photographic and movie films until the mid 1930s.[21]

1.2.2 Hemicellulose

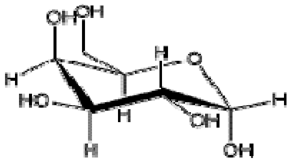
The second composition of biomass is hemicelluloses; it is a polymeric material, although it is lower in molecular weight than cellulose. Hemicelluloses consist of C6-sugars (glucose, mannose and galactose) and C5-sugars (mainly arabinose and xylose). The structure of these mono sugars are shown in **Figure 1.3.**



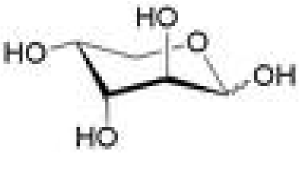
D- glucose



D- mannose



D- galactose



D- arabinose

D- xylose

Fig (1.3): Monomers of Hemicelluloses

Hemicellulose consists of shorter chains composed of about 200 sugar units of those shown in **Figure 1.3**. In contrast to cellulose, hemicellulose is branched, whereas cellulose is unbranched, and crystalline, strong, and resistant to hydrolysis. Hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid, base, or enzyme. [22] These enzymes are commercially important because they open the structure of wood for easier bleaching, the older methods of bleaching consume larger amounts of chemicals such as chlorine that are bad for the environment.

Enzymatic hydrolysis of hemicellulose is preferred since it does not produce toxic products.[23] Acid treatment is effective in solubilizing the hemicellulose components of biomass. Proper combinations of pH, temperature, and reaction time can result in high yields of sugars, primarily xylose.[24] Treatment with dilute acid at moderate temperatures (the first stage of acid hydrolysis) has proven to be an efficient means of producing a mixture of sugars with xylose as the major component. In the hydrolysis of hemicellulose with acid some toxic and non toxic by-products are generated, such as acetic acid, furfural, phenolic compounds.[25]

1.2.3 Lignin

The third component of biomass is lignin. It is actually not one compound but a mixture of several compounds. All are complex, amorphous, three-dimensional polymers that have in common a phenylpropane structure, that is, a benzene ring with a tail of three carbons.[26] It is highly cross-linked made as shown in **Figure 1.4**. It acts as glue, holding together the cellulose fiber and hemicellulose polymer. The building blocks of hemciellulose are shown previously in **Figure 1.4**.[27]

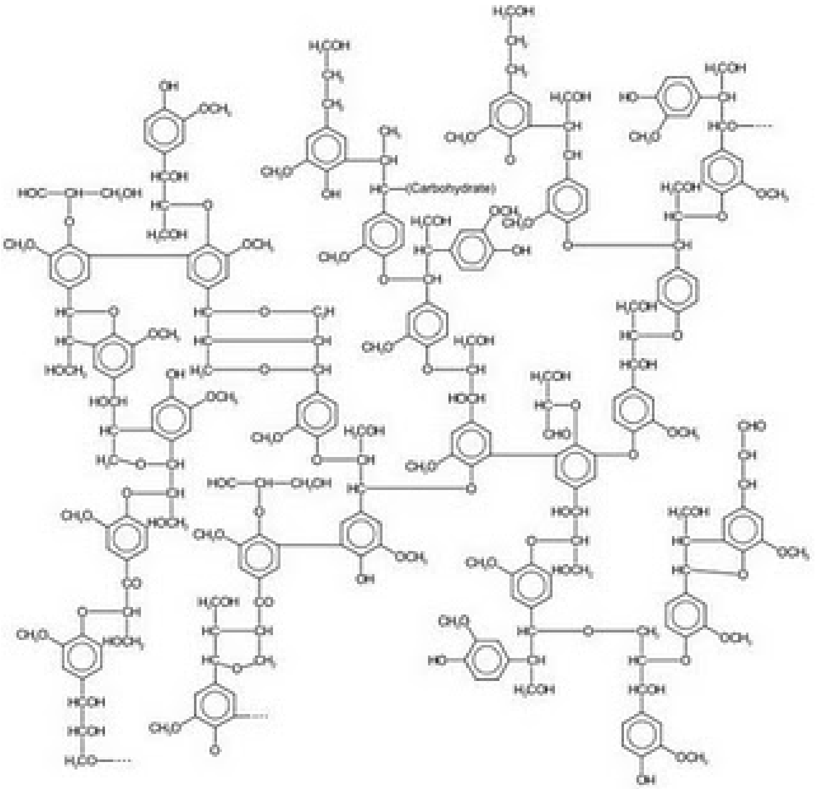


Fig (1.4): Possible Molecular Structures of Lignin

Lignin is very resistant to degradation, being held together with strong chemical bonds. It has hydroxyl, methoxy functional groups bondend to aromatics; because of these functional groups , lignin has high density of internal hydrogen bonds. It is bonded in complex and various ways to carbohydrates (hemicelluloses and cellulose) in wood. Lignins in their natural unprocessed form, they are so complex that none of them has ever been completely described, and they have average molecular weights that may reach 15,000 or more. One of the suggested models about the biosynthesis of lignin states that, lignin is formed by removal of water from sugars to create aromatic structures.[28]These reactions are not reversible. There are many possible monomers of lignin, and the types and proportions depend on the source in nature. Some typical monomers are shown **Figure 1.5**.

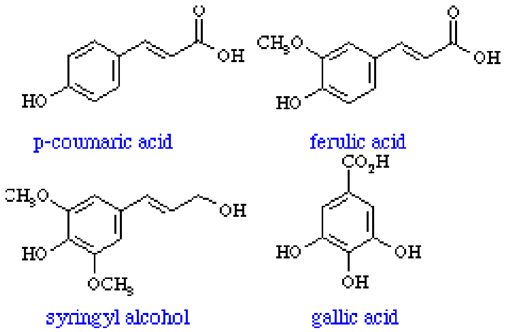


Fig (1.5): Typical Monomers of Lignin's

Sometimes lignin is isolated as a brown powder, but more often it is a gummy mixture of lignins with a wide range of molecular weights. [29]Lignin resists attack by most microorganisms, and anaerobic processes tend not to attack the aromatic rings at all. Aerobic breakdown of lignin is slow and may take many days.[30] Lignin is nature's cement along with hemicellulose to exploit the strength of cellulose while conferring flexibility. Lignin contains both hydrophilic and hydrophobic groups.

1.3 Conversion of Biomass into Value Added Products

The conversion of biomass into value added products with industrial applications has initiated an intensive research and development activities in various countries. As a result of that, unlimited number of novel products that have unlimited enormous applications in the industry have been developed. Among these are: Cellulose ester, Cellulose ethers, and nitrocellulose which are mentioned previously.

One of the most novel materials made from cellulose is Ethanol.

1.3.1 Ethanol from biomass

Ethanol can be produced from lignocellulosic biomass by several ways. Ethanol has a number of industrial, fuel, and fuel additives uses. When added to fuel it boosts octane number and reduces pollution. combination of gasoline and ethanol is the well-known commercial product called "gasohol." It has been proposed to eliminate gasoline completely from the fuel to burn ethanol alone.[31] Such fuel would produce considerably less air pollution by not forming as much carbon monoxide or hydrocarbon emissions. Furthermore, gasoline is produced from crude oil; which fluctuates in price and availability. As mentioned earlier, it has been estimated that about 1×10^{9} tons biomass wastes are produced every year. This amount exceeds the total amount of crude oil consumed per year. Consequently, cellulose and hemicellulose represent a readily available potential source for ethanol. Among the techniques proposed for the production of fuel grade ethanol include the hydrloysis of cellulose and hemicellulose to produce sugars which is then fermented to ethanol.

An intensive research in the area of cellulose hydrolysis has resulted in a novel concept known as biorefining.[27, 32-33] A biorefinery is a facility concerned with conversion of biomass into fuels, and chemicals .[34] Example on that is the American National Renewable Energy Laboratory

(NREL). The process of the biorefinary could be summarized into the following two stages:

1. Separation of the biomass into its components (cellulose, hemicelluloses, lignin, proteins, pure plant oil, minerals, fine chemicals and pharmaceutical compounds) in a primary fractionation/de-polymerization unit. Typical technologies applied in this stage are traditional separation processes like filtration, solvent extraction and distillation.

2. Conversion of the intermediate fractions to valuable end products (e.g., bio-fuels) and chemical intermediates is performed in a secondary refinery process. Examples of chemical intermediates are conventional intermediates, such as alcohols or acids, and platform chemicals.

A schematic representation of a biorefinery process is shown in **Figure 1.6**.

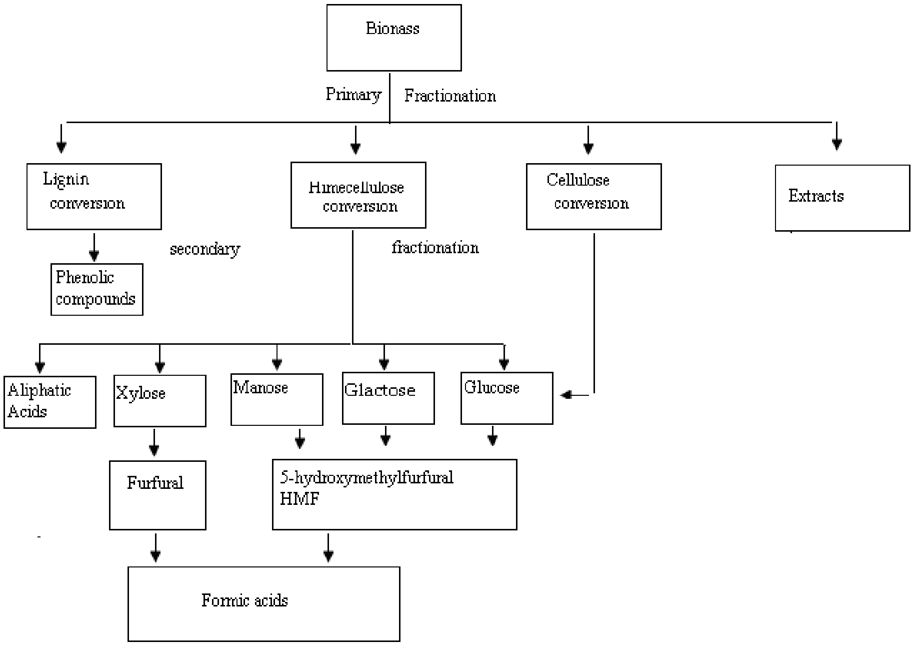


Fig (1.6): Scheme Shows the Concept of a Biorefinery.

An important application of ethanol is as a fuel to power Direct-ethanol fuel cells (DEFC) in order to produce electricity and by-products (water) and carbon dioxide (CO_2).[35] A vehicle using a DEFC was used in the Shell Eco-Marathon 2007 by a team from Offenburg (Germany)which achieved an efficiency of 2716 kilometers per liter (6388 miles per gallon).

Another important application of ethanol is that, it is used as a feedstock for chemicals such ethyl halides, ethyl esters, diethyl ether, acetic acid, butadiene, and ethyl amines.

Ethanol is also used in medical wipes and in most common antibacterial hand sensitizer gels at a concentration of about 62% (percentage by volume) as an antiseptic. Ethanol kills organisms by denaturing their proteins and dissolving their lipids and is effective against most bacteria and fungi, and many viruses, but is ineffective against bacterial spores.[36]

Ethanol can be used as an antidote for poisoning by other toxic alcohols, in particular methanol and ethylene glycol. Antidote is a substance which can counteract a form of poisoning. Ethanol competes with other alcohols for the alcohol dehydrogenase enzyme, preventing metabolism into toxic aldehyde and carboxylic acid derivatives.[37]

Scope of the Thesis

Jeft which is one of the residues of olive oil industry attracts scientists and researchers with a greater challenge to utilize and convert this waste material into useful and low-cost marketable products. Jeft consists of four main components: extractives, hemicelluloses, lignin (polyphenols), and mainly carbohydrate (specifically cellulose). The last three components have unlimited number of commercial applications as shown in the introduction.

About 66% of the volume coming out from the olive mill is olive pulp; in another word almost 40% of the olive is carbohydrate (cellulose).

Every year there is about 35.0 thousand MT of Jeft produced in Palestine alone, which contains about 20.0 million pounds of carbohydrates? This amount of carbohydrate is more than enough to supply the existing number of factories and research institutes in Palestine with their requirements of cellulose and fine chemicals.

The primary objective of this thesis is to define optimum reagents, and reaction conditions for the conversion of olive waste (Jeft) or cellulose extracted from Jeft into monomeric sugar glucose. In this project ,the following process for conversion of Jeft or cellulose to glucose will be evaluated. The process involves several treatments that together form a unique reaction network.

These reactions could be summarized as follows:

1. Activation

Activation could be accomplished by pretreatment process which includes solubilization and separation of one or more of the four major components of Jeft (hemicelluloses, cellulose, lignin, and extractives) to make the remaining solid biomass more accessible to hydrolysis.

2. Hydrolysis

In this process, acids or enzymes or a combination of both are used to catalyze the conversion complex polysaccharides in Jeft to simple sugar. After the pretreatment process, Jeft will be subjected to hydrolysis by one of the following two processes acid (dilute and concentrated) or enzymatic.

a) Acid Hydrolysis

There are two acid hydrolysis processes commonly used: dilute acid and concentrated acid. The dilute acid process is conducted under high temperature and pressure with a reaction time in the range of seconds or minutes. The concentrated acid process is relatively carried out at mild temperatures and low pressure. Reaction times are typically much longer than for dilute acid.

The dilute acid process involves a solution of about 1% sulfuric acid at a high temperature (about 215°C).

Concentrated acid hydrolysis, include treatment with concentrated sulfuric acid followed by a dilution with water to dissolve and hydrolyze or convert the substrate into sugar. This process provides a complete and rapid conversion of cellulose to glucose and hemicelluloses to 5-carbon sugars. The concentrated acid process uses a solution of 70% sulfuric acid at room temperature for 2 to 6 hours. The low temperature and pressure minimizes the degradation of sugars.

In the current work, the two acid process will be tried and the one, produces higher yield and is more economic, will be adopted.

b) Enzyme Hydrolysis

In this process ,biological hydrolysis of cellulose will be carried out using enzyme. Enzyme treatment is expected to have the potential to improve conversion efficiencies and production economics.

For enzymes to work efficiently, they must obtain access to the molecules to be hydrolyzed. This requires some kind of pretreatment process to remove hemicelluloses and break down the cellulose or removal of the lignin to expose the cellulose and hemicelluloses molecules to enzyme.

After the process is evaluated, conditions for conversion of Jeft into monomeric sugar glucose will be optimized to obtain maximum yield at low cost.

The Future work will be:

1. Scale up the bench process into a large scale process.
2. Determine the economic viability of the developed process.
3. Develop a single step process for converting Jeft into ethanol.

CHAPTER TWO
EXPERIMENTAL

2.1 General experimental

All reagents were purchased from Aldrich Chemical Company and used without any further purification unless otherwise specified. Kraft pulping was performed using a high Parr Reactor model: Buchiglasuste, bmd 300. Fresh Jeft was obtained from an olive factory from the city of Tulkarm in Palestine and stored in a freezer at about -5 ^{o}C to 0 ^{o}C. IR analysis was performed on. HPLC analysis was performed on L-2400-2-Lachrom Flite HPLC System connected to a refractive index (R I) detractor and equipped with an Amino column with dimensions of 150 x 4.6mm. Mobile solvent used in the analysis composed of acetonitrile and a buffer solution of NaH_2PO_4 / Na_2HPO_4 (1.15 gm) in water (1 L) at ratio of 80:20.

Cellulose was extracted from Jeft then converted into sugar using the following methods combined or separated:

1. Extraction of residual materials
2. Pulping
3. Acid Hydrolysis

2.2 Removal of Extractable Materials from Jeft

Residual materials were removed using soxhlet extraction method. Jeft (200.0 g, OD (oven dry) weight 80%) was placed in a round bottom flask (1.0 L) of soxhlet extractor and subjected to extraction with ethyl acetate (500 mL). The extraction was continued for about 12 hr. Then ethyl acetate solvent was removed under reduced pressure using rotary evaporator to afford 10.0 g (10% based on Jeft weight) of pale yellow residual liquid, which was saved for future analysis.

2. 3 Pulping

Pulping method involves removal of lignin and hemicelluloses from Jeft. The pulping was conducted in a high Parr Reactor of one liter capacity. Jeft (100 g) and a solution of sodium hydroxide (25.0 g) and sodium sulfide (11.05 g) in 260 mL water were placed in a stainless-steel reactor vessel, which was then attached to the high barr reactor. The vessel and contents were then heated by an outer jacket containing electrical wires. The vessel contents were mixed with a mixer that is rotating in the reactor via a motor that was connected through a rotary axle to a control unit containing the required instruments for the measurement and control of the pressure and the temperature. The temperature was measured with a thermometric probe that was accommodated inside the reactor. The reactor was pressurized to 50 psi using N_2 gas , and heated to 130-160 ^oC gradually over a period of 30 min. The contents of the reactor were kept under these conditions for about 2 hr. At the end of the pulping process, produced pulp (cellulose left over after the pulping process) was removed from the reaction mixture by suction filtration, washed several times with tap water, air dried at room temperature, and stored in plastic bags for further use.

Yield was calculated according to equation 2.1 by dividing the dry weight of the produced pulp by the dry weight of the starting Jeft.

$$\%\text{Yield} = \frac{\text{Weight of produced pulp (g)}}{\text{Weight of Used Jefft (g)}} * 100\ \% \qquad \text{Eq 2.1}$$

Under the above pulping conditions ,the weight of cellulose obtained from 100.0 g Jefft was 46.5 g; accordingly the yield was 46.5 %.

Obtained Cellulose was subjected to analysis by IR, HPLC, and electronic microscope. Refer to the Result and Discussion chapter for IR results and electronic microscope images.

2.3.1 Analysis of Purified Cellulose by HPLC

Sample of pulped cellulose (1.0 g) was hydrolyzed by conc. sulfuric acid (50 ml) at 50 ^{o}C and produced clear pale yellow solution was analyzed by HPLC. Results are summarized in chromatogram shown in **Chapter 3 (Fig 3.2)**.

2.4 Acid Hydrolysis of Extracted Cellulose and Jefft

Hydrolysis was performed on a raw material of Jeft after and before extraction and on cellulose extracted from Jeft by pulping.

Acid hydrolysis was performed using the followings:

1. Diluted acid
2. Concentrated acid
3. Mixture of acid and catalyst.

2.4.1 Hydrolysis by Diluted Acid

Two types of acid were used in this study: sulfuric acid and hydrochloric acid

2.4.1.1 Hydrolysis by Diluted H_2SO_4

Cellulose (pulp) or raw material of Jeft (1.0 g) was placed in a round bottom flask (100 mL) fitted with a condenser and a magnet stirrer bar. To the flask contents, was added 10 mL of diluted H_2SO_4. Hydrolysis was performed at various conc. of H_2SO_4 ranging from 3% to 7%. Produced mixture was stirred at various temperatures (room temperature to 90 ^{o}C) for various periods of time ranging from 2 hr to 24 hr. After the period of time was over, the reaction mixture was neutralized with 25% NaOH solution. Produced solution was filtered using simple filtration method, and then filtered again through a special filter for HPLC, clear filtrate was then subjected to analysis by HPLC to determine the amount of produced sugar using pre-prepared calibration curve. Volume of filtrate obtained by gravity filtration was recorded and used in the calculation of sugar weight and percentage.

Results from this experiment are summarized in **Tables 2.1, 2. 2**.

Table (2.1): Results for Hydrolysis of Jeft Using 3% H_2SO_4

Hydrolysis time (hr)	Concentration of sugar (g/ml)
2	$9.724 X10^{-05}$
4	$3.066 X10^{-05}$
6	nothing
8	nothing

Table (2.2): Results for Hydrolysis of Jeft Using 7% H_2SO_4

Hydrolysis time (hr)	Concentration of sugar (g/ml)
2	$3.445X10^{-03}$
4	$3.018X10^{-03}$
6	$1.005 X10^{-03}$
8	$2.038 X10^{-03}$

2.4.1.2 Hydrolysis by Diluted HCl

The same procedure was followed as that for hydrolysis by diluted H_2SO_4 except that, in this experiment, hydrolysis was performed at various conc. of diluted HCl acid that is ranging from 2% to 10%**.** Hydrolysis was performed at various temperatures (room temperature to 90 ^oC) and for various periods of time ranging from 2 hr to 24 hr. Results are summarized in **Tables 2.3 , 2.4, 2.5, 2.6, and 2.7.**

Table (2.3): Results for Hydrolysis of Jeft Using 3%HCl

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)
2	$2.178 X10^{-02}$
4	$2.268 X10^{-02}$
6	$2.480X10^{-02}$
8	$1.887 X10^{-02}$

Table (2.4): Results for Hydrolysis of Jeft Using 7%HCl

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)
2	$1.832 \text{X}10^{-02}$
4	$1.344 \text{X}10^{-02}$
6	$0.8865 \text{X}10^{-02}$
8	$0.619\text{X}10^{-02}$

Table (2.5): Results for Hydrolysis of Jeft Using 5%HCl

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Sugar (g)	Conversion %
2	$9.66\text{X}10^{-02}$	0.1207	12.07
3	$5.99 \text{X}10^{-02}$	0.08396	8.39

Table (2.6): Results for Hydrolysis of Washed Jeft Using 5%HCl

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	$7.10 \text{X}10^{-02}$	.0675	6.753
3	$6.68 \text{X}10^{-02}$	0.06015	6.015

Table (2.7): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using 5% HCl

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	$6.88\text{X}10^{-02}$	.0963	9.632
3	$6.52 \text{X}10^{-02}$	.09135	9.135

2.4.2 Procedure for Hydrolysis by Concentrated Acid

2.4.2.1 Hydrolysis by Concentrated sulfuric acid

Cellulose or raw material of Jeft (1.0 g) was placed in a round bottom flask (100 mL) fitted with a condenser and a magnet stirrer bar. Then 10 mL of 70% H_2SO_4 were added To the flask. The mixture was stirred at room temperature for various periods of time ranging from 2 hr to 24 hr. At the end of the reaction, the mixture was neutralized with 25% NaOH solution to pH 7. Produced solution was filtered using regular simple filtration method then through special filter for HPLC and subjected to analysis by HPLC. The Produced filtered solution was analyzed by HPLC and the peaks were analyzed to determine sugar concentration using the pre-prepared calibration curve.

Results from this experiment are summarized in **Table 2.8 .**

Table (2.8): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using Concentrated H_2SO_4

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)
2	0.301×10^{-04}
4	4.84×10^{-03}
6	2.58×10^{-04}

2.4.2.2 Hydrolysis by Concentrated HCl

The same procedure was followed as the one before for hydrolysis by H_2SO_4, except that in this experiment, conc. HCl was used**.** It was performed on extracted cellulose. Results from this experiment are summarized in **Tables 2.9, 2.10, 2.11.**

Table (2.9): Results for Hydrolysis of Jeft Using Concentrated HCl

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	25.61×10^{-02}	0.5187	51.87
4	28.82×10^{-02}	0.4610	46.10

Table (2.10): Results for Hydrolysis of Washed Jeft Using Concentrated HCl

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	28.24×10^{-02}	0.6496	64.96
4	27.48×10^{-02}	0.4248	42.48

Table (2.11): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using Concentrated HCl

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	$25.61X10^{-02}$	0.6260	62.60
4	$32.94X10^{-02}$	0.5889	58.89

2.4.3 Procedure for Hydrolysis by a Mixture of Acid and a Catalyst

Cellulose or raw material of Jeft (1.0 g) was placed in a round bottom flask (10 mL) fitted with a condenser and a magnet stirrer bar. To the flask contents was added 10 mL diluted HCl and catalyst such as zinc chloride or magnesium chloride. Hydrolysis was performed at various conc. of HCl ranging from 2% to 10% and various concentration of catalyst ranging form 10-20%. The reaction mixture was stirred at various temperatures (room temperature to 90 ^{o}C) for various periods of time was applied ranging from 2 hr to 24 hr. At the end of the reaction, reaction mixture was neutralized with 25% NaOH solution to pH 7. The reaction mixture was filtered by a hot filtration then another filtration by special filter for HPLC and then subjected to analysis by HPLC to determine sugar concentration using pre-prepared calibration curve. Results from this experiment are summarized in **Tables:- 2.12 2.13, 2.14, 2.15, 2.16, 2.17, 2.18, 2.191, 2.20, 2.21, 2.22, 2.23, 2.24, 2.25, 2.26, 2.27, 2.28, 2.29, 2.30, 2.31, 2.32, 2.33, 2.34, 2.35.**

Table (2.12): Results for Hydrolysis of Jeft Using a Mixture of 5% HCl and 10%ZnCl$_2$

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	.49 X10^{-02}	0.0103	1.033
1	6.40X10-^{02}	0.1408	14.08
2	9.244 X10^{-02}	0.1894	18.94

Table (2.13): Results for Hydrolysis of Washed Jeft using a Mixture of HCl (5%) and ZnCl$_2$ (10%)

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	7.910X10^{-02}	0.1423	14.23
1	9.33 X10^{-02}	0.1865	18.65
2	10.05 X10^{-02}	0.2110	21.10

Table (2.14): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 5% HCl and 10% ZnCl$_2$

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	5.924 X10^{-02}	0. 6013	6.01
1	7.182 X10^{-02}	0.1221	12.2
2	9.84 X10^{-02}	0.2066	20.6

Table (2.15): Results for Hydrolysis of Jeft Using a Mixture of 10%HCl and 10% ZnCl$_2$

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
0.5	14.07X10^{-02}	0.2251	22.51
1	16.14 X10^{-02}	0.3201	32.0
2	21.67 X10^{-02}	0.4552	45.52

Table (2.16): Results for Hydrolysis of Washed Jeft Using a Mixture of 10%HCl and 10%ZnCl$_2$

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
0.5	10.95X10^{-02}	0.2059	20.59
1	15.36 X10^{-02}	0.2996	29.96
2	16.24X10^{-02}	0.3493	34.93

Table (2.17): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 10% HCl and 10% $ZnCl_2$

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
0.5	13.03 X10^{-02}	0.2411	24.11
1	14.15X10^{-02}	0.3255	32.55
2	21.51 X10^{-02}	0.4839	48.93

Table (2.18): Results for Hydrolysis of Jeft Using a Mixture of 5%HCl and 20% $ZnCl_2$

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	14.31 X10-02	0.2720	27.20
1	16.16 X10-02	0.3393	33.93
2	23.39 X10-02	0.4561	45.61

Table (2.19): Results for Hydrolysis of Washed Jeft Using a Mixture of 5%HCl and 20% $ZnCl_2$

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	8.43X10-02	0.1264	12.64
1	13.34 X10-02	0.2802	28.02
2	23.93X10-02	0.3111	31.11

Table (2.20): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 5% HCl and 20% $ZnCl_2$

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	Conversion %
.5	15.21 X10-02	0.3194	31.94
1	23.18X10-02	0.3477	34.77
2	23.41 X10-02	0.4917	49.1

Table (2.21): Results for Hydrolysis of Jeft Using a Mixture of 10 % HCl and 20% $ZnCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	8.43 X10-02	0.1264	12.64
1	23.15 X10-02	0.322	30.22
2	23.93X10-02	0.3111	31.11

Table (2.22): Results for Hydrolysis of Washed Jeft Using a Mixture of 10% HCl and 20% $ZnCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	16.01 X10-02	0.3204	32.04
1	19.87 X10-02	0.3179	31.79
2	23.75 X10-02	0.4989	49.89

Table (2.23): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 10% HCl and 20% $ZnCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	Conversion %
.5	14.34X10-02	0.2438	24.38
1	14.44 X10-02	0.3322	33.22
2	18.30X10-02	0.3661	36.61

Table (2.24): Results for Hydrolysis of Jeft Using a Mixture of 5%HCl and 10%$CaCl_2$

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	0.0883X10-02	0.18549	18.549
1	11.16 X10-02	0.2344	23.44
2	13.10 X10-02	0.2621	26.21

Table (2.25): Results for Hydrolysis of washed jeft using a Mixture of 5%HCl and 10%$CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	6.90 X10-02	0.1453	14.5
1	8.0865 X10-02	0.1698	16.98
2	9.053 X10-02	0.19013	19.013

Table (2.26): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 5% HCl and 10 %$CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	11.948 X10-02	0.1656	16.56
1	12.4603 X10-02	0.2330	23.30
2	8.280 X10-02	0.26167	26.166

Table (2.27): Results for Hydrolysis Results Jeft Using a Mixture of 10% HCl and 10% $CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	8.2739 X10-02	0.15307	15.3006
1	9.175 X10-02	0.1835	18.35
2	9.6717 X10-02	0.19013	19.013

Table (2.28): Results for Hydrolysis of Washed from Jeft Using a Mixture of 10% HCl and 10% $CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
1	5.9223X10-02	0.0947	9.4746
2	13.251 X10-02	0.2452	24.52

Table (2.29): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 10%HCl and 10% $CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	8.123 X10-02	0.1218	22.46
1	9.46 X10-02	14.67	29.35
2	11.38 X10-02	0.1702	34.144

Table (2.30): Results for Hydrolysis of Jeft Using a Mixture of 5% HCl and 20% $CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	26.688 X10-02	0.13095	13.095
1	7.482 X10-02	0.20251	20.25
2	10.94 X10-02	0.4003	40.03

Table (2.31): Results for Hydrolysis of Washed Jeft Using a Mixture of 5%HCl and 20% $CaCl_2$.

Hydrolysis Time (hr)	Concentration of Ssugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	24.19 X10-02	0.1786	17.86
1	11.906 X10-02	0.26612	26.61
2	20.45 X10-02	0.3068	30.68

Table (2.32): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 5%HCl and 20% $CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	1.682 X10-02	0.2234	0.2234
1	11.75 X10-02	0.2246	22.46
2	13.614X10-02	0.3196	31.96

Table (2.33): Results for Hydrolysis of Jeft using a Mixture of 10% HCl and 20% $CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	7.07 X10-02	0.1520	15.20
1	14.522 X10-02	0.2686	26.86
2	20.47 X10-02	0.3275	32.75

Table (2.34): Results for Hydrolysis of Washed Jeft Using a Mixture of 10% HCl and 20% $CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	14.839X10-02	0.2335	23.35
1	15.56 X10-02	0.2596	25.96
2	21.402 X10-02	0.4494	44.94

Table (2.35): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 10% HCl and 20% $CaCl_2$.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
.5	26.57 X10-02	0.1170	11.70
1	14.11X10-02	0.1411	14.11
2	5.70 X10-02	0.5049	50.498

2.4.4 Procedure for Hydrolysis by a Mixture of Acid and Hydrogen Peroxide

2.4.4.1 Procedure for Hydrolysis by a Mixture of Dilute Acid and Hydrogen Peroxide

To 1.0 g of Cellulose or raw material of Jeft in a round bottom (100 mL) flask fitted with a condenser and a magnetic stir bar was added 10 mL of an aqueous solution containing 5%HCl and 2.5%hydrogen peroxide. Hydrolysis was performed at 60 °C for various periods of time ranging from 2 hr to 4 hr. After each period of time was over, the reaction mixture was neutralized with25% NaOH solution to pH 7. The solution was filtered using hot filtration then through special filter for HPLC and then subjected to HPLC analysis to determine produced sugar using pre-prepared calibration curve.

Results from this experiment are summarized in **Tables:-2.36, 2.37, 2.38**.

Table (2.36): Results for Hydrolysis of Jeft Using a Mixture of 5% HCl and 2.5% H_2O_2.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	7.07 X10-02	0.990	9.90
4	10.11 X10-02	0.1871	18.71

Table (2.37): Results for Hydrolysis of Washed Jeft Using a Mixture of 5% HCl and 2.5% H_2O_2.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	8.84X10-02	0.1104	11.04
4	0.14195 X10-02	0.1632	16.32

Table (2.38): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 5%HCl and 2.5% H_2O_2.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	9.26X10-02	0.06943	6.943
4	9.40 X10-02	0.1223	12.23

2.4.4.2 Procedure for Hydrolysis by a Mixture of Concentrated Acid and Hydrogen Peroxide

To 1.0 g of Cellulose or raw material Jeft in a round bottom (100 mL) flask fitted with a condenser and a magnet stirrer bar, then was added 10 mL of an aqueous solution of conc. HCl and hydrogen peroxide (2.5%). Hydrolysis was performed at room temperature for various periods of time ranging from 2 hr to 4 hr. After the reaction time was over, the reaction mixture was neutralized with 25% NaOH solution to pH = 7. The reaction mixture was heated to dissolve the inorganic precipitate then filtered while hot by gravity filtration. Then through special filter for HPLC**.** The filtrate was subjected for HPLC Analysis to determine the amount of sugar using pre-prepared calibration curve**.**

Results from this experiment are summarized in **Tables:-2.39, 2.40, 2.41.**

Table (2.39): Results for Hydrolysis of Jeft Using a Mixture of Conc. HCl and 2.5% H_2O_2.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	26.44X10-02	0.5157	51.57
4	25.113 X10-02	0.4269	42.69

Table (2.40): Results for Hydrolysis of Washed Jeft Using a Mixture of Conc. HCl and 2.5% H_2O_2.

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	22.55X10-02	0.3947	39.47
4	19.74 X10-02	0.3159	31.159

Table (2.41): Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of Conc. HCl and 2.5% H_2O_2.

H2O2

Hydrolysis Time (hr)	Concentration of Sugar (g/ml)	Weight of Produced Sugar (g)	% Conversion
2	26.67 X10 -02	0.4934	49.34
4	22.06X10 -02	0.3088	30.88

2.5 Determination of Sugar Concentration by HPLC

2.5.1 Preparation of Calibration Curve

The calibration curve was prepared according to the following procedure: a series of standard solutions of sugar ranging from concentrations 0.005 g/ml to 0.2 g/ml were prepared. Then analyzed they were by HPLC to determine their retention time and peak area. Results are summarized in **Table 2.42**.

Table (2.42): HPLC Analysis of Samples of Sugar with Known Concentrations

Sugar Sample (g/mL)	Peak Area
0.005	3.39 X1006
.01	6.71 X1006
.02	1.33X1007
.05	3.35 X1007
.1	7.10 X1007
.2	1.49 X1008

Calibration curve is depicted in **Figure 3.8**. It was drawn by plotting the peak area against sugar concentration.

CHAPTER THREE

RESULTS AND DISCUSSION

As shown in the introduction (chapter 1), hydrolysis of cellulose into glucose usually performed using one of the following two methods:

- Non-biological (Chemical) Hydrolysis
- Biological (Enzyme) Hydrolysis

In this study ,we have only used the chemical hydrolysis method. In this method, raw material of cellulose (Jeft) or purified cellulose is exposed to chemicals at specific concentration and temperature for a period of time which results in depolymerization of cellulose and formation of sugar monomers such as glucose. The chemicals we have tried in this study were various acids of hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) with or without a catalyst.

Acid hydrolysis method that has been tried could be divided into three categories:

1. Diluted acid
2. Concentrated acid
3. Mixture of acid and a catalyst.

3.1 Extraction of cellulose form Jeft

The first step, is to extract cellulose from Jeft by a method known as Kraft pulping. Where Jeft was suspended in an aqueous solution containing sodium hydroxide (NaOH) and sodium sulfide (Na_2S) then heated to about 130-160 °C for 2 hr under pressure as shown in the experimental part.

The Kraft process is the most frequently used in pulping.

The success of Kraft processes is due to the selectivity of Kraft chemicals on attacking Jeft constituents other than cellulose.

Chemicals used in pulping process alter the structure of the lignin in such a way that soluble fragments of polymer are produced. Pulping chemicals act on lignin structure in two ways to enhance dissolution. In the first one, lignin is degraded into smaller units by cleaving inter-linkage **Fig 3.1**. The second is by introducing hydrophilic groups into lignin polymer and fragments, rendering it more soluble in the pulping solution. Fragmentation shown in **Figure 3.1** results from the cleavage of aryl ether linkage, this cleavage assists in the dissolution by creating additional phenolic groups.

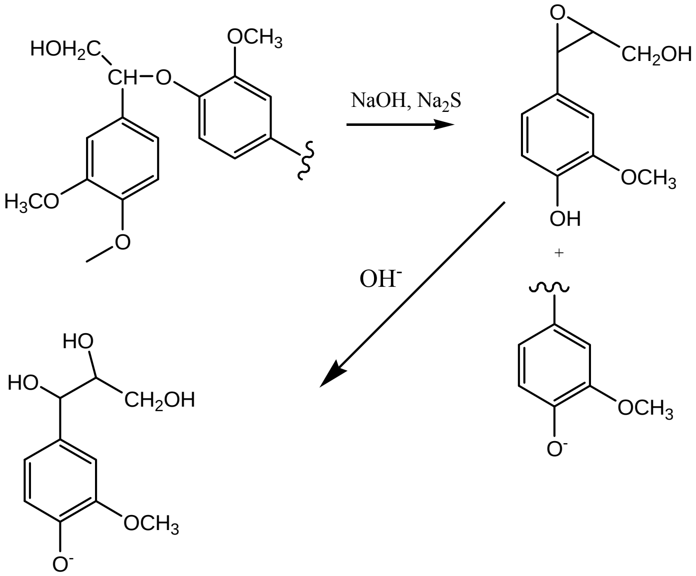


Fig (3.1): Fragmentation of Lignin by Kraft Pulping Chemicals

As shown in the experimental part, produced cellulose was washed several times with water to remove any leftover Pulping chemicals. Produced cellulose was subjected to bleaching processes to remove residual lignin and hemicelluloses. In this project, bleaching was performed only on a small sample of cellulose to obtain sample of cellulose with high purity for analysis. However, for hydrolysis of cellulose to sugar high purity cellulose is unnecessary.

Cellulose sample obtained after pulping and bleaching was subjected to analysis by various techniques:

3.2 Analysis of cellulose extracted from Jeft

With above method we were able to extract about 35-45% of pure cellulose. The extracted cellulose was subjected to analysis by various methods shown below.

3.2.1 Intrinsic Viscosity

Intrinsic viscosity was determined to be about 1.6. This result indicates that extracted cellulose has similar molecular weight to microcrystalline cellulose.

3.2.2 Sugar Analysis

Sugar analysis was also performed on extracted cellulose. The hydrolysis method is shown in the experimental part **Chapter 2** The results are shown in HPLC chromatogram **Figure 3.2**. As can be seen from

HPLC chromatogram **Figure 3.2**, hydrolysis of cellulose by 70%sulfuric acid is producing almost pure glucose. Traces of other sugars are also shown in the chromatogram. Which are usually produced from the hydrolysis of hemicelluloses. These results indicate that traces of hemicelluloses are present along with cellulose and also indicate that extracted cellulose will be a valuable source of sugar which then could be converted into ethanol.

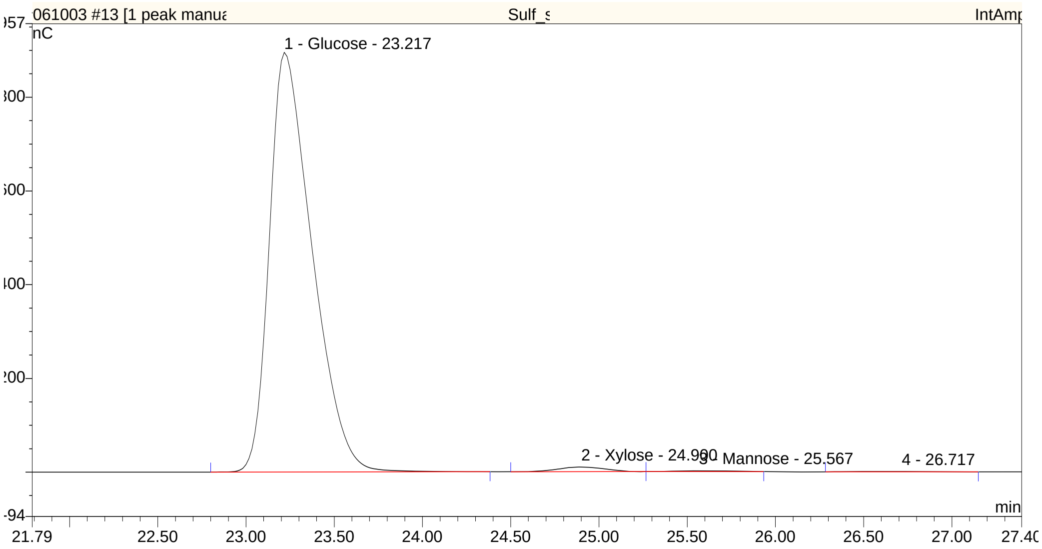


Fig (3.2): HPLC of the Hydrolysis of Jeft Cellulose

3.2.3 Infrared Spectroscopy

Analysis of Jeft cellulose by IR produces the IR spectrum that is shown in **Figure 3.3**. The figure shows two IR spectra, the upper one is for cellulose extracted from Jeft and the lower one is for microcrystalline cellulose obtained from Aldrich Chemical Company. As can be seen from the figure, the two IR spectra are in complete match. This is an indication that the material extracted from Jeft is highly pure microcrystalline cellulose .

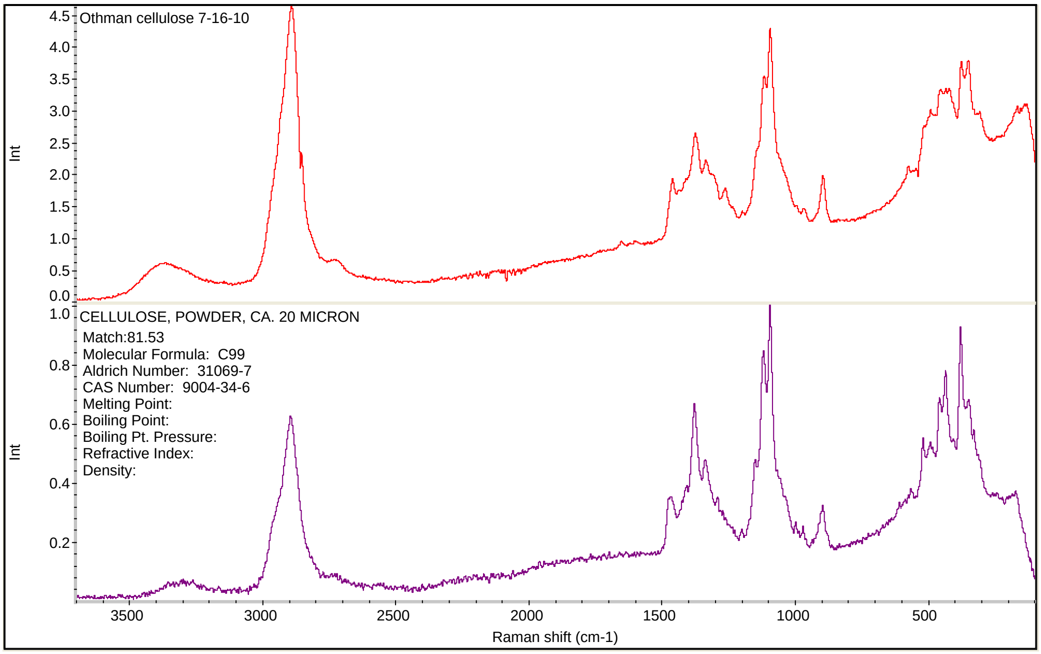


Fig (3.3): IR Spectra of Jeft Cellulose and Microcrystalline Cellulose

3.2.4 Scanning Electronic Microscope (SEM)

Extracted cellulose was also subjected to analysis by electronic microscope. The following photographs at magnification of 50x **Figure 3.4**, magnification of 1500x **Figure 3.5**, and 200x **Figure 3.6** show the morphology of extracted cellulose which is similar to that of microcrystalline cellulose **Figure 3.7**.[38]

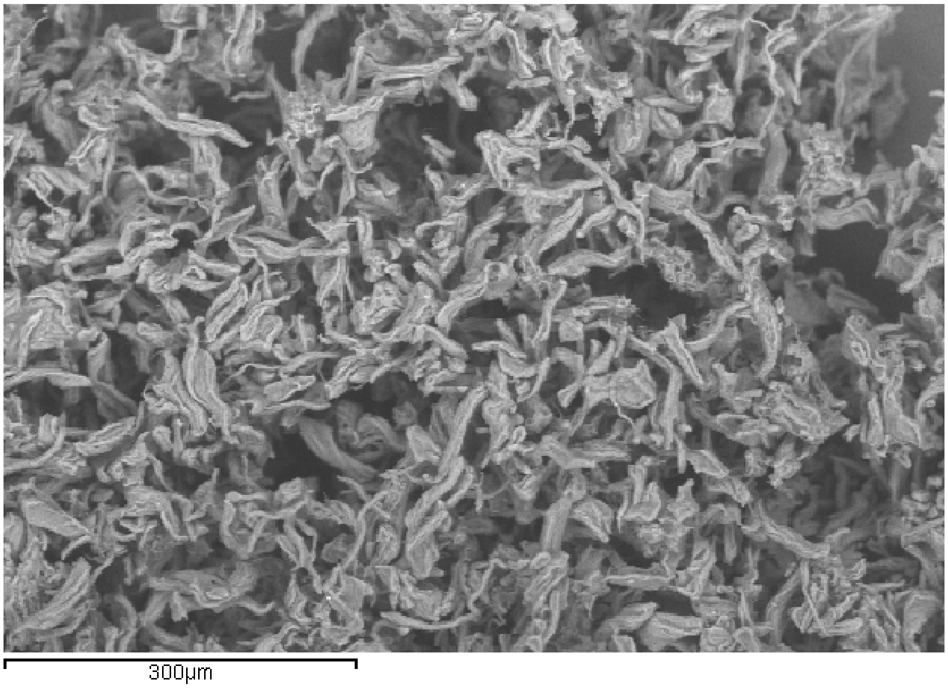


Fig (3.4): SEM Photo of Jeft Cellulose at Magnification of 50X

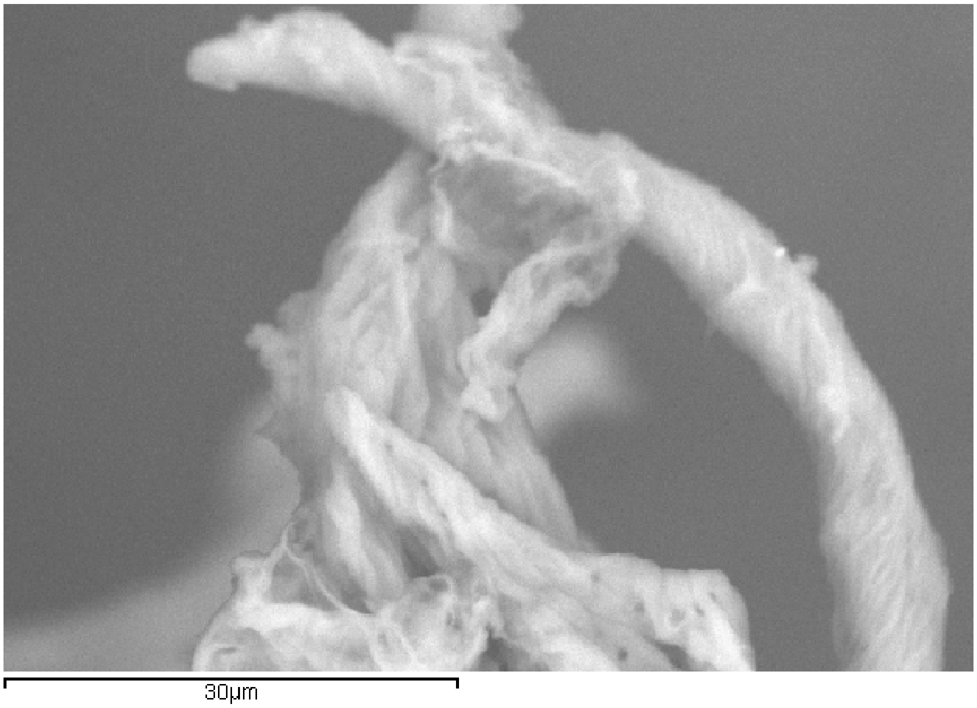


Fig (3.5): SEM Photo of Jeft Cellulose at Magnification of 1.5kX

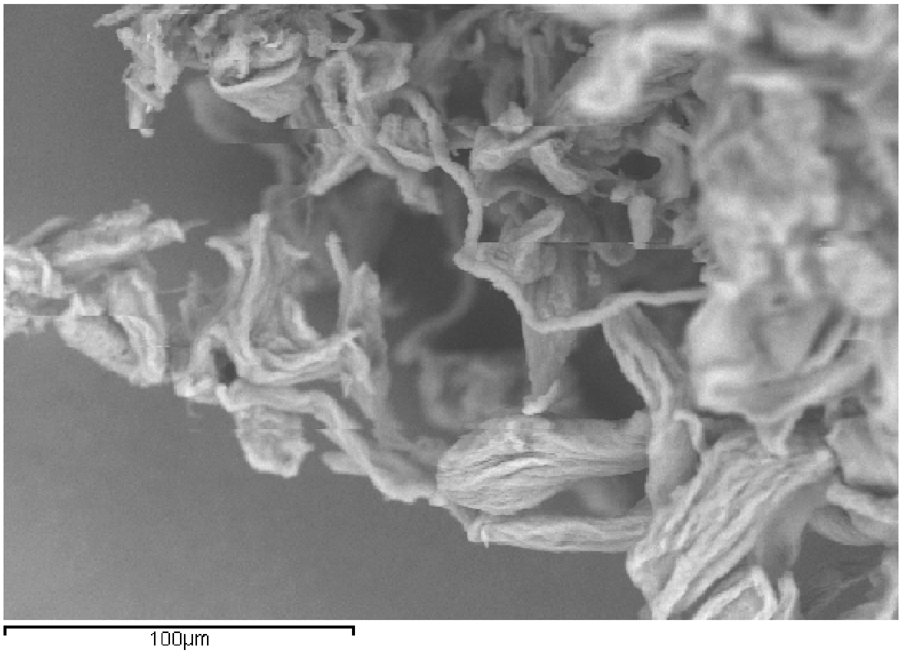


Fig (3.6): SEM Photo of Jeft Cellulose at Magnification of 200X

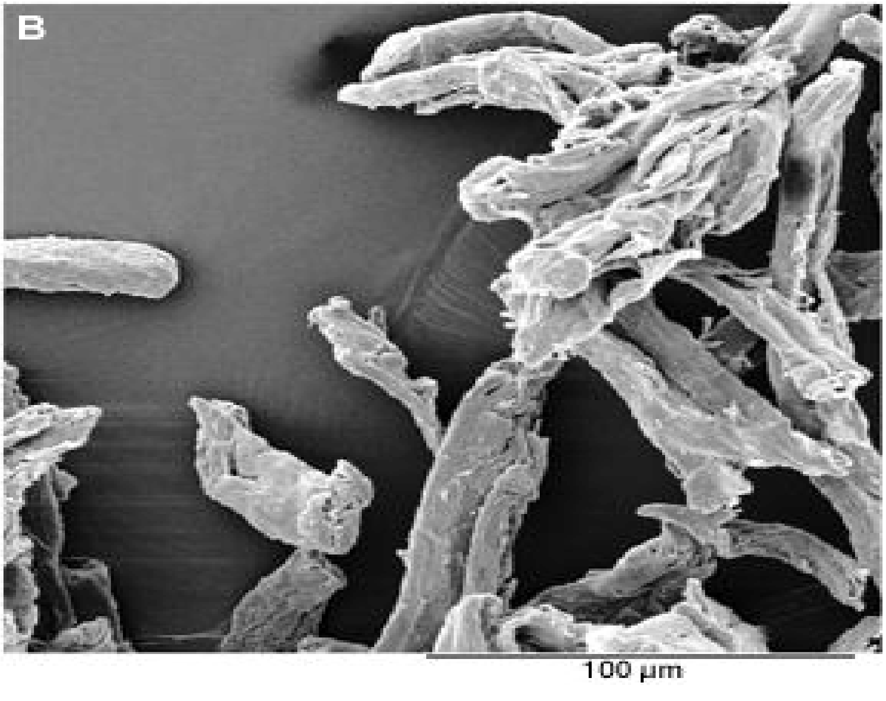


Fig (3.7): Morphology for (Microcrystalline Cellulose (DP = 300)

3.3 Hydrolysis of Jeft into Glucose

3.3.1 Diluted Acid Method

In this method, both diluted sulfuric acid and hydrochloric acid have been evaluated. The hydrolysis was performed on Jeft and cellulose extracted from Jeft.

The hydrolysis was performed on two types of raw material of Jeft, one was used as received from the olive mill factory without any kind of treatment and the other was extracted with ethyl acetate to remove residual olive oil and other extractive (washed jeft). This was performed to study the effect of presence of the residual olive oil and extractives on rate of hydrolysis of cellulose.

3.3.1.1 Hydrolysis of Raw Jeft into Glucose Using Diluted H_2SO_4

Samples of Jeft were treated with solution of acid at various concentrations ranging from 3.0% to a highly concentrated. The treatment was performed at a consistency of 10%. Consistency, as shown in following **Eq: 3.1,** is defined as weight of solid over weight of total reaction mixture.

$$\text{Consistency} = \frac{\text{Weight of pulp}}{\text{Total Weight of reaction mixture}} \qquad \text{Eq. 3.1}$$

The first two treatments were performed using H_2SO_4 (3%), at 90 ^{o}C for 2 hr and 4 hr periods.

Analysis of the hydrolysis product was performed using HPLC as shown in the experimental part. The concentration of produced sugar was calculated from a calibration curve shown in **Figure 3.8**.

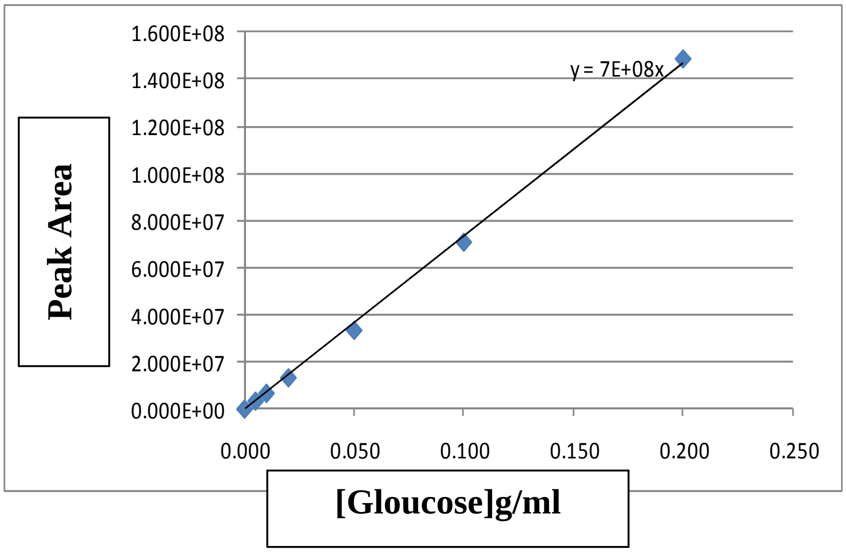


Fig (3.8): Calibration Curve

Calibration curve was generated by measuring the absorbency of standard samples of glucose with known concentrations. Detailed procedure for the generation of the calibration curve is shown in the experimental part **Chapter 2**.

The glucose peak produced from the hydrolysis of cellulose with 3% sulfuric acid was identified by comparing its retention time in the chromatogram with that of the standard samples.

The concentration of glucose was determined to be $9.7X10^{-05}$ g/mL, 3.1 $X10^{-4}$ g/mL for 2 hr and 4 hr, respectively **Table 2.1**. The weight of produced sugar was calculated according to equation 3.2. HPLC results of samples hydrolyzed by sulfuric acid (3%) for 2 hr are shown in the appendix part **Fig 1.** Hydrolysis rate was very low, so higher concentrations of sulfuric acid were tried as shown below. However, these results indicate that there is a direct proportional between sugar concentration and treatment time.

The effect of increasing the concentration of acid on rate of hydrolysis was then studied. So the second hydrolysis was performed using a solution of 7%H_2SO_4. The treatment was also performed at temperature of 90 ^oC for 2, 4 and 8 hr period. HPLC chromatogram of samples hydrolyzed by 7% sulfuric acid for 2 hr is shown in the appendix part **Fig 2**. Results are summarized in **Table 2.2** and shown in Figure 3.10. As can be seen from **Figure 3.10**, the concentration of glucose was 3. 5X10^{-03} g/mL and dropped to to 1.005 X10^{-03}g/mL after 8 hr. The decrease in the concentration of glucose could be attributed to conversion of glucose produced from hydrolysis to other chemicals such as furfural as shown in the litrature.[39] So far best the result was obtained using 7% H_2SO_4 at treatment time for2 hr as shown in **Fig 3.10**.

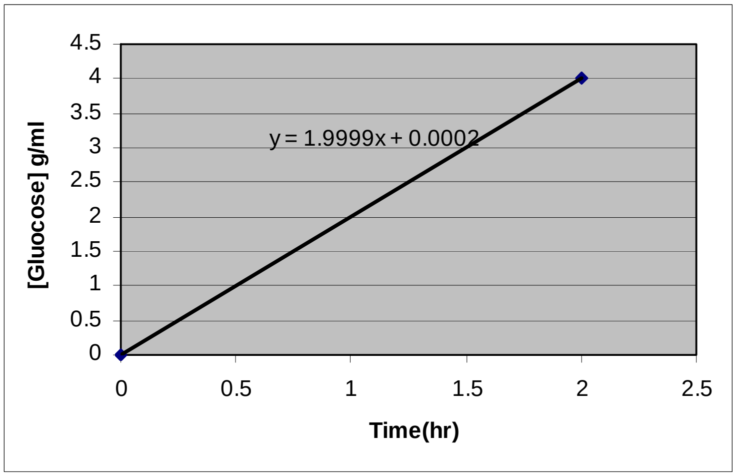


Fig (3.9): Results for Hydrolysis of Jeft Using 3%H2SO4

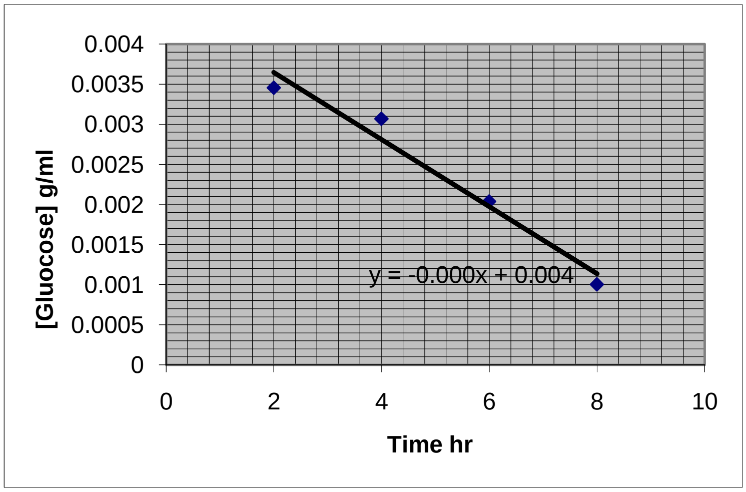


Fig (3.10): Results for Hydrolysis of Jeft Using 7%H2SO4

3.3.1.2 Hydrolysis of Raw Jeft into Glucose Using Diluted HCl

The first treatment was performed in 3% solution of HCl; the treatment was performed at temperature 90 ^{o}C for 2, 4, 6 and 8 hr period. Results are summarized in **Figure 3.11**,which shows that concentration of glucose decreased by increasing the reaction time from 2.5X10^{-02} at 2 hr to 1.887X10^{-02} at 8 hr.

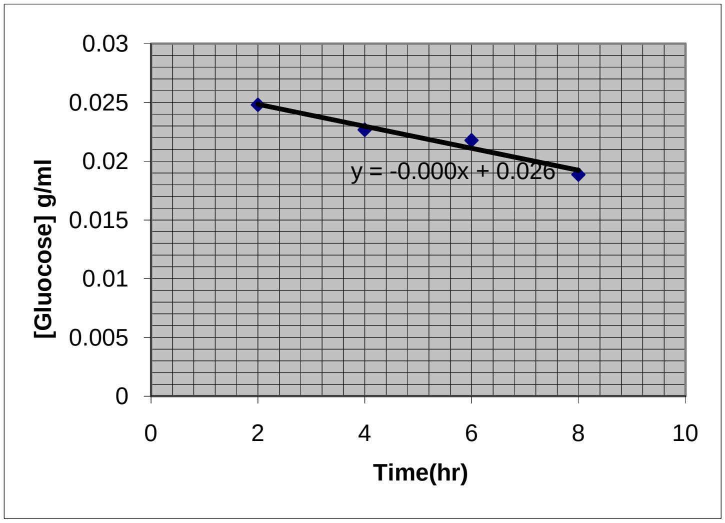


Fig (3.11): Results for Hydrolysis of Jeft Using 3%HCl

Then the hydrolysis was performed at higher concentration of 7%HCl, the treatment was also performed at temperature 90 ^{o}C for 2, 4, 6 , and 8 hr period. Results are summarized in **Figure 3.12** and **Table 2.3**. Such results show that the concentration of glucose decreased by increasing reaction time from 2 hr to 8 hr. At reaction time of about 8 hr, the concentration of sugar dropped to .619 X10^{-02}, which could be attributed to the hydrolysis of sugar to other materials such as furfural as mentioned earlier. HPLC results for hydrolysis of jeft using 7% HCl for 2hr are shown in the appendix part **Fig 4.**

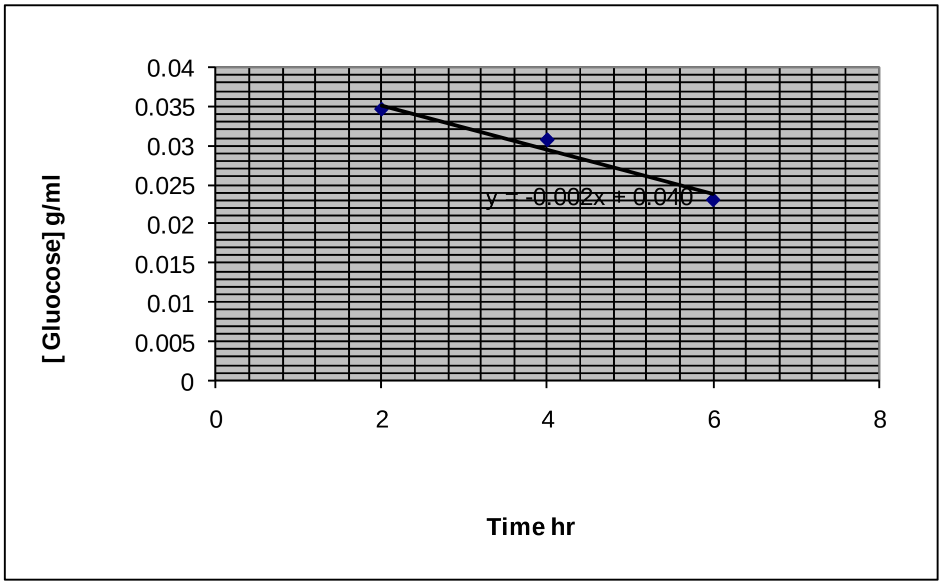


Fig (3.12): Results for Hydrolysis of Extracted Cellulose Using 7%HCl

So far ,the results indicated that HCl is more effective than H_2SO_4 at 90 ^{o}C.

Hydrolysis was also performed on Jeft using 5% HCl. Results are summarized in **Figure 3.13**, that shows that the concentration of glucose decreased by increasing hydrolysis time from 2 to 4 hr. The weight of produced cellulosed was calculated according to equation 3.2. The results of weight of produced sugar and percent conversion are summarized in **Table 2.5**. HPLC for hydrolysis of jeft using by 5% hydrochloric acid for 2 hr are shown in the appendix part **Fig 5**.

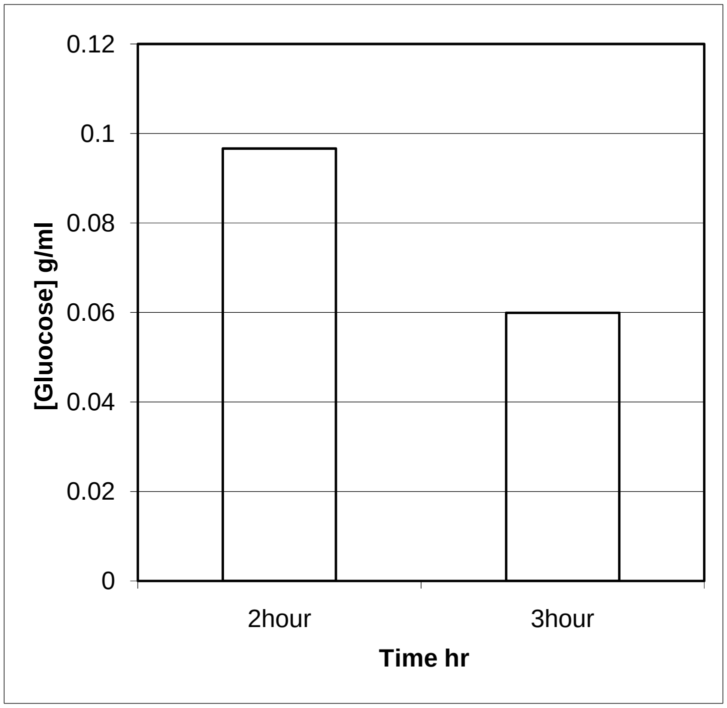


Fig (3.13): Results for Hydrolysis of Jeft Using 5%HCl

3.3.1.3. Hydrolysis of Jeft Washed with Ethyl Acetate Using Diluted HCl

The results of this run are summarized in **Table 2.6** and in **Fig 3.14**. As shown in Figure 3.14 the results indicated that residual materials in jeft have no effect on the rate of jeft hydrolysis, since the % sugar produced from hydrolysis of Jeft before and after washing with ethyl acetate is almost similar. HPLC results for the hydrolysis of jeft using 5%hydrochloric acid for 2hr are shown in the appendix part Fig 6.

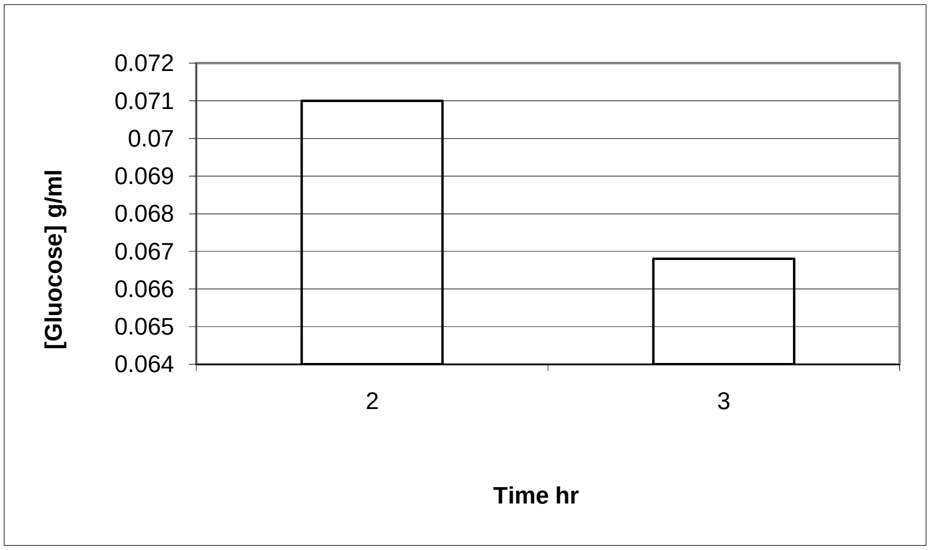


Fig (3.14): Results for Hydrolysis of Jeft Washed with Ethyl acetate Using 5%HCl

3.3.1.4. Hydrolysis of Purified Cellulose Extracted from Jeft Using Diluted HCl

As can be seen from **Figure 3.15** the concentration of glucose decreases from $6.9X10^{-02}$ to about $6.5X10^{-02}$ by increasing reaction time of hydrolysis from 2 to 3 hr. The weight of produced cellulose was calculated according to **Eq. 3.2**. The results of weight of produced sugar and %conversion are summarized in **Table 2.7**. HPLC results for hydrolysis of jeft using 5% hydrochloric acid for 2 hr are shown in the appendix part **Fig 7**.

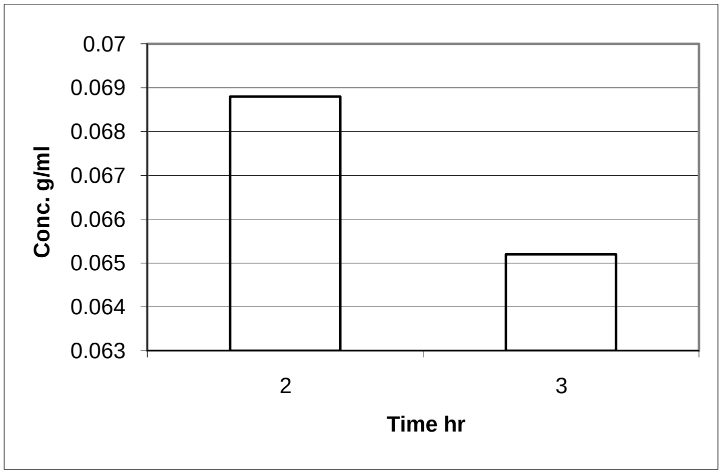


Fig (3.15): Results for Hydrolysis of purified Cellulose Extracted from Jeft Using 5% HCl

3.3.2 Concentrated Acid Method

3.3.2.1 Concentrated Hydrochloric Acid Method

In this method, concentrated hydrochloric acid was used. The hydrolysis was performed at 25 ^{0}C for 2, 4, and 6 hours. As before, the hydrolysis was performed on three types of raw materials: Jeft, Jeft washed with ethyl acetate and purified cellulose. Results of this study are summarized in **Figures 3.16-3.18**. Results from hydrolysis of Jeft are shown in Figure 3.21 and **Table 2.9**. A decrease was observed in sugar concentration by changing the hydrolysis time from 2 to 4 hr. As mentioned earlier, the drop could be attributed to hydrolysis of sugar to furfural in presence of acid, which usually started showing up after a long period of time of exposure of sugar to acid. The conversion becomes faster by increasing acid concentration. After 2 hr period, sugar produced at concentration of 28.8 X10^{-02}, while with 4 hr period it was 25.6X10^{-02}.

HPLC results of hydrolysis of jeft using concentrated hydrochloric acid for 2 hr are shown in the appendix part **Fig 8.**

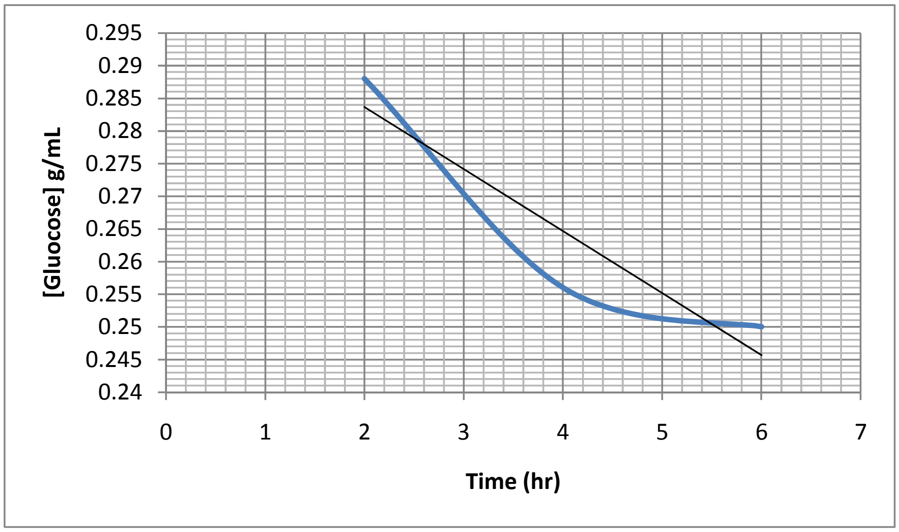


Fig (3.16): Results for Hydrolysis of Jeft Using Concentrated HCl

3.3.2.2 Results of Hydrolysis of Washed Jeft Using Concentrated HCl

Similar trend to that observed form hydrolysis of jeft was observed in this experiment . Also , as shown from the results no major difference between the results of hydrolysis before or after washing Jeft with ethyl acetate. The concentration of sugar at 2 and 4 hr time period was 28.2X10^{-02} and decreased to 27.4 X10^{-02} after 4 hr of hydrolysis. Results of this study are summarized in **Figure 3.17** and **Table2.10**. HPLC results for hydrolysis of washed jeft using concentrated hydrochloric acid for 2 hr are shown in the appendix part Fig 9.

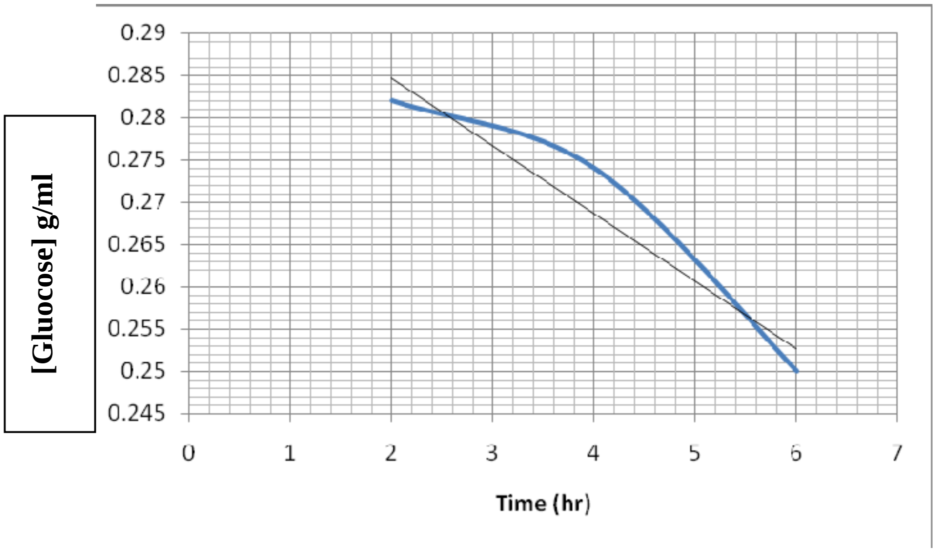


Fig (3.17): Results for Hydrolysis of Jeft Washed with Ethyl acetate Using Concentrated HCl

3.3.2.3 Hydrolysis of Purified Cellulose Using Concentrated HCl

In this experiment, the concentration of sugar decreases by increasing the hydrolysis time from 2 to 4 hr period. Hydrolysis for 2 hr produces 25.6 X10^{-02} of sugar while hydrolysis at 4 hr period produces 21.9 X10^{-02}. Another important observation is that, both Jeft and washed jeft produced higher concentration of sugar than purified cellulose upon hydrolysis with strong acid. This could be attributed to the presence of amorphous cellulose which is present in Jeft and absent in purified cellulose as it is removed during the process of pulping and bleaching of jeft. Since amorphous cellulose is easily hydrolyzed into sugar. HPLC results for hydrolysis of purified cellulose using concentrated hydrochloric acid for 2hr are shown in the appendix part **Fig 10**

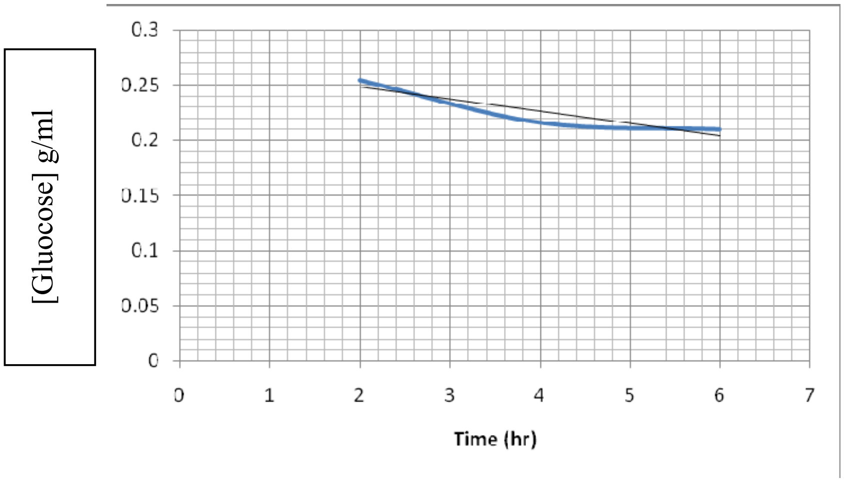


Fig (3.18): Results for hydrolysis of Purified Cellulose Using Concentrated HCl

3.3.2.1 Hydrolysis of Purified Cellulose Extracted from jeft Using Concentrated acid H_2SO_4

In another study, similar to that with concentrated HCl, concentrated sulfuric acid was used in hydrolysis of purified cellulose. In this case, the sugar yield was very low. This could be due to converting of produced sugar into coal tar by H_2SO_4. A best result was obtained at a hydrolysis of 4 hr. Results are summarized in **Tables 2.8**. HPLC results for hydrolysis of purified Cellulose using concentrated sulfuric acid for 2 hr are shown in the appendix part **Fig 11**.

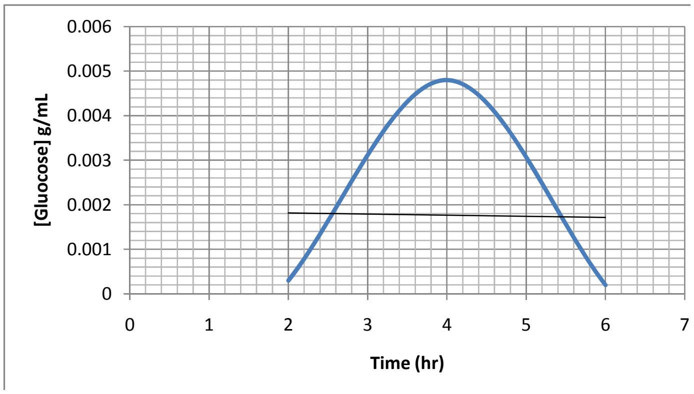


Fig (3.19): Results for Hydrolysis of Purified Cellulose by Pulping Hydrolysis Using Concentrated H_2SO_4

So far, the highest rate of hydrolysis and highest concentration of sugar was obtained using concentrated HCl with cellulose purified by pulping and bleaching processes. In another study, we tried to enhance the rate of hydrolysis using Lewis acid catalyst along with HCl.

3.3.3.1 Hydrolysis Using a Mixture of acid and Lewis acid Catalyst

The study was conducted at various concentrations of HCl ranging from 5% to 20% along with various concentrations of Lewis acids (Zinc chloride and calcium chloride). The hydrolysis was conducted at various periods of time. The temperature in this study was kept constant at about 90 ^{0}C. Chromatogram of this exp. for 1hr are shown in appendix part in **Figures 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35**. Results of this study are summarized in Figures **3.20, 3.21, 3.22 , 3.23,3.24, 3.25, 3.26**. As shown in Figure 3.20 and Figure 3.22 best results were obtained using high concentration of $ZnCl_2$. Another important conclusion is that the hydrolysis time of about 2 hr could produce good yield of sugar (49.89%). The low rate of hydrolysis using acid alone could be attributed to the crystalline structure of cellulose extracted from Jeft.[40] Cellulose structure consists of two regions, one amorphous and the other is crystalline and the crystalline structure is resistant to chemicals. The analysis results mentioned previously (IR, SEM, and sugar analysis) indicated that the cellulose we extracted from Jeft has microcrystalline structure. Results also show that all three materials Jeft, washed Jeft, and cellulose extracted from jeft produce almost equal amount of sugar. So, big improvement was shown using a combination of Lewis acid and HCl at low to medium concentration. Actually, the results were expected since as reported in the literature, Lewis acid opens the crystalline region of cellulose structure and makes it more accessible to chemicals. For this reason, the rate of hydrolysis increased by using Lewis acid such as $ZnCl_2$ even in the presence of low concentration of HCl. So with these results we could claim a new efficient method for hydrolysis of cellulose into sugar.

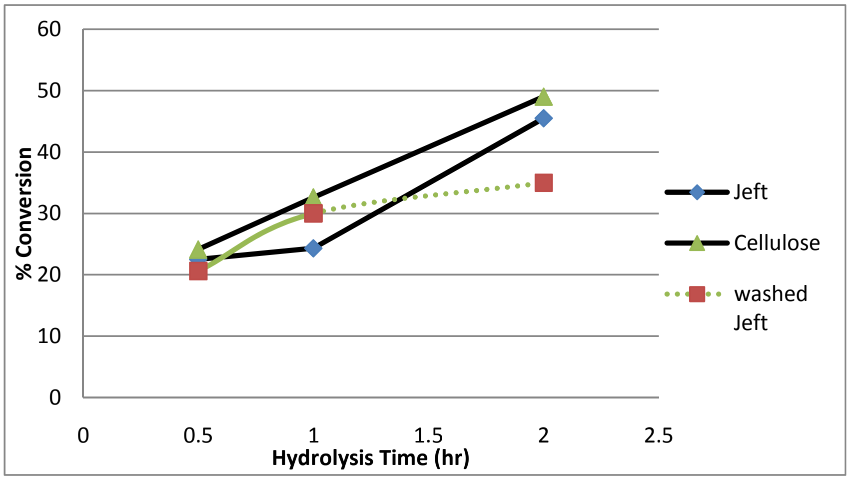


Fig (3.20): Results for Hydrolysis of Jeft, Washed Jeft, and Purified Cellulose Extracted from Jeft Using a Solution of 10%HCl and 10% $ZnCl_2$

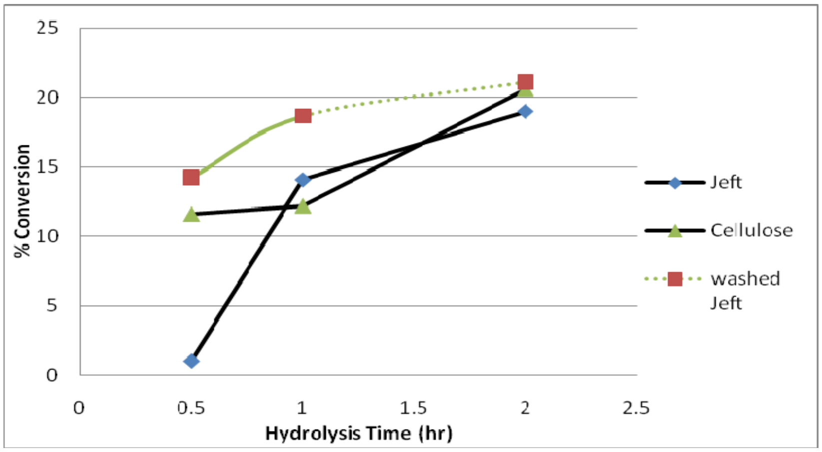


Fig (3.21): Results for Hydrolysis of Jeft, Washed Jeft, and Purified Cellulose Extracted from Jeft Using a Solution of 5%HCl and 10%$ZnCl_2$

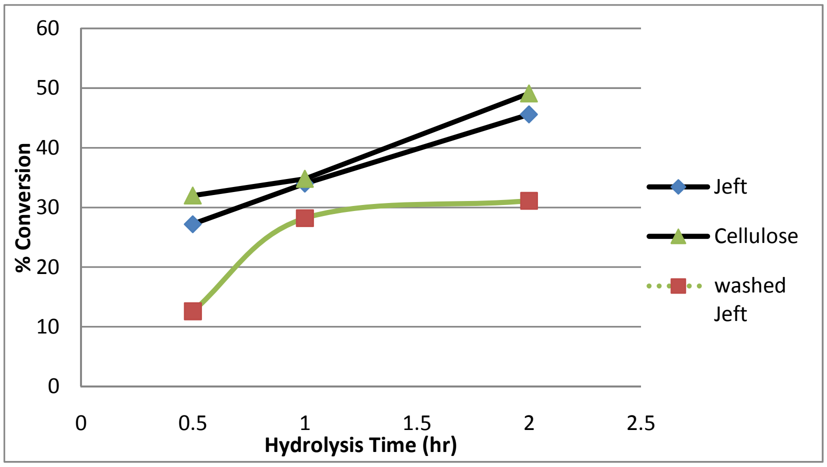


Fig (3.22): Results for Hydrolysis of Jeft, Washed Jeft, and Purified Cellulose Extracted from Jeft Using a Solution of 5% HCl and 20%$ZnCl_2$

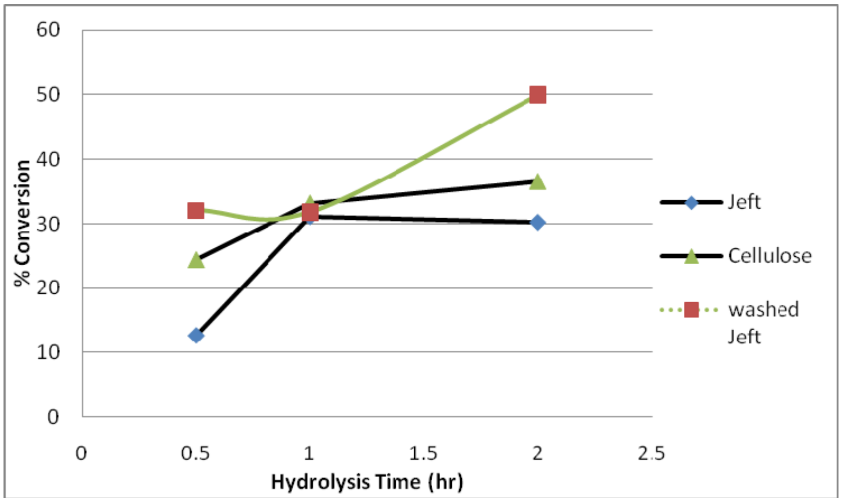


Fig (3.23): Results for Hydrolysis of Jeft, Washed Jeft, and Purified Cellulose Extracted from Jeft Using a Solution of 10% HCl and 20% $ZnCl_2$

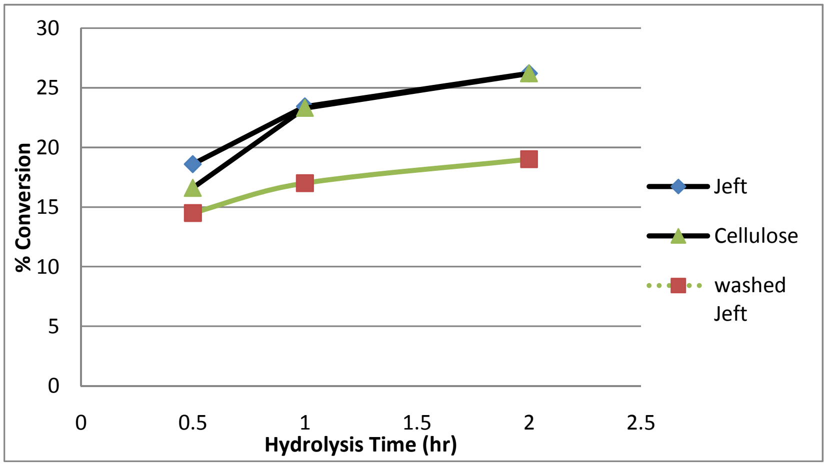


Fig (3.24): Results for Hydrolysis of Jeft, Washed Jeft, and Purified Cellulose Extracted from Jeft Using a Solution of 5%HCl and 10%$CaCl_2$

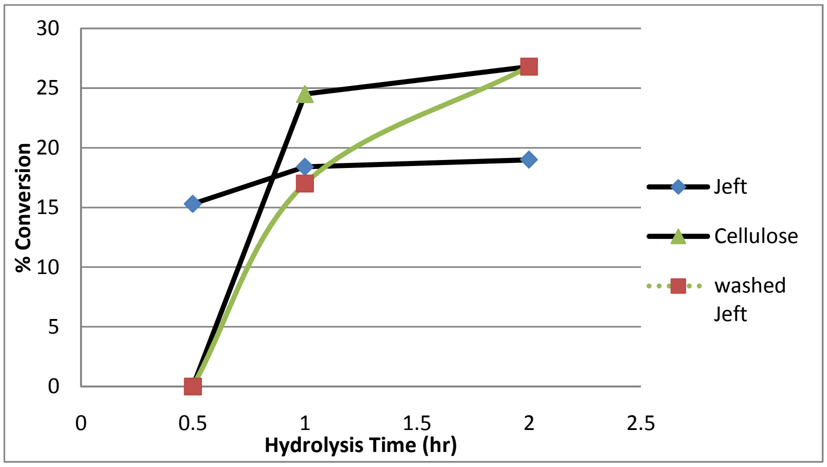


Fig (3.25): Results for Hydrolysis of Jeft, Washed Jeft, and Purified Cellulose Extracted from Jeft Using a Solution of 10%HCl and 10%CaCl$_2$

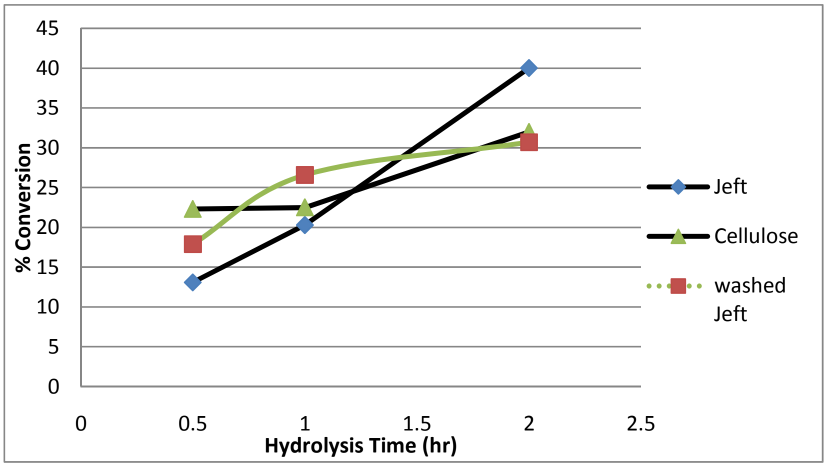


Fig (3.26): Results for Hydrolysis of Jeft, Washed Jeft, and Purified Cellulose Extracted from Jeft Using a Solution of 5%HCl and 20%CaCl$_2$

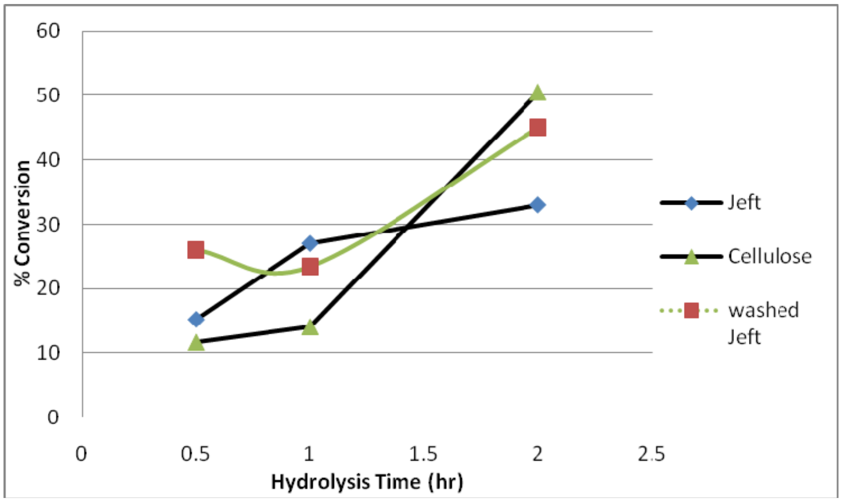


Fig (3.27): Results for Hydrolysis of Jeft, Washed Jeft, and Purified Cellulose Extracted from Jeft Using a Solution of 10%HCl and 20%CaCl$_2$

The study was extended to include $MgCl_2$, but lower of rate of hydrolysis of cellulose to sugar was observed.

In another study, hydrogen peroxide was used along with HCl hoping to enhance the rate of hydrolysis.

3.3.3.2 Hydrolysis Using a Mixture of acid and Hydrogen Peroxide H_2O_2

Hydrogen peroxide is colorless and odorless oxidizing agent that can mix with soluble organic solvent and water. Hydrogen peroxide has been used for pretreatment of biomass.[41]

This hydrolysis study was performed on various Jeft materials as before using various concentrations of HCl ranging from 5% to 35% in the presence of hydrogen peroxide at concentration of 2.5%. The hydrolysis was conducted at 60 ^{o}C and at room temperature for various periods of time. Results of this study are summarized in **Table 3.1**. Using hydrogen peroxide didn’t improve the yield even at high concentration of HCl. This could be due to running the hydrolysis at low temperature and fast decomposition of hydrogen peroxide at temperature over room temperature. The highest concentration was obtained from the hydrolysis where concentrated HCl and 2.5% H_2O_2 was used. An actually similar result was obtained using concentrated HCl alone.

Table (3.1): Summary of the Hydrolysis Results Using Mixture of Acid and Hydrogen Peroxide H_2O_2

Material Hydrolyzed	% H_2O_2	% HCl	Hydrolysis Time (hr)	Sugar Yield	
				Conc. Sugar	%Yield
Jeft	2.5	5[1]	2	$7.07\ X10^{-02}$	9.90
Jeft	2.5	5	4	$10.11\ X10^{-02}$	18.71
Washed Jeft	2.5	5[2]	2	$8.837X10^{-02}$	11.04
Washed Jeft	2.5	5	4	$.947X10^{-02}$	1.089
Purified Cellulose	2.5	5[3]	2	$9.26X10^{-02}$	6.943
Purified Cellulose	2.5	5	4	$9.406\ X10^{-02}$	12.23
Jeft	2.5	Conc.[4]	2	$26.44X10^{-02}$	51.57
Jeft	2.5	Conc.	4	$25.11\ X10^{-02}$	42.69
Washed Jeft	2.5	Conc.[5]	2	$22.55X10\text{-}^{02}$	39.47
Washed Jeft	2.5	Conc.	4	$19.74\ X10\text{-}^{02}$	31.59
Purified Cellulose	2.5	Conc.[6]	2	$26.67X10\ ^{-02}$	49.34
Purified Cellulose	2.5	Conc.	4	$22.06\ X10\text{-}^{02}$	30.88

1. Chromatogram of this exp. Is shown in appendix part Fig 36
2. Chromatogram of this exp. Is shown in appendix part Fig 37
3. Chromatogram of this exp. Is shown in appendix part Fig 38
4. Chromatogram of this exp. Is shown in appendix part Fig 39
5. Chromatogram of this exp. Is shown in appendix part Fig 40
6. Chromatogram of this exp. Is shown in appendix part Fig 41

From the above results ,we conclude that, Jeft could be used as a source of sugar as it is without any further purification. More work should be conducted in this area in order to accomplish two important criteria:

1. Improve the rate of hydrolysis of Jeft and to enhance the yield of sugar.
2. To determine the drop point (the point at which the rate of hydrolysis reach the maximum and start decreasing), since as shown in the graphs

in the previous figures, the rate of hydrolysis is increasing with time. But the maximum rate of hydrolysis was never determined.

The mechanism of acid-catalyzed hydrolysis of cellulose (cleavage of β-1-4-glycosidic bond) could occur as shown by the mechanism in Figure **3.27**. The acid hydrolysis proceeds in three steps: firstly,the reaction starts with protonation of the terminal glycosidic oxygen linking two sugar units, forming a protonated cellulose (conjugate acid),Secondaly, the nuleophilic water attacks on the protonated cellulose which breaks down to the cyclic carbonium ion,thirdly, after a rapid addition of water, free sugar and a proton are liberated.[42] It has been shown in previous studies that the formation of the intermediate carbonium ion takes place more rapidly at the end than in the middle of the polysaccharide chain.

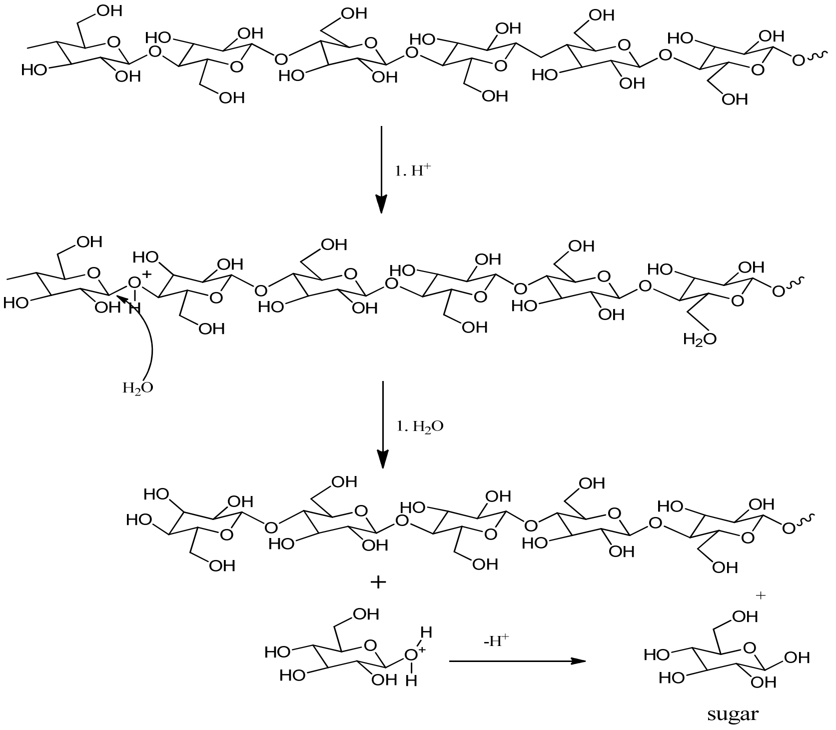


Fig (3.27): Mechanism of hydrolysis of cellulose in acidic medium

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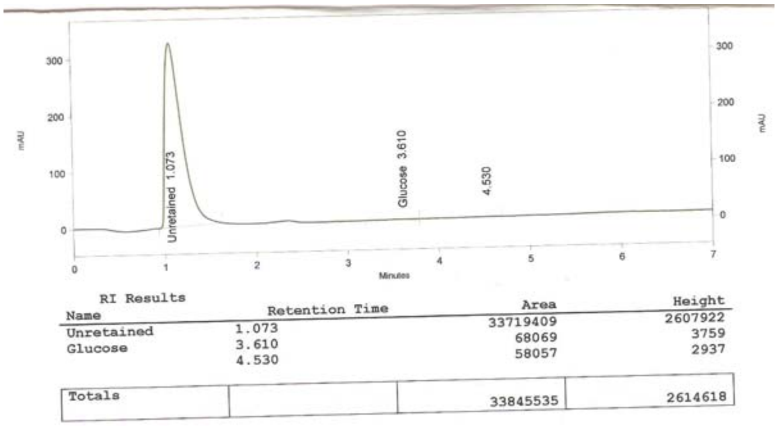
APPENDIX

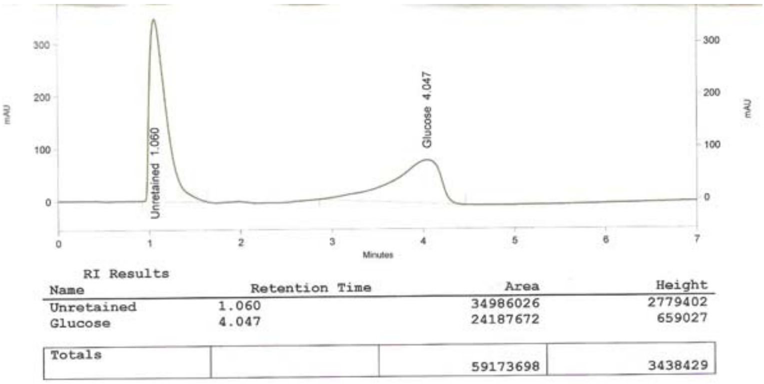
HPLC CHROMATOGRAMS



RI Results

Name	Retention Time	Area	Height
Unretained	1.073	33719409	2607922
Glucose	3.610	68069	3759
	4.530	58057	2937
Totals		33845535	2614618

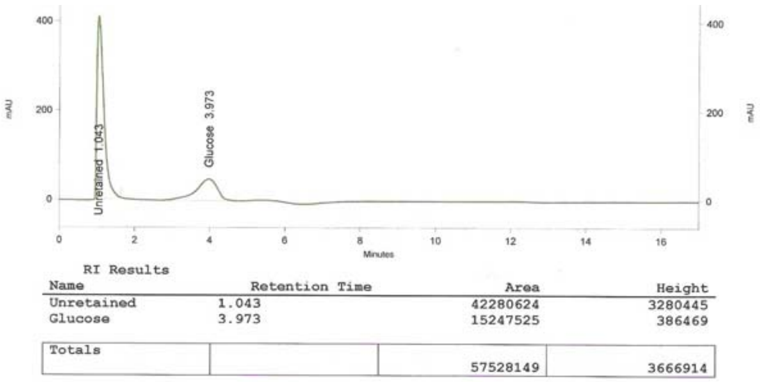
Fig 1: HPLC Chromatogram Results for Hydrolysis of Jeft Using 3% H_2SO_4 for (2 hr)



RI Results

Name	Retention Time	Area	Height
Unretained	1.060	34986026	2779402
Glucose	4.047	24187672	659027
Totals		59173698	3438429

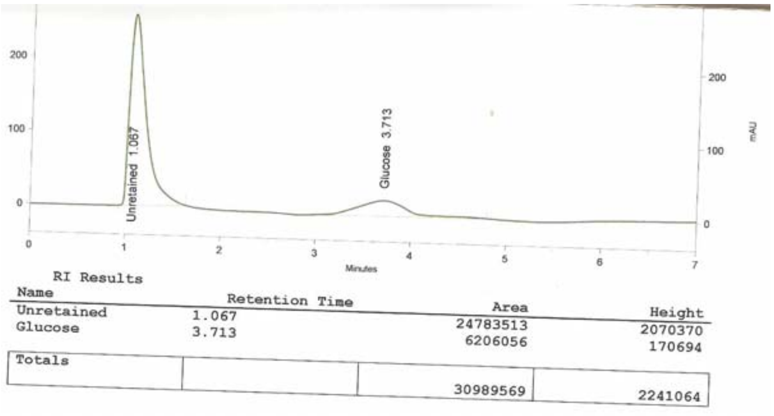
Fig 2: HPLC Chromatogram Results for Hydrolysis of Jeft Using 7% H_2SO_4 for (2 hr)



RI Results

Name	Retention Time	Area	Height
Unretained	1.043	42280624	3280445
Glucose	3.973	15247525	386469
Totals		57528149	3666914

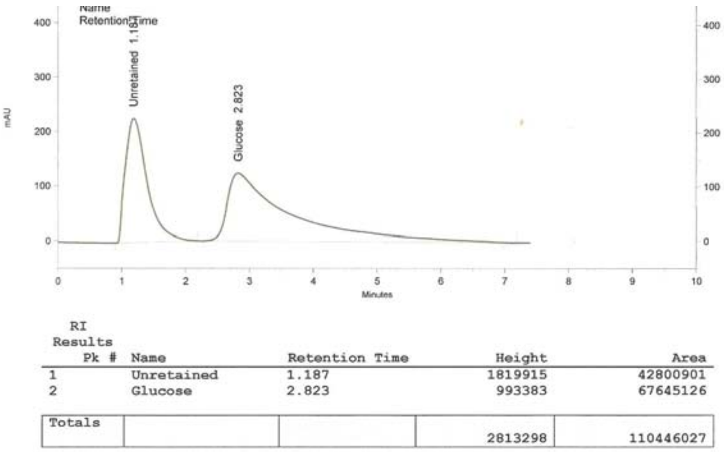
Fig 3: HPLC Chromatogram Results for Hydrolysis of Jeft Using 3% HCl for (2 hr)



RI Results

Name	Retention Time	Area	Height
Unretained	1.067	24783513	2070370
Glucose	3.713	6206056	170694
Totals		30989569	2241064

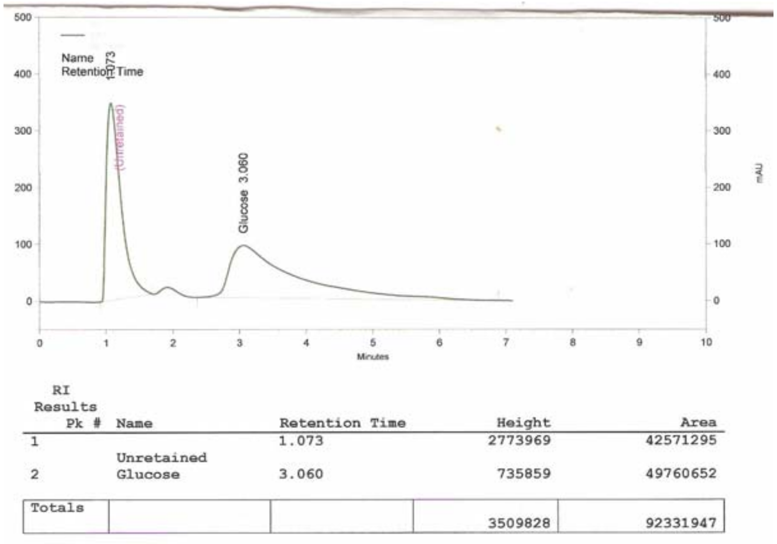
Fig 4: HPLC Chromatogram Results for Hydrolysis of Jeft Using 7%HCl for (2 hr)



RI Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.187	1819915	42800901
2	Glucose	2.823	993383	67645126
Totals			2813298	110446027

Fig 5: HPLC Chromatogram Results for Hydrolysis of Jeft Using 5% HCl for (2 hr)

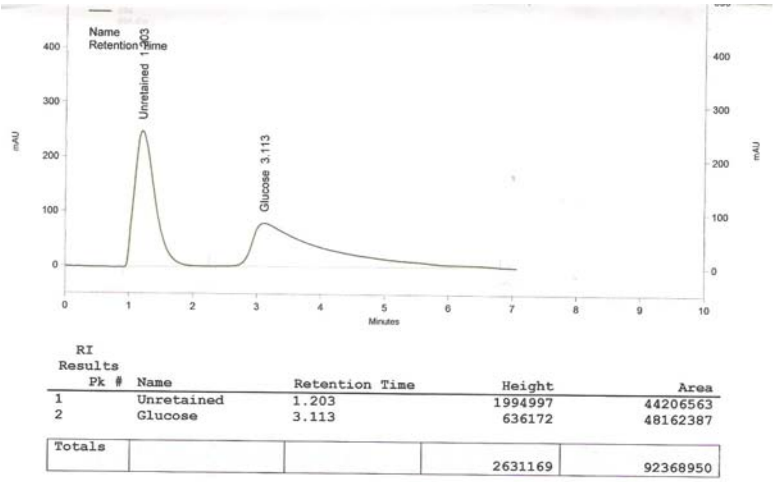


RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.073	2773969	42571295
2	Glucose	3.060	735859	49760652

Totals				
			3509828	92331947

Fig 6: HPLC Chromatogram Results for Hydrolysis of Washed Jeft Using 5% HCl for (2 hr)

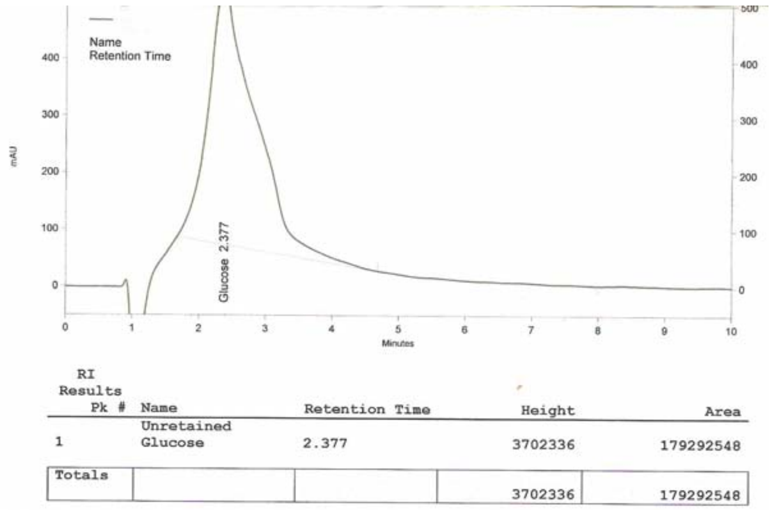


RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.203	1994997	44206563
2	Glucose	3.113	636172	48162387

Totals				
			2631169	92368950

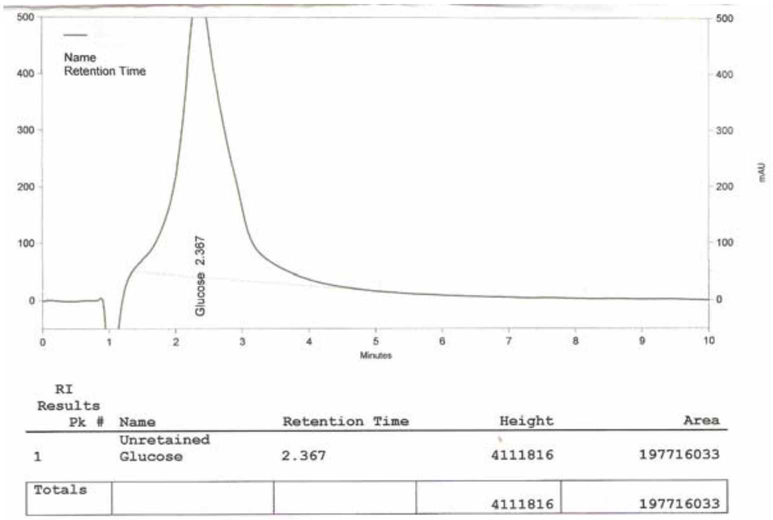
Fig 7: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Extracted from Jeft by Using 5% HCl for (2 hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained Glucose	2.377	3702336	179292548
Totals			3702336	179292548

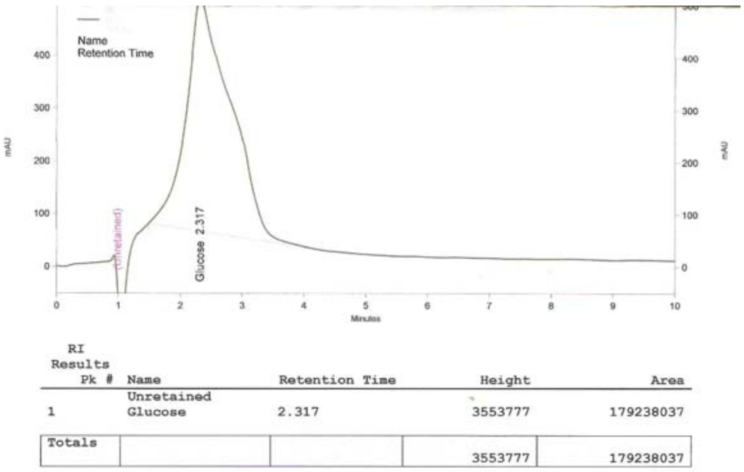
Fig 8: HPLC Chromatogram Results for Hydrolysis of Jeft Using Conc. HCl for (2 hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained Glucose	2.367	4111816	197716033
Totals			4111816	197716033

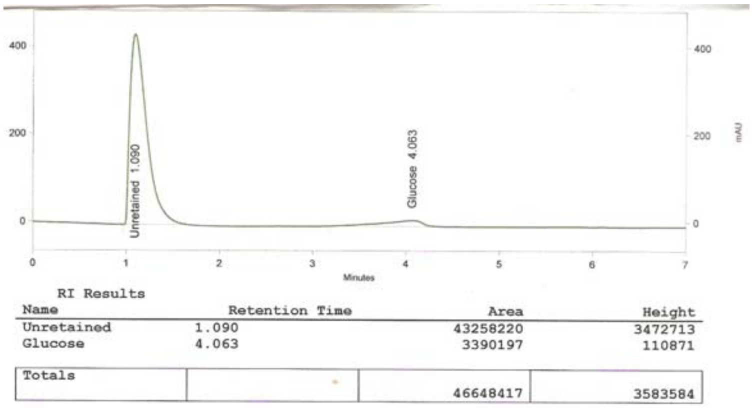
Fig 9: HPLC chromatogram Results for Hydrolysis of Washed Jeft Using Conc. HCl for (2 hr)



RI Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1	Glucose	2.317	3553777	179238037
Totals			3553777	179238037

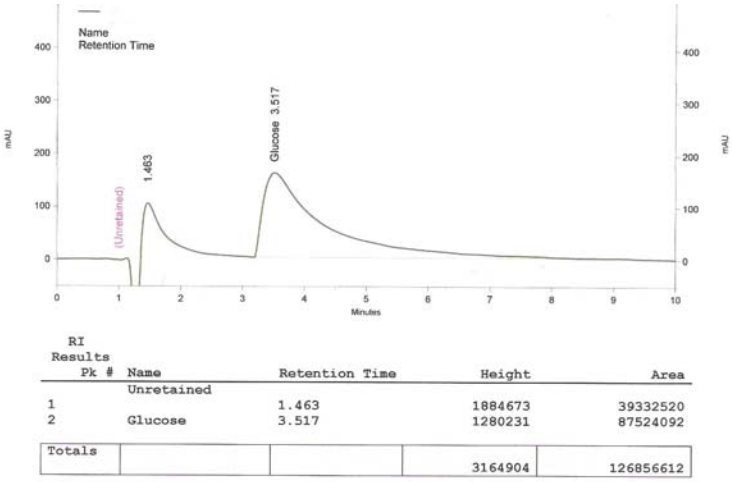
Fig 10: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using Conc. HCl for (2 hr)



RI Results

Name	Retention Time	Area	Height
Unretained	1.090	43258220	3472713
Glucose	4.063	3390197	110871
Totals		46648417	3583584

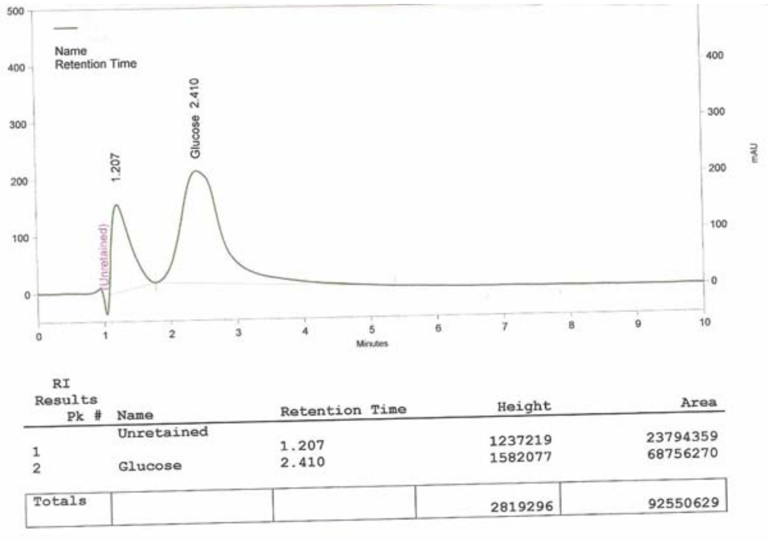
Fig 11: HPLC Chromatogram Results for Hydrolysis Purified Cellulose Extracted from Jeft Using 70% H_2SO_4 for (2 hr)



RI Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1		1.463	1884673	39332520
2	Glucose	3.517	1280231	87524092
Totals			3164904	126856612

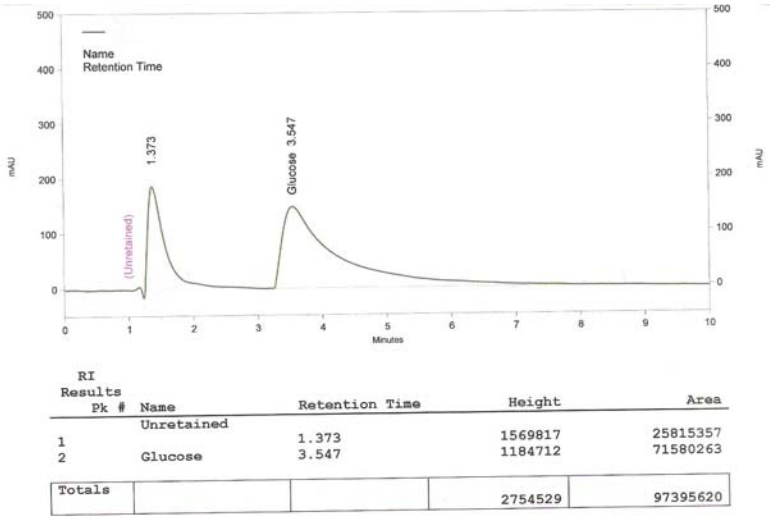
Fig 12: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of 5%HCl and 10% $ZnCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1		1.207	1237219	23794359
2	Glucose	2.410	1582077	68756270
Totals			2819296	92550629

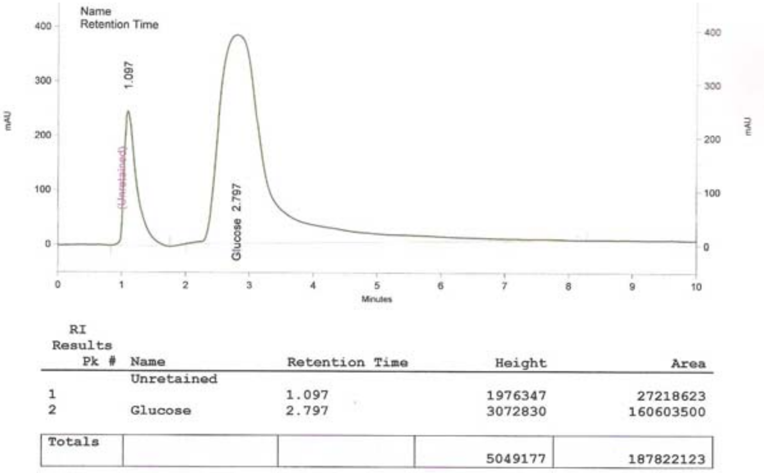
Fig 13: HPLCChromatogram Results for Hydrolysis of Washed Jeft Using a Mixture of 5% HCl and 10% Zn Cl_2 for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1		1.373	1569817	25815357
2	Glucose	3.547	1184712	71580263
Totals			2754529	97395620

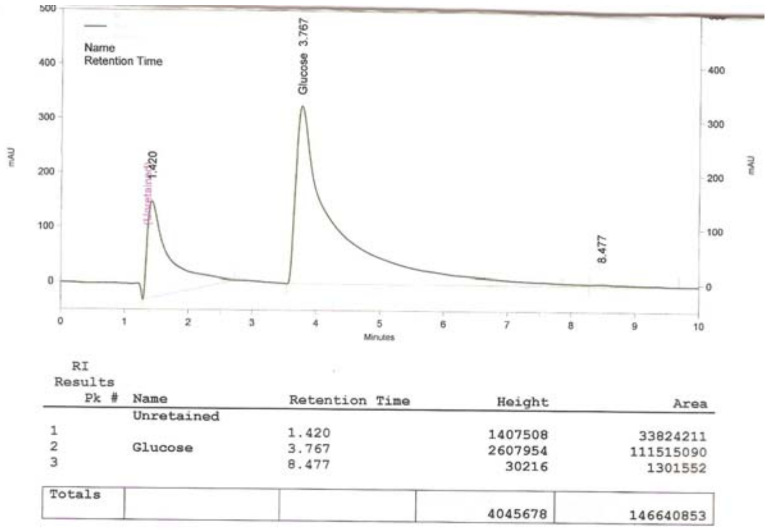
Fig 14: HPLC Chromatogram Results for Hydrolysis Purified Cellulose Extracted from Jeft by Using a Mixture of 5%HCl and 10%$ZnCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1		1.097	1976347	27218623
2	Glucose	2.797	3072830	160603500
Totals			5049177	187822123

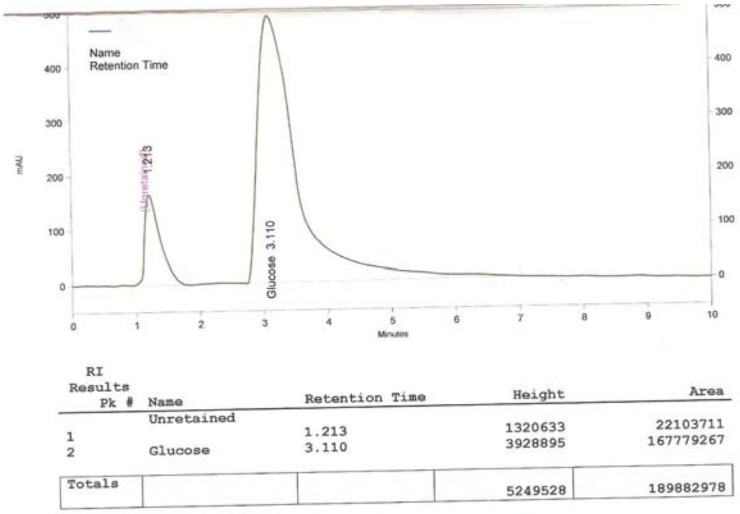
Fig 15: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of 10% HCl and 10% $ZnCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1		1.420	1407508	33824211
2	Glucose	3.767	2607954	111515090
3		8.477	30216	1301552
Totals			4045678	146640853

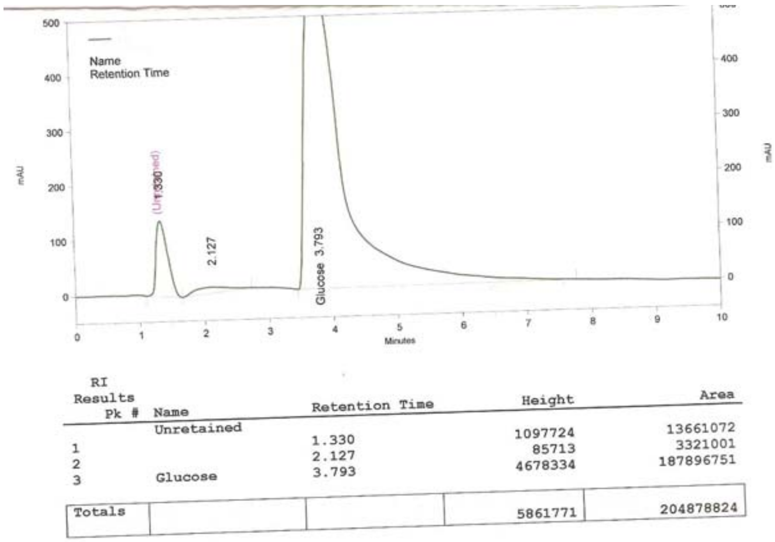
Fig 16: HPLC Chromatogram Results for Hydrolysis of Washed Jeft a Using Mixture of 10%HCl and 10% $ZnCl_2$ for (1hr)



RI Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.213	1320633	22103711
2	Glucose	3.110	3928895	167779267
Totals			5249528	189882978

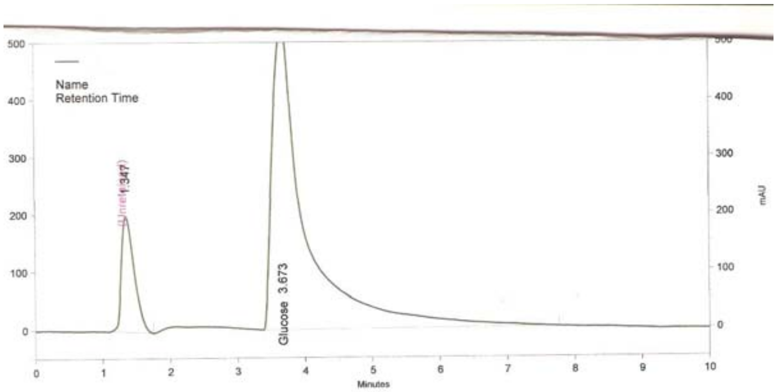
Fig 17: HPLC Chromatogram Results for Hydrolysis of purified Cellulose Using a Mixture of 10% HCl and 10% $ZnCl_2$ for (1hr)



RI Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.330	1097724	13661072
2		2.127	85713	3321001
3	Glucose	3.793	4678334	187896751
Totals			5861771	204878824

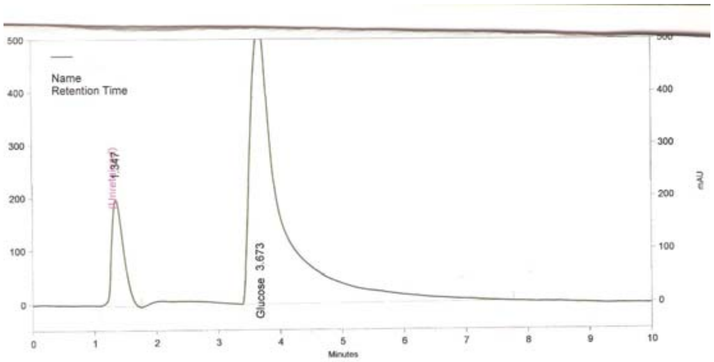
Fig 18: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of 5% HCl and 20% $ZnCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.347	1600011	21031711
2	Glucose	3.673	4241008	146314927
Totals			5841019	167346638

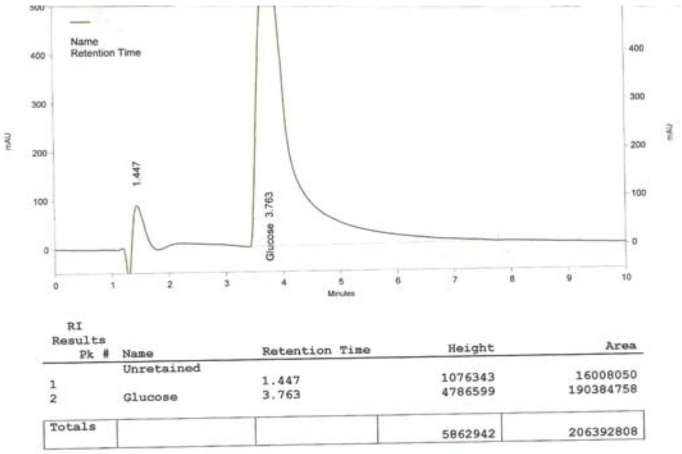
Fig 19: HPLC Chromatogram Results for Hydrolysis of Washed Jeft Using a Mixture of 5% HCl and 20% $ZnCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.347	1600011	21031711
2	Glucose	3.673	4241008	146314927
Totals			5841019	167346638

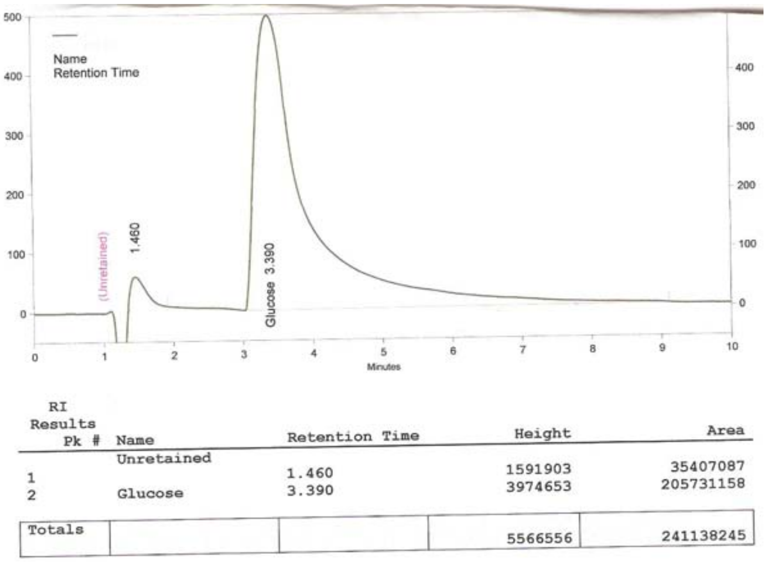
Fig 20: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 5% HCl and 20% $ZnCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.447	1076343	16008050
2	Glucose	3.763	4786599	190384758
Totals			5862942	206392808

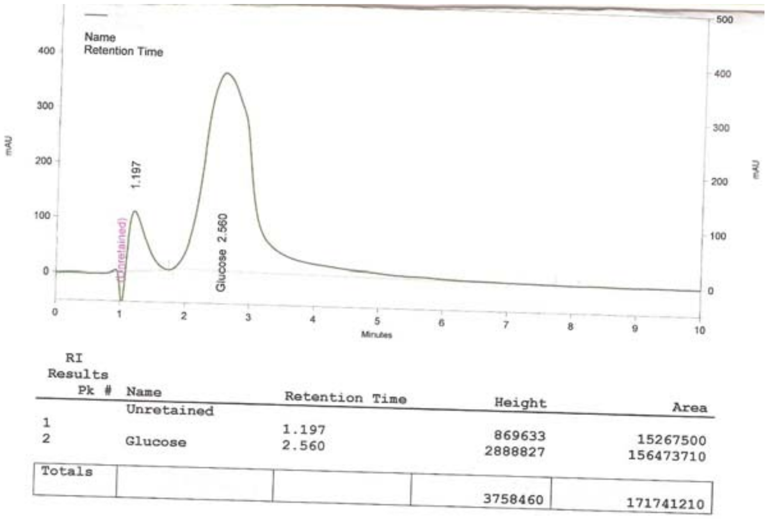
Fig 21: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of 10%HCl and 20%$ZnCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.460	1591903	35407087
2	Glucose	3.390	3974653	205731158
Totals			5566556	241138245

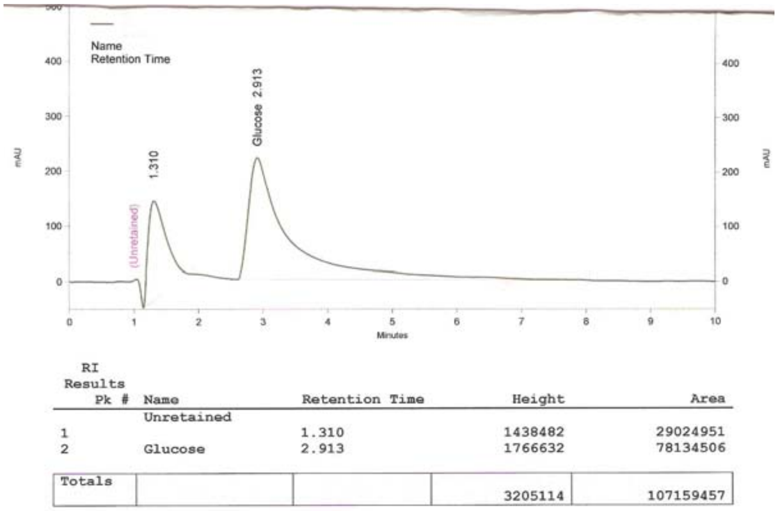
Fig 22: HPLC Chromatogram Results for Hydrolysis of Washed Jeft Using a Mixture of 10% HCl and 20% $ZnCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.197	869633	15267500
2	Glucose	2.560	2888827	156473710
Totals			3758460	171741210

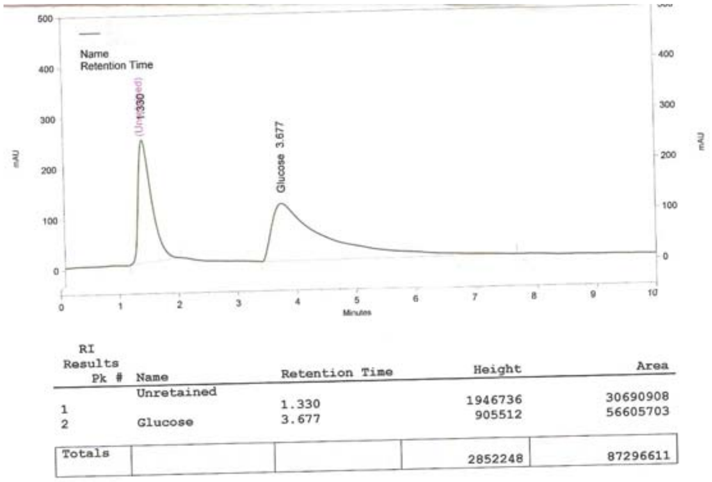
Fig 23: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of HCl and 20%$ZnCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.310	1438482	29024951
2	Glucose	2.913	1766632	78134506
Totals			3205114	107159457

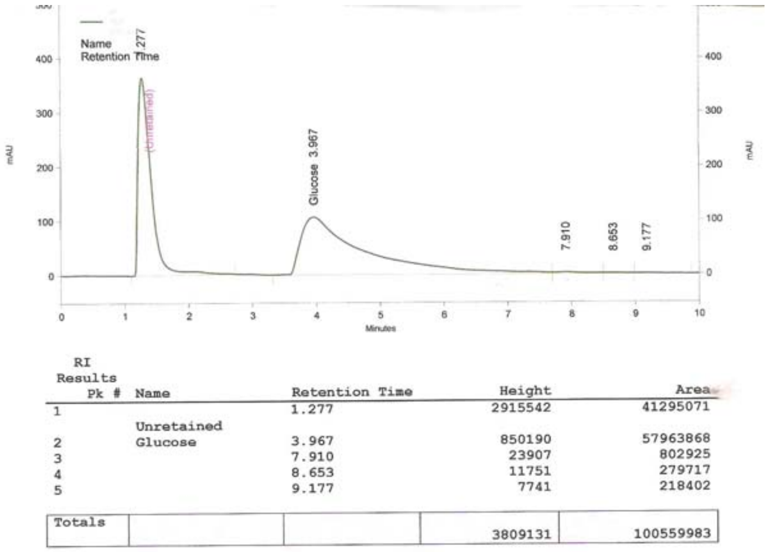
Fig 24: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of 5% HCl and 10% $CaCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.330	1946736	30690908
2	Glucose	3.677	905512	56605703
Totals			2852248	87296611

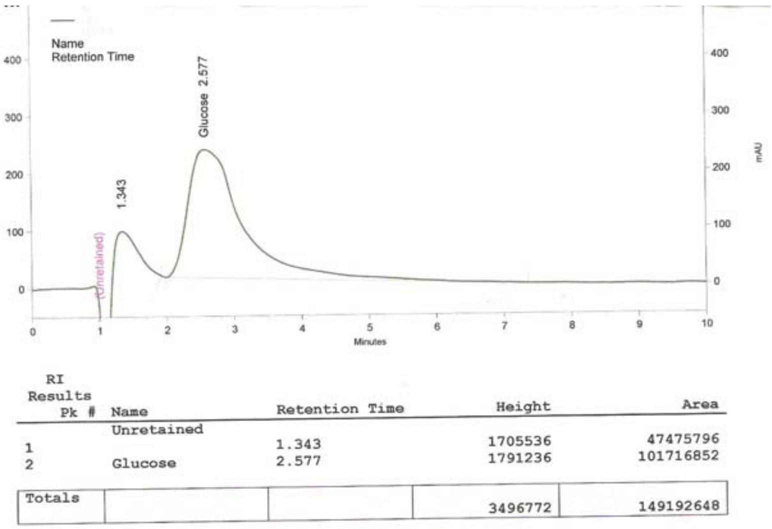
Fig 25: HPLC Chromatogram Results for Hydrolysis of Washed Jeft Using a Mixture of 5% HCl and 10% $CaCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.277	2915542	41295071
2	Glucose	3.967	850190	57963868
3		7.910	23907	802925
4		8.653	11751	279717
5		9.177	7741	218402
Totals			3809131	100559983

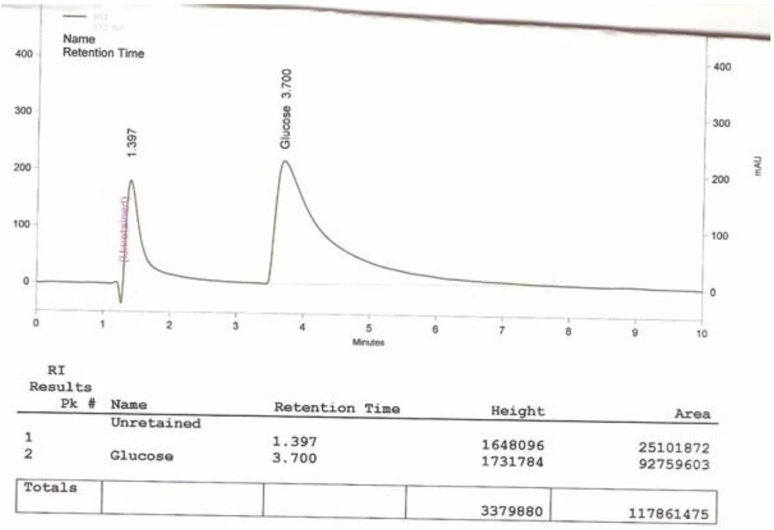
Fig 26: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Eextracted from Jeft Using a Mixture of 5% HCl and 10 % $CaCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1		1.343	1705536	47475796
2	Glucose	2.577	1791236	101716852
Totals			3496772	149192648

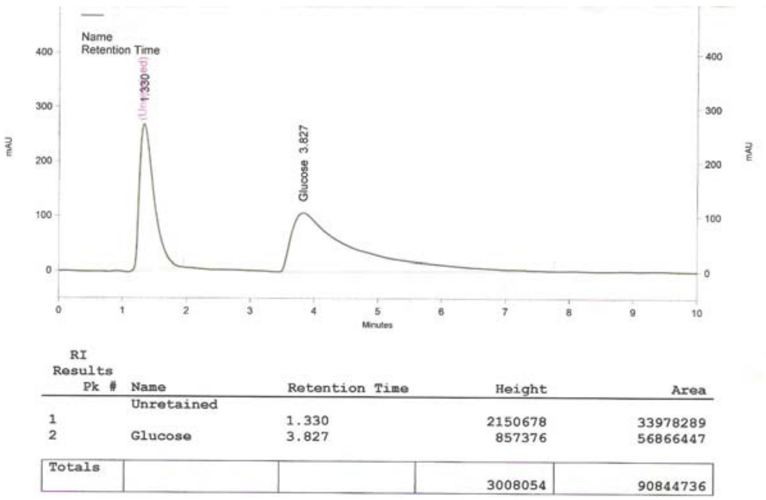
Fig 27: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of 10% HCl and 10% $CaCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1		1.397	1648096	25101872
2	Glucose	3.700	1731784	92759603
Totals			3379880	117861475

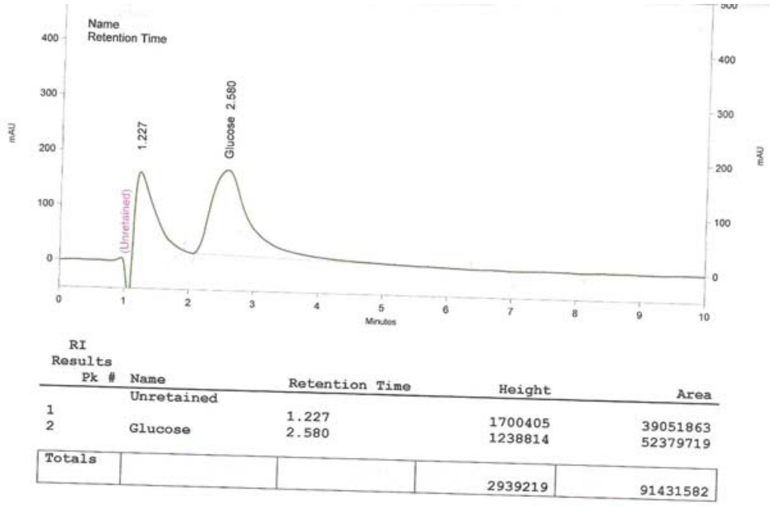
Fig 28: HPLC Chromatogram Results for Hydrolysis of Washed Jeft Using a Mixture of 10% HCl and 10% $CaCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.330	2150678	33978289
2	Glucose	3.827	857376	56866447
Totals			3008054	90844736

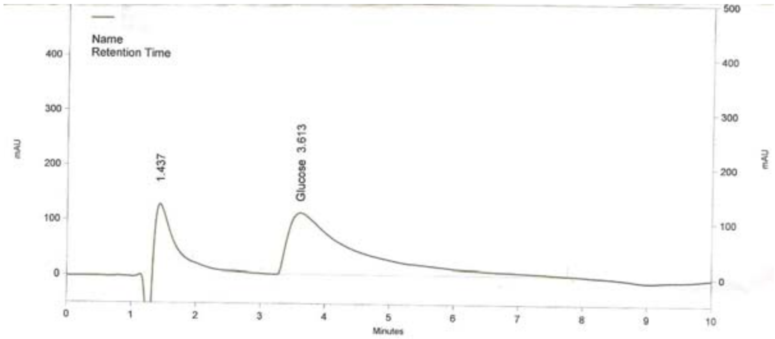
Fig 29: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 10% HCl and 10% CaCl$_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.227	1700405	39051863
2	Glucose	2.580	1238814	52379719
Totals			2939219	91431582

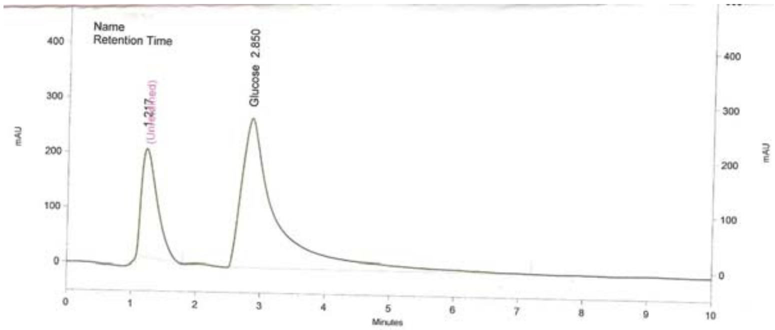
Fig 30: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of 5% HCl and 20% CaCl$_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1		1.437	1805745	36554419
2	Glucose	3.613	888529	63376078
Totals			2694274	99930497

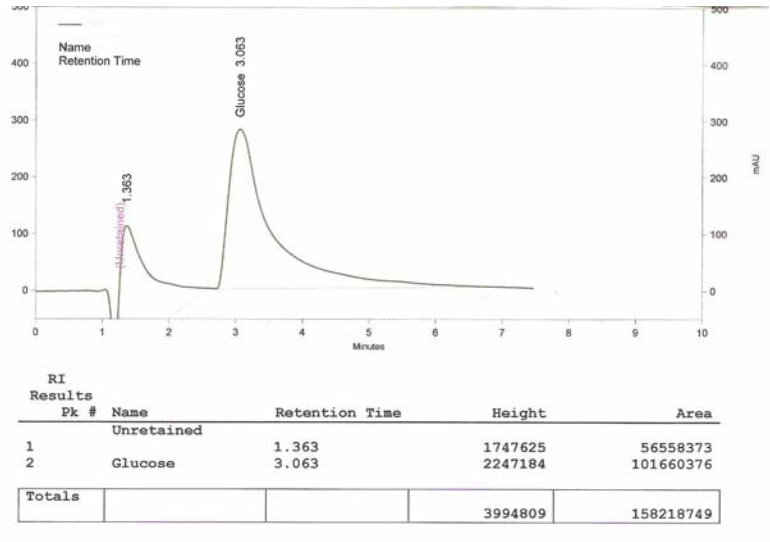
Fig 31: HPLC Chromatogram Results for Hydrolysis of Washed Jeft Using a Mixture of 5% HCl and 20% $CaCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.217	1577014	26840606
2	Glucose	2.850	2174582	82315705
Totals			3751596	109156311

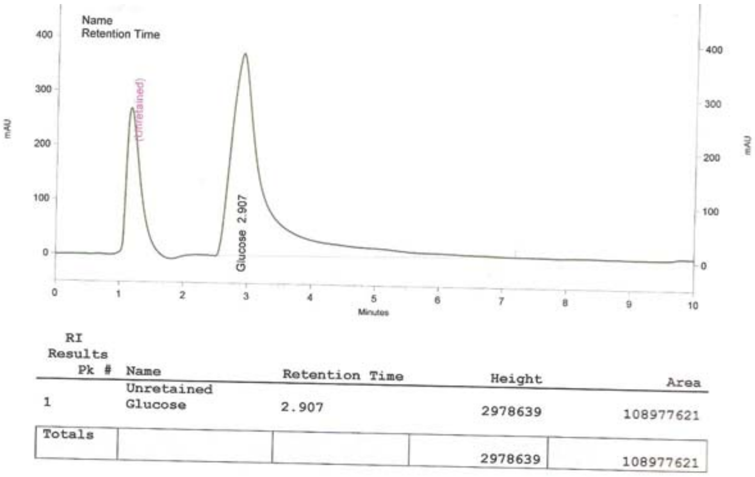
Fig 32: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 5% HCl and 20% $CaCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.363	1747625	56558373
2	Glucose	3.063	2247184	101660376
Totals			3994809	158218749

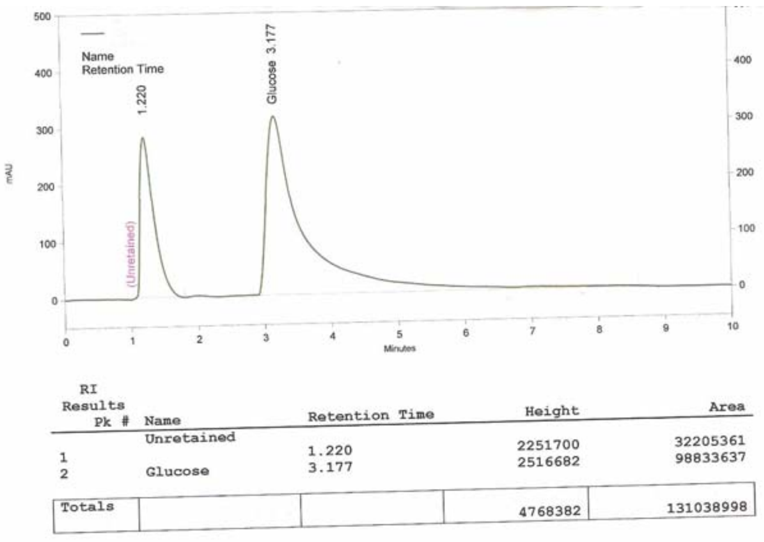
Fig 33: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of 10% HCl and 20% $CaCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained Glucose	2.907	2978639	108977621
Totals			2978639	108977621

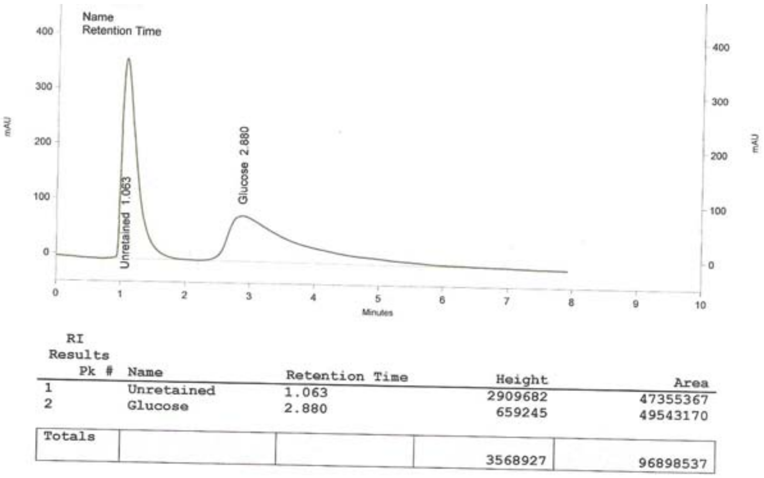
Fig 34: HPLC Chromatogram Results for Hydrolysis of Washed Jeft Using a Mixture of 10% HCl and 20% $CaCl_2$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.220	2251700	32205361
2	Glucose	3.177	2516682	98833637
Totals			4768382	131038998

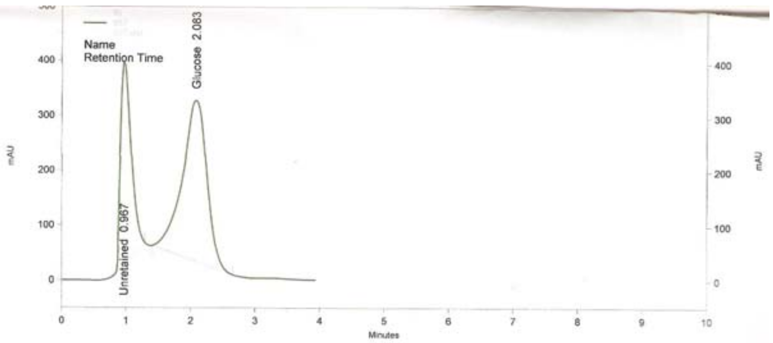
Fig 35: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 10% HCl and 20%CaC$_{l2}$ for (1hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.063	2909682	47355367
2	Glucose	2.880	659245	49543170
Totals			3568927	96898537

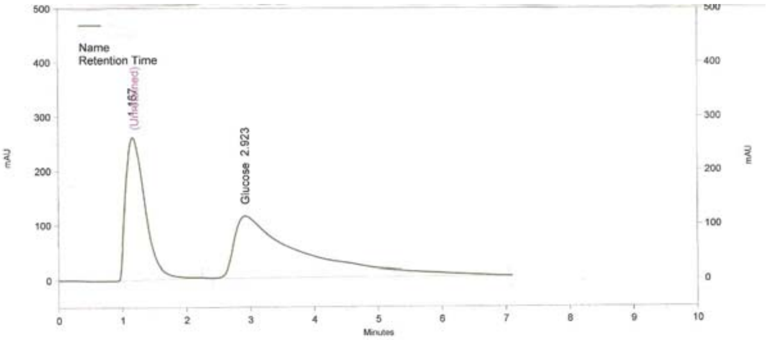
Fig 36: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of 5% HCl and 2.5% H_2O_2 for(2hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	0.967	2952572	34199456
2	Glucose	2.083	2345994	61862015
Totals			5298566	96061471

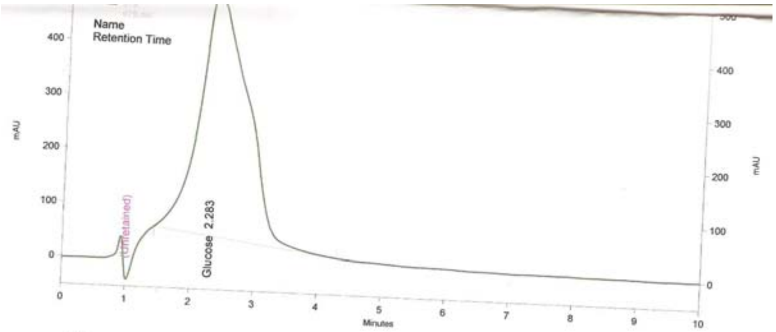
Fig 37: HPLC Chromatogram Results for Hydrolysis of of Washed Jeft Using a Mixture of 5% HCl and 2.5% H_2O_2 for(2hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.167	2092077	44112244
2	Glucose	2.923	902717	64822265
Totals			2994794	108934509

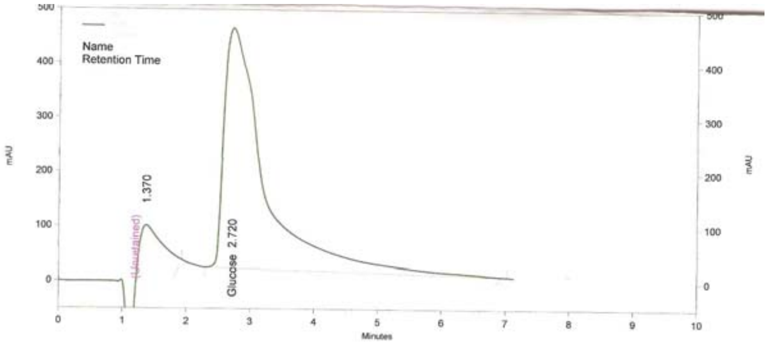
Fig 38: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of 5%HCl and 2.5% H_2O_2 for(2hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1	Glucose	2.283	3505161	185147463
Totals			3505161	185147463

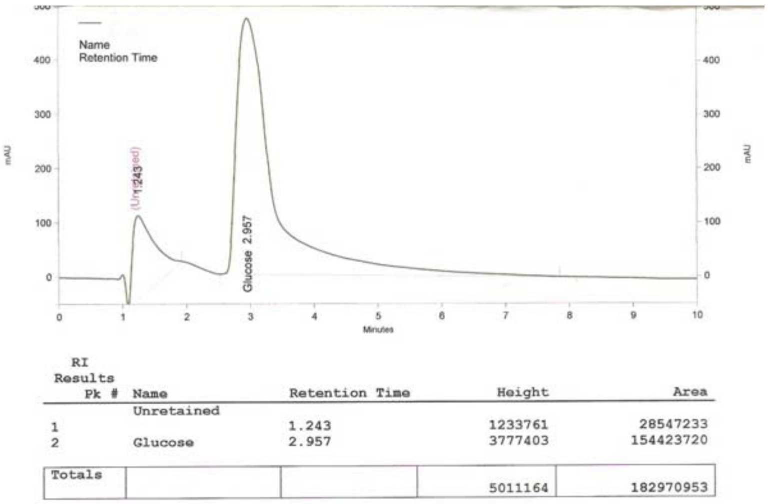
Fig 39: HPLC Chromatogram Results for Hydrolysis of Jeft Using a Mixture of Conc. HCl and 2.5% H_2O_2 for(2hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
	Unretained			
1		1.370	1700952	46013623
2	Glucose	2.720	3535440	157895409
Totals			5236392	203909032

Fig 40: HPLC Chromatogram Results for Hydrolysis of Washed Jeft Using a Mixture of Conc. HCl and 2.5% H_2O_2 for(2hr)



RI
Results

Pk #	Name	Retention Time	Height	Area
1	Unretained	1.243	1233761	28547233
2	Glucose	2.957	3777403	154423720
Totals			5011164	182970953

Fig 41: HPLC Chromatogram Results for Hydrolysis of Purified Cellulose Extracted from Jeft Using a Mixture of Conc. HCl and 2.5% H_2O_2 for(2hr)

جامعة النجاح الوطنية
كلية الدراسات العليا

إنتاج الكحول الحيوي من جفت الزيتون

إعداد
آمال عمر حسني شلبي

إشراف
د.عثمان حامد
د.شحده جوده

قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2011م

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الملخص

الجفت هو احد النواتج الفرعية التي تصاحب عملية عصر الزيتون, ويتكون من المواد التي يتكون منها الخشب مثل السليلوز واللجنيين, وشبه السليلوز, حيث نجحنا في استخلاص من 40-45%, من السليلوز الموجود في الجفت, تم إجراء بعض التحاليل للسليلوز المستخلص من الجفت.(RI, SEM,VI) وهي (microcrystalline structure) ونتاج هذه التحاليل تبين أن السليلوز الموجود في الجفت له قليله وهذه الخاصية جعلت استخدامه مثاليا في صناعة العقاقير والأغذيه, وفي هذه الدراسة الجفت والسليلوز المستخلص قد عولجا باستخدام حمض الهيدوكلوريك وثم حمض الكبريتيك وذلك لتحويل السكر المستخلص إلى إيثانول للاستفادة منه كوقود. ولقد تم الحصول على أعلى نسبه من السكر وكانت تساوي 27% باستخدام حمض الهيدوكلوريك المركز. ثم تم استخدام حمض الهيدروكلوريك المخفف وقاعدة لويس كلوريد الزنك وحصلنا على كمية51% من كمية السكر وهذه النتائج جاءت مكمله لنتائج التحاليل السابقة. والنسبة القليلة التي ظهرت معنا هي نتيجة ارتفاع درجة التبلور الخاصية العالية التي يتمتع بها السيليولوز. والتي قللت من تعرضه لعامل التحلل.