An-Najah National University
Faculty of Graduate Studies

METHODS OF EXTRACTING CELLULOSIC MATERIAL FROM OLIVE PULP

By

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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.

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This thesis was defended successfully on 29/12 /2009, and approved by:

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3. Dr. Abdallah Walwil. (External Examiner) **…………….**

DEDICATION

To my beloved husband Mohammed and my daughter
Leen for their inspiration

Acknowledgement

Praise and thanks to Allah, the most metrical for assisting and directing me to the right path, without his help my effort would have gone astray. Special thanks are due to my research supervisor Dr. Othman Hamed, for the opportunity to work with him in his research group. I am deeply grateful to him for his constant presence, his willingness to help at any time and his encouragement throughout this research project. I also thank the thesis committee member, Dr. Mohammed Alnuri, Dr. Shehdeh Jaodeh, and Dr. Abdullah Walwil for their consent to read my thesis and provide useful suggestions.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحت عنوان

Methods of Extracting Cellulosic Material From Olive Pulp

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

Declaration

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

Student's name: **اسم الطالب:**

Signature: **التوقيع:**

Date: **التاريخ:**

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METHODS OF EXTRACTING CELLULOSIC MATERIAL FROM OLIVE PULP

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Abstract

Jefft is an important solid waste generated in large quantities every year from olive oil extraction process. Jefft is considered a lignocellulosic material, so it consists of components similar to that of wood such as cellulose, lignin, and hemicellulose. Jefft is produced from natural product, so it is considered a renewable source of cellulose. In this study about 30% of pure cellulose was extracted from Jefft. The separation of cellulose from Jefft was performed in four stage : extraction, pre-hydrolysis, pulping, and bleaching. Our study showed that two steps of pulping and bleaching could be as good as the four steps one. In the extraction step, the extractable materials such as residual olive oil were removed. In the second step the Jefft was subjected to treatment with diluted solution of sulfuric acid (5%) or sodium hydroxide (5%) under a pressure of about 5 psi. This step was useful in opening the Jefft structure and make it more accessible to pulping and bleaching chemicals. Then Jefft was subjected to pulping by either acid or Kraft pulping process. Results indicate that Kraft pulping is considered to be more suitable to used in this study, since with the Kraft process higher yield of cellulose was obtained, in addition chemicals used in this study was recyclable. Recycling of chemicals is a very important factor in this study, since we are planning in scaling up the process to a multi-ton process. In the Kraft process, Jefft was treated with a solution of sodium hydroxide and sodium sulfide under a pressure (5 psi). Resulting cellulose was then subjected to treatment with various oxidizing agents in a process called bleaching process. Various sequences of oxidizing agents each consisting of at least four oxidizing agents were studied. The best results were achieved when using the sequence of CEHP which consists of the four oxidizing agents: chlorine, sodium hydroxide, hypochlorite, and hydrogen peroxide. Cellulose produced, using this sequence, showed the lowest contents of lignin as was determined by Kappa No. procedure. Viscosity was determined to cellulose produced from CEHP bleaching sequence, from the viscosity, the DP was determined to be about 315. These results indicate that, cellulose extracted from Jefft has a structure that could be similar to that of microcrystalline cellulose (MCC).

Results summarized in this thesis indicate that we have succeeded in converting waste solid Jefft into valued added product MCC. MCC is a valuable natural polymer that is very useful in unlimited numbers of commercial applications such as food, medicine, construction, absorbents, and many others.

CHAPTER I

INTRODUCTION

1.1 Background

Oil recovery from olives is a major industry in Palestine, usually occurs by a conventional batch process wherein olive is pressed and oil and water are collected then oil is separated form water by centrifuge and decantation. With this method olive oil usually requires no further processing.

In addition to olive oil, solid waste is generated during the press process. The solid waste is known as Jefft. A considerable amount of Jefft is generated from olive mills every year in Palestine and all over the world.

This waste material possesses a challenge in waste management to the olive mills and a concern to the environmentalists. It presents a serious disposal problem. Usually the Jefft is left to rot or burned.

Jefft consists of several components, the components are expected to be similar to that found in wood which consists mainly of three polymers: cellulose, hemicelluloses, and lignin. Wood also contains small amounts of extractives and inorganic material. The main constituent, cellulose, is a linear homopolysaccharide composed of β-D-glucopyranose units linked together by β-1,4-linkages, Figure 1.1. The cellulose chains consist of about 10,000 monomer units, grouped together in bundles called microfibers, which form either ordered (crystalline) or less ordered (amorphous) regions. Microfibers build up fibrils and finally cellulose fibers.

Chemically, cellulose is very stable and extremely insoluble polymer.[1] Cellulose has no taste, odorless, hydrophilic, insoluble in water and in most organic solvents, chiral, and is biodegradable.

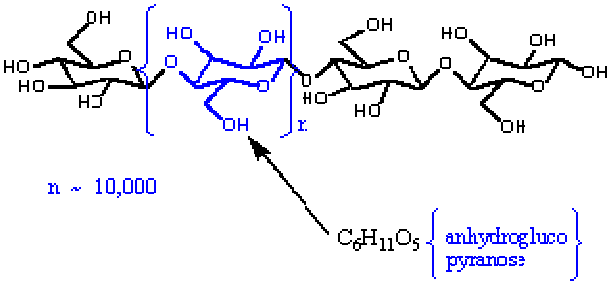
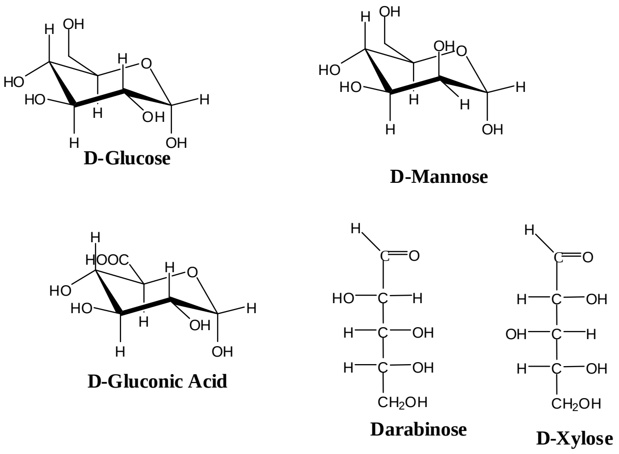


Figure 1.1

The uniqueness of the chemical structure and macromolecules configurations make cellulose rigid, highly crystalline material which is difficult to dissolve in common organic solvents. This property serves it well as a structural engineering material. Polymer solubility and flexibility are very important criteria for materials to be used in pharmacy. To meet these criteria, chemical modification of cellulose is essential so that it can be transformed into water soluble, organo soluble, or meltable derivatives. This would improve its processability and performance for specific applications in the broad field of pharmacy. Being natural polymers, cellulose and cellulose derivatives are generally recognized as safe nontoxic material, noncarcinogenic, biocompatible, and in no way harmful in the biological environment. Because of that, cellulose have gained wide acceptance in medical application as well as in pharmaceutical, cosmetic, food and packaging uses. [2,3,4]

The second main component of wood is hemicelluloses, that is a group of heteropolysaccharides built up of different types of monosaccharides. The chains of hemicellulose are shorter than those of cellulose, with a degree of polymerization of about 100 to 200.[5] Like cellulose, most hemicelluloses function as supporting material in the cell walls. Hemicelluloses are relatively easily hydrolyzed by acids to their main monomers consisting of glucose, mannose, xylose, galactose, arabinose and rhamnose: The structure of these monosugers are shown in Figure 1.2 below. In addition some hemicelluloses contain uronic acids. The compositions and structures of the hemicelluloses depend on the source.



D-Glucose

D-Mannose

D-Gluconic Acid

Darabinose

D-Xylose

Figure 1.2

The third main component of wood is lignin, the material that binds the cellulose fiber together in wood and it differs from cellulose and hemicelluloses in many ways. It has no obvious repeating unit building up of its structure and the structure of lignin can in the broadest sense be described as three dimensional net work as shown in Figure 1.3.

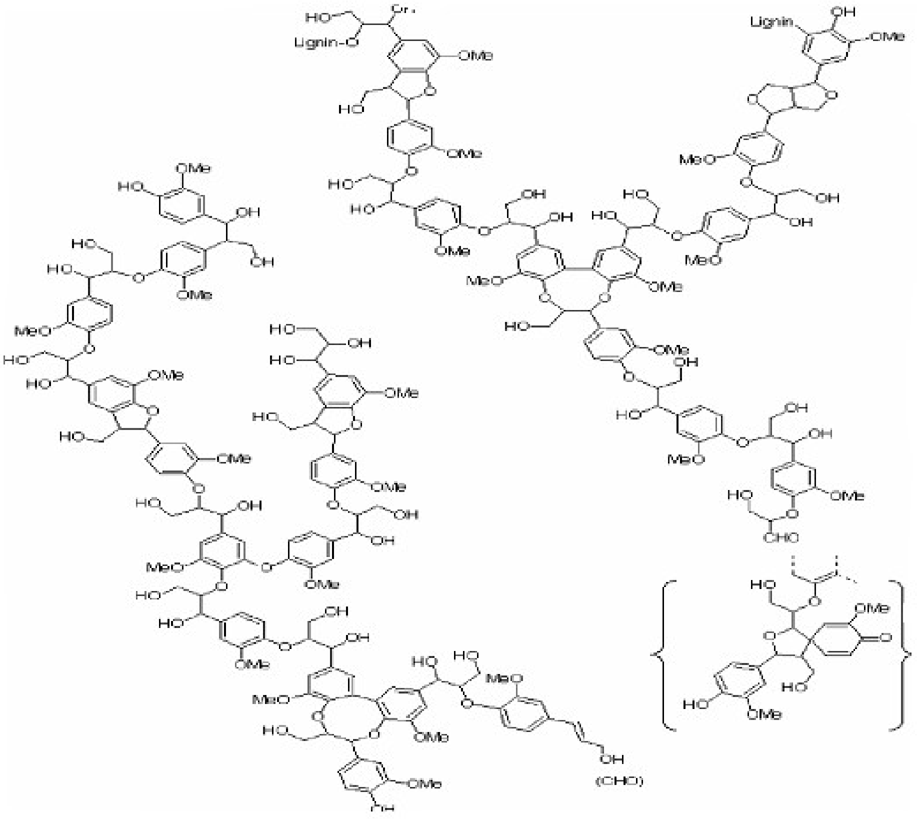


Figure 1.3

The lignin is built up of hydroxyphenylpropane units and is phenolic in character. The hydroxyphenylpropane units are connected by various types of bonds, of which arylglycerol-β-arylethers (β-O-4) are the most frequent.[6] The chemical structure of lignin is irregular in the sense that the structural elements are not linked to each other in any systematic order. Lignin is a result of the radical polymerization of three hydroxyphenylpropane units shown in Figure 1.4.[7]

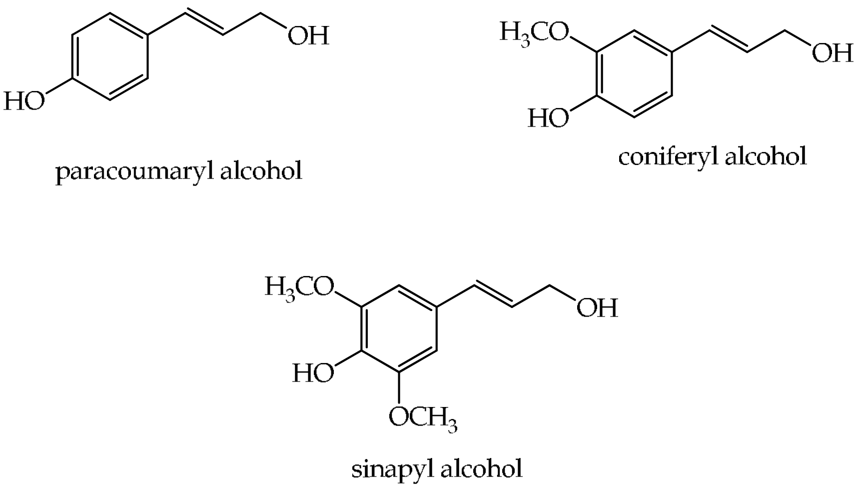


Figure 1.4

1.2 Cellulose Structure and Properties

Cellulose is a linear polymer made of the monomer D-glucose units that are linked successively through glycosidic linkage in the β-configuration between carbon 1 and carbon 4 of adjacent unit to form a polymeric chain (Fig 1.1). Because of the β-configuration of the intermonomer links, the glucose units effectively alternate up and down in the chain, as a results of that cellobiose (Figure 1.5) is considered to be the repeating unit of cellulose, on which a syndiotactic configuration of the macromolecule is formed. The size of the cellulose molecule occurring in natural indicated by its degree polymerization (DP) and is dependent heavily on its source, Table 1.1.[8]

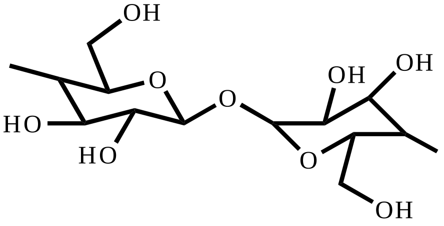


Figure1.5

Pure cellulose inevitably loses some of its molecular weight (MW) during isolation and purification. The DP of cellulose typically- ranges from 1,000 to 10,000, and cellulose chains are composed entirely of anhydrous D-glucose units. Cellulose is unlike starch, no coiling occurs, and the molecule adopts an extended stiff rod-like conformation (Fig 1). The multiple hydroxyl groups on the glucose residues from one chain form hydrogen bonds with oxygen molecules on adjacent chain, holding the chains firmly together side-by-side and forming microfibrils with high tensile_strength. Compared to starch, cellulose is composed of two regions (crystalline and amorphous) while starch is an amorphous. Cellulose requires a temperature of 320 °C and pressure of 25 mPa to become amorphous in water.[9]

Table (1.1) Degree of polymerization of cellulose from various sources

Source	**Degree of polymerization**
Acetobactor xylinum	2,000-3,700
Acetobactercellulose	600
Bacterial cellulose	2700
Bagasse	700-900
Bast fibers	1,000-5,000
Cotton fibers	8,000-14,000
Cotton linters	1,000-6,500
Flax fibers	7,000-8,000
Ramie fibers	9,000-11,000
Pulp cellulose (bleached)	5,00-2,100
Wood fibers	8,000-,9,000
Valonia	25,000-27,000

Cellulose crystalline region is accessible for only certain chemicals such as strong bases and acids. It is considered as an inert material and only soluble in certain solutions such as aqueous N-methylmorpholine-Noxide (NMNO ~0.8 mol water/mol also dissolves up to 30% by wt cellulose at 100°C in LiCl/*N,N'*-dimethylacetamide, or ionic liquid.

Many properties of cellulose depend on its degree of polymerization, the number of glucose units that make up one polymer molecule. [10] Molecules with very small chain length resulting from the break down of cellulose are known as cellodextrins; in contrast to long-chain cellulose, cellodextrins are typically soluble in water and organic solvents.

1.3 Cellulose Derivatives

Once the cellulose polymer becomes amorphous and the hydroxyl groups on the D-anhydroglucopyranose units are become accessible to varius chemicals, they offer a variety of possibilities for making useful derivatives [11,12,13] .The properties of the derivatives depend heavily on the type, distribution, and uniformity of the substitution group. The average number of hydroxyl groups replaced by the substituent is known by degree of substitution (DS), the maximum is 3 substituents per D-anhydroglucopyranose unit. For example, in a cellulose ether with DS of 1.5, 50% hydroxyl groups are converted to ether and 50 % remain free.

Properties that are most strongly affected by DS are the solubility and plasticity, which are essential properties for pharmaceutical products. Solution properties and rheological characteristics are function of the degree of substitution and substituents distribution. Derivatives of a low DS are often more sensitive to water and may even be dispersive in water.

In derivatives with a high DS of nonpolar substituents, the water absorptivity and solubility are decreased, and the solubility in organic solvents is increased. Moreover, with an increase in DS of non-polar groups, the plasticity is increased.

The quality and stability of the cellulose derivatives can be enhanced by etherification, esterification, cross-linking , or graft copolymerization. In graft copolymerization, cellulose ester is used in by far the greatest volume, but cellulose ether is more important in pharmacy, medicine, cosmetics, and food.

1.4 Cellulose Applications

Cellulose in its polymeric form can be employed for manufacture of paper and industrial feedstocks or converted into large number of derivatives with unlimited number of commercial applications, and also in the production of ethanol when chemically or enzymatically hydrolyzed into glucose. For instance cellulose acetate is a plastic collodion useful in medicinal applications.

Cellulose ethers like hydroxypropylmethyl cellulose (HPMC) are generally applied to many areas of industry and domestic life. Its spectrum of applications ranging from auxiliaries in large-scale emulsion or suspension polymerization, through to additives for paints and wall papers adhesives, to viscosity enhancers in cosmetics and food-stuffs.

The worldwide industrial manufacture of cellulose ethers has presently arrived at a level of over half a million tons annually. The most important properties of cellulose ethers are their solubility, chemical stability and non-toxicity.

Cellulose also is the raw material in the manufacture of nitrocellulose (cellulose nitrate) which was historically used in smokeless gunpowder and as the base material for celluloid used for photographic and movie films until the mid 1930s.

Another important application for cellulose is in the laboratory as the stationary phase for thin layer chromatography.

Cellulose insulation made from recycled newsprint is becoming popular as an environmentally preferable material for building insulation.

Cellulose is also used to make hydrophilic and superabsorbent sponges, as well as water-soluble adhesives and binders such as methyl cellulose and carboxymethyl cellulose which are used in wallpaper paste.

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. [14]

Despite the fact that humans (and many other animals) cannot digest cellulose (meaning that their digestive systems cannot break it down into its basic constituents), cellulose is a very important part of the healthy human diet. This is because it forms a major part of the dietary fiber that we know is important for proper digestion. Since human bodies cannot break cellulose down and it passes through our systems basically unchanged, and that makes called bulk or roughage that helps the bowel movements .

In fact, crystallite cellulose is added to some foods to reduce the caloric value. [15]

Another important form of cellulose is microcrystalline cellulose and powdered cellulose. Microcrystalline cellulose (MCC) is a partially depolymerized cellulose prepared by treating cellulose with hydrochloric acid. [16] The microcrystalline cellulose occurs as a fine , white, odorless crystalline powder usually used as inactive ingredients fillers in medicine tablets and as thickeners and stabilizers in processed foods. [17] Microcrystalline cellulose used as an excipient to assist in the flow, lubrication, and bonding properties of the ingredients to be tableted; to improve the stability of the drugs in tablet form; and especially to provide for rapid disintegration in the stomach. It also contributes stability to many pharmaceutical formulation.

When properly dispersed in water to formed stable colloidal gels and dispersions, MCC can be used in cosmetics and pharmaceuticals for both creams and solid suspensions. [17,18] It is also used to prepare reduced–lipid or lipid-free ice cream and mayonnaise like products and low-and no-oil pourable salad dressings, it also strengthens and stabilizes foams.

1.5 Method of obtaining cellulose from its sources

Cellulose in its native form is distributed throughout the plants kingdom. In wood pulp or cotton fibers (cotton fibers are a biological source of almost pure cellulose). Cotton fibers are about 98% cellulose, while wood is 40-50% cellulose, Table 1.2 [19]

Cellulose can also be produced from various other plant, such as corn cobs or stalks, soybean hulls, bagasse (sugar cane stalks), oat hulls, rice hulls, wheat straw, sugar beet pulp, bamboo, and fibers such as jute, flax, and ramie among others. [20]

Commercial cellulose production concentrates on the highly pure sources such as cotton or the easily harvested sources such as wood. The isolation of cellulose from wood is more difficult than its isolation from most of its other sources. It is usually performed by a pulping process.

Table (1.2): A Summary of Natural Sources of Cellulose

Source	Cellulose Content (%)
Baggbasse	35-45
Bamboo	40-55
Cotton	90-99
Flax	70-75
Hemp	75-80
Jute	60-65
Kapok	70-75
Ramie	70-75
Straw	40-45

1.5.1 Pulping Process

Generally pulping process involves treating wood with chemical in aqueous solution at elevated temperature and pressure. There are two major types of chemical pulping known in the art : Kraft pulping and Sulfite pulping.

1. Kraft process: In this process wood is treated with a solution of sodium hydroxide and sodium sulfide at elevated temperature and pressure. The output products are separated pulp and solution that contains degraded lignin and hemicellulsose. Today, the Kraft process is the dominating process for the production of chemical pulps in the world, accounting for more than 90 % of the world's total manufacture of bleached chemical pulps. The Kraft process produces a strong pulp, thereby the name – Kraft – coming from the German and Swedish words for strength. Some drawbacks of the Kraft process compared to the Sulfite process are the formation of malodorous gases which cause environmental concern, lower yield and a much darker pulp.

2. Sulfite process: This process relies on acid solution of sulfurous acid (H_2SO_3) and bisulfate ion to break the bond between cellulose and lignin.

The pulping process separates the cellulose from the lignin and hemicellulose leaving it in a fibrous form that is purified, dried, and shipped in large rolls.

Cellulose produces from pulping usually contain small amount of lignin which cause it to have some brown discoloration. Further purification of cellulose is performed by several steps known as bleaching and alkali extraction.

1.5.2 Bleaching of pulp

The lignin cannot be removed from the wood by pulping alone because of poor selectivity. The pulping process is therefore interrupted after the dissolution of approximately 90 % of the lignin originally present in the wood. The pulping is often followed by an oxygen delignification stage. After the oxygen delignification stage, about 1.5 % (on wood) of the lignin remains in the pulp. The left over lignin present as impurities and cause some discoloration to pulp, since it contains large number of chromophores, which are usually removed by subjecting pulp to multi-bleaching process.

Bleaching is desirable for several reasons. First, a bright pulp is necessary for good contrast. Second, bleaching of the pulp makes it more resistant to aging. Another purpose of bleaching is to improve the cleanliness of the pulp by removing extractives. Chemically and biologically pure pulps are required especially in the production of hygiene products and packages for food. The light absorption (color) of pulp is mainly associated with its lignin component. To reach an acceptable brightness level, the residual lignin should thus either be removed from the pulp or, alternatively, freed from strongly light-absorbing groups (chromophores) as completely as possible.

The bleaching is carried out in a number of consecutive stages, chlorine dioxide, hydrogen peroxide, ozone and/or peracetic acid as bleaching agents, with a minor use of the latter two.

Bleaching may include up to twelve steps of chlorination, hypochlorite bleaching, chlorine dioxide bleaching, and extraction with concentrated sodium hydroxide along with intermediate alkaline extraction (washing) after each oxidative stage.

Scope

The overall aim of the work described in this thesis is to convert solid waste [Olive industry solid waste (Jefft)] into valuable commercial material cellulose. Cellulose is a classical natural polymer with unique chemical, physical, and mechanical properties. Its physical arrangement of macromolecules makes cellulose rigid structural material. The utilization of its three hydroxyl group can transform this practically insoluble polymer into soluble derivatives in water and organic solvents. This endeavor also opens up the opportunity for cellulose derivatives to be used in pharmaceuticals, cosmetics, and medical fields. Although cellulose and its derivatives have contributed immeasurably to the welfare and health of human race, the renaissance of cellulose chemistry in recent years, due to its biocompatibility and renewability, has allowed continued significant progress in the arena of biomaterials and medicines. It is believed that more novel cellulose derivatives with unique properties are to come.

In this thesis, we offer a new source of cellulose that is the olive pulp (Jefft). A considerable amount of olive pulp (*Jefft*) is generated from olive mills every year in Palestine and all over the world. Jefft is considered as a waste material that possesses a challenge in waste management to the olive mills and a concern to the environmentalists (which presents a serious disposal problem). Usually Jefft is left to rot or burned.

About 70% of the volume coming out from the olive mill is olive pulp, in other words, almost 40-45% of the olive is carbohydrate (cellulose).

Every year there is about 40 thousand MT of Jefft produced in Palestine alone. This means over 1.5 million pounds of carbohydrate waste generated from olive every year. This amount of carbohydrate is more than enough to supply all of the existing of factories and research institutions in Palestine with the cellulose and fine chemicals requirements .

In this work, developed methods of separating and purifying cellulose from Jefft, along with same and ways of analyzing are presented.

Chapter II

Results and Discussion

Olive oil industry represents an economic and social industrial activity that is highly significant in Palestine and other Mediterranean countries. Despite its economical value, olive oil industry has quite a large environmental impact due to the production of highly polluted wastewater and waste solid residue (Jefft). Jefft is considered a lignocellulosic material, so it is a rich source of valuable components. Jefft composition is similar to that of wood, it consists of four main components: 1) extractive, 2) cellulose; 3) lignin; and 4) hemicellulose.

The main purpose of this study is to develop a fractionation method to separate Jefft into its components in order to convert low value biomass Jefft into commercially useful products.

2.1 Extraction of Jefft

Jefft, before purification, was subjected to Soxhlet extraction with ethyl acetate. After extraction, ethyl acetate was removed under reduced pressure, weight of the residue indicates that about 20% of the Jefft mass is extractives. The major component of extractives is olive oil, our results are consistent with a published results which shows that about 80% of the extractives is olive oil.[21] All Jefft samples in this study were subjected to moisture analysis. In this step, moisture contents was determined based on a procedure listed in the experimental section. This was necessary for determining accurate pulping and bleaching conditions. Moisture contents assessment was performed using oven drying technique. A known weight of Jefft sample was dried in an oven at about 110 °C until constant weight, then oven dry weight was calculated according to equation 2.1.

$$\textbf{Mositure content \%} = \frac{\textbf{Weight Loss}}{\textbf{Wet sample weigh}} \times 100\% \qquad \textbf{Eq. 2.1}$$

Results show that moisture contents of Jefft ranged from 15-20%.

2.2 Jefft Pre-Treatment (Pre-Hydrolysis)

After extraction, Jefft was subjected to pre-hydrolysis.

Pre-treatment refers to the partial separation of one or more of the four major components of biomass hemicellulose, cellulose, lignin, and extractives to make the remaining solid biomass more accessible to further chemical or biological treatment. Some separation and hydrolysis of hemicellulose also may occur during pre-treatment.

The most common chemical pre-treatment used for cellulosic feedstocks are dilute acid, alkaline, organic solvent, ammonia, sulfur dioxide, carbon dioxide or other chemicals.

Biological pre-treatments are sometimes used in combination with chemical treatments to solubilize the lignin in order to make cellulose more accessible to hydrolysis.

In acid pre-hydrolysis, the Jefft was suspended in a solution of sulfuric acid (0.5%) and heated for a period of 2 hours. In basic pre-hydrolysis the Jefft was suspended in a solution of sodium hydroxide (2%) and heated for about 2 hours. Results indicate that there is some loss of cellulose during pre- acid and base hydrolysis stages. The yield of pulp for both process 65% and 74%, respectively.

Pre-hydrolysis with acid was more effective than with base, pre-hydrolysis with base gave higher yields, however Kappa No. for the sample pre-hydrolyzed with acid was lower, which means lower contents of lignin. These results indicate that more lignin could be removed by pre-treatment with acid reagent. Pulp produced by acid hydrolysis expected to produce cellulose that is cleaner and brighter even at lower concentration of bleaching agents.

The yield from acid pre-hydrolysis was lower than the basic one by about (10-15%), as shown in the experimental part. The low yield in the acid pulping could be related to acid hydrolysis of cellulose to sugar monomer as shown in the following figure 2.1.[22] The mechanism of acid-catalyzed hydrolysis of cellulose (cleavage of β-1-4-glycosidic bond) follows the pattern outlined in Fig. 2.1**.** Acid hydrolysis proceeds in three steps. The reaction starts with a protonation of the glycosidic oxygen linking two sugar units, forming a protonated cellulose (conjugate acid). Then water makes a nuleophilic attack on the protonated cellulose which breakdown to the cyclic carbonium ion. After a rapid addition of water, free sugar and a proton are liberated. 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.

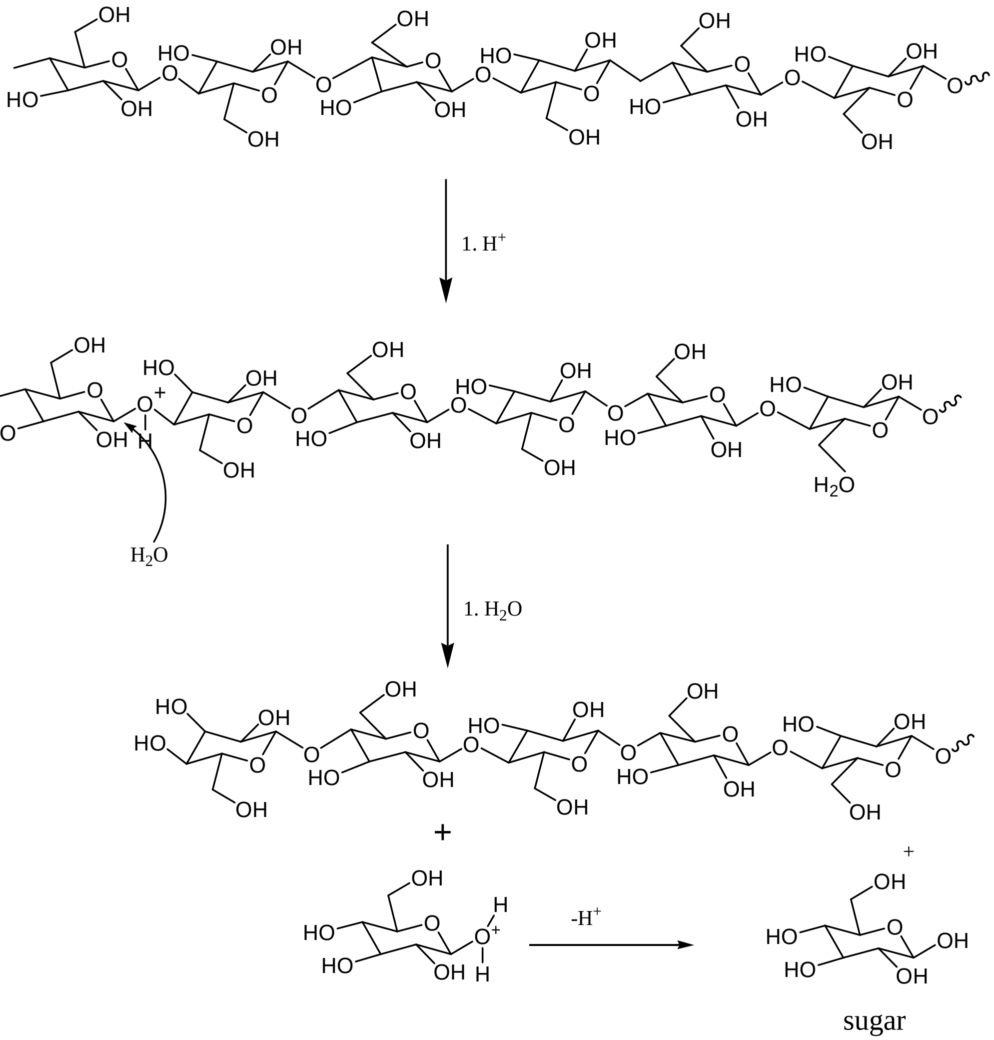


Figure 2.1 (the mechanism of acid hydrolysis of cellulose)

Pre-Treatment process is important in the removal of lignin, and producing cellulose with high purity.

After pre-Treatment Jefft was then subjected to purification by pulping and bleaching techniques. The pulping process separates the cellulose from the lignin and hemicellulose, leaving it in a fibrous form that is then purified by bleaching, dried, shipped for consumers.

2.3 Pulping of Jefft

2.3.1 Acid pulping

Pulping was performed using the two techniques: a) acid pulping, and b) Kraft pulping.

In acid pulping, Jefft was suspended in a solution of acetic acid and hydrochloric acid with various percentage weights as shown in Table 3.1 in the experimental part, then heated for periods of time varied form 2 to 4 hrs. In yield assessment, two factors were considered: 1) produced pulp weight; and 2) pulp whiteness and purity. Yield was calculated according to equation 2.2.

$$\%\ \text{Yield} = \frac{\text{Oven dry wieght of produced cellulose}}{\text{Oven dry weight of raw Jefft}} \times 100\ \% \qquad \text{Eq.2.2}$$

At higher concentration of HCl, produced cellulose looked whiter and contains fewer of unbroken particles of Jefft (barks). Based on these observations, samples 2, 3, 4, and 5 showed higher percentage yields and cleaner cellulose products. After pulping, produced cellulose usually has a light brown color, which is related to small amount of lignin left over on the pulping. The amount of lignin remains in cellulose after pulping and bleaching usually estimated by Kappa number as shown in equation 2.3.

wt.% of lignin = 0.15 x Kappa Number Eq. 2.3

Kappa number was determined according to procedure shown in the experimental part.

2.3.2 Kraft Pulping of Jefft

In Kraft pulping Jefft was suspended in a solution of sodium hydroxide and sodium sulfide with various ratio as shown in the experimental part.

The Kraft process is the most frequently used process in pulping.

The success of Kraft processes and its widespread are due to several reasons. Among these, Kraft chemicals are selective in their attack on Jefft constituents and the pulps produced are notably stronger than those from other processes.

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 degrades into smaller units by cleaving inter-linkage. The second by introducing a hydrophilic groups into lignin polymer and fragments, rendering it more soluble in the pulping solution. An example on lignin fragmentation is shown in Figure 2.2 Fragmentation shown in Figure 2.2 results from the cleavage of aryl ether linkage, this cleavage assist in the dissolution by creating additional phenolic groups. After pulping the remaining linkage are principally the C-C bond types.[23]

Structure changes of lignin polymer was proved by Kiringstad and Morck, they studied the course of the reaction by ^{13}C-NMR. In their study they proved that aryl ether linkage was interupted. [24]

Residual lignin is believed to be attached to cellulose as shown in Figure 2.3, which may influence its dissolution during pulping process. The residual lignin is usually removed by bleaching process. [25]

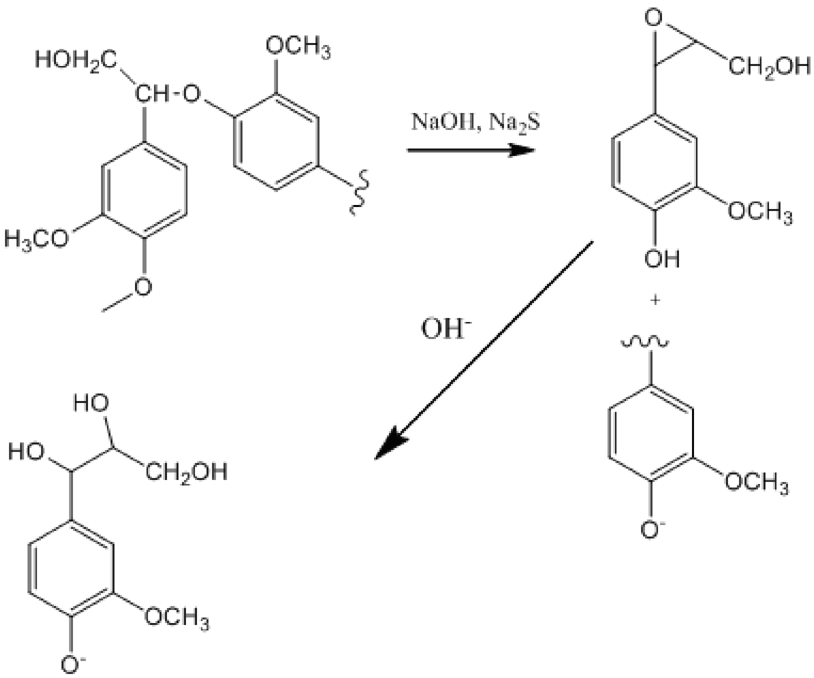


Figure 2.2(An example of degrading process of Lignin into smaller units)

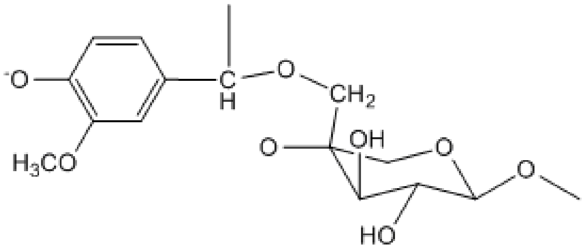


Figure 2.3(An example of the attaching residual lignin with cellulose)

The Kraft process is also flexible, it is amenable to many different type of raw cellulosic materials (wood, grass, bagass, and others) and can tolerate contaminants frequently found in Jefft. Lignin removal rates are high in the Kraft process (up to 90 percent) allowing high levels of brightness (whiteness) without pulp degradation. Finally, the chemicals used in Kraft pulping are readily recovered within the process, making it very economical and reducing potential environmental releases.

In the Kraft pulping of Jeff, a sodium-based alkaline was used. The active ingredients in the Kraft process are sodium sulfide (Na_2S) and sodium hydroxide (NaOH). Fresh solution of NaOH and Na_2S usually called white liquor. Total weight of Na_2S and NaOH in gram per liter of liquid is expressed as active alkali. This white liquor was mixed with the Jefft. A mixture of Jefft and white liquor was heated at 140-160 ^{o}C for various times under a high pressure. At the end of the process, cellulose is separated and hemicellulose and lignin are dissolved in the white liquor. The white liquor at this stage changed to a black liquor.

Kraft and acid pulping conditions, yield , and Kappa numbers for various samples are listed in Table 2.1.

Table (2.1): Comparison between results of organic acid and Kraft pulping

No.Sample	Conditions Pulping	%Yield	Number Kappa
3	Organic acid	23	3.75
5	Organic acid	23	0.225
9	Kraft pulping	44	1.5
10	Kraft pulping	46	1.16

Cellulose produced by Kraft pulping, showed similar quality to that of cellulose produced by organic acid pulping; however the yield from Kraft pulping was much higher.

The yield from Kraft pulping is higher, due to the absence of degradation reaction caused by acid as shown in Figure 2.1.

Results indicate that pulping time is an important factor in purity of produced pulp. As shown in Table 2.2, Jefft that is treated with pulping solution for longer time showed lower Kappa number. Jefft treated for about 3 hrs showed Kappa number of about 2.16, while sample treated for 2 hrs showed Kappa number of about 5.3. These results indicate that, the amount of residual lignin in the pulp generally decreases with increasing pulping time. Also by looking at the produced pulp visually, one can tell that higher brightness (less yellowish) could be achieved with longer pulping time.

Results also show that pulping time has an adverse effect on pulp yield as can be seen from Table 2.2. Yield decreases with pulping time; for instance, a sample treated for 2 hr gave higher yield than sample 19 which was treated for 3 hr . These results indicate that cellulose undergoes de-polymerization: to form water soluble species as pulping time increases.

Table (2.2): Comparison between results of pulping time

Sample #	Reaction Time (hr)	Kappa number	%Yield
9	2	5.3	55
19	3	2.16	46

2.4 Bleaching

Pulping process alone is not enough to produce cellulose suitable for food and pharmaceutical applications. After pulping, cellulose must be subjected to further purification. In this work, cellulose extracted from Jefft by pulping process was subjected to bleaching by various oxidizing agents. Bleaching agents used in the bleaching process selectively oxidize leftover lignin that is attached to cellulose chain (Figure 2.5) rendering it more water soluble.[26] Various bleaching processes are known in the art and among these are the elemental chlorine free (ECF) and the total chlorine free (TCF) bleaching sequences which are based on oxygen-derived chemicals, among which hydrogen peroxide has received much attention.

Peroxide bleaching may either be carried out as a single-stage process, or may be preceded by a pretreatment to eliminate peroxide decomposition catalysts. It may also be preceded or followed by conventional bleaching stages. The bleach liquor strength, expressed in terms of peroxide content, is usually in the range of 1–3% hydrogen peroxide.[27]

Bleaching is usually performed in a multistep process, some of these steps are summarized in Table 2.3

As mentioned earlier, the goal of bleaching is to reduce the kappa number without drastically decreasing the degree of polymerization of the cellulose.

Table (2.3): Bleaching steps

Process Used	**Letter Designation**
Chlorine	C
Sodium hypochlorite	H
sodium hydroxide	E
hydrogen peroxide	P

All tested pulps were bleached under equal conditions with a simple three-stage, four-stage or five stage process, without oxygen pre-bleaching. The conditions applied (including time, temperature and chemical charge) were kept the same for each stage in different sequences. Two different bleaching combinations were applied, namely CEHEH and CEHP bleaching sequences.

All bleaching stages were successively performed in sealed plastic bags plunged into an agitated water bath with controlled heating. After each bleaching stage, the pulps were thoroughly washed by distilled water and analyzed for yield, viscosity and residual lignin contents (Kappa number).

The first sequence to be tried was CEHEH which is chlorine, sodium hydroxide extraction, hypochlorite, sodium hydroxide extraction, and hypochlorite. In the first step pulp was subjected to bleaching with chlorine water (C-stage). Pulp was suspended in a solution of chlorine-water (2%) at about 10% consistency. The mixture was agitated for about

1 hr at 70 °C. Chlorine (Cl_2) breaks lignin bonds and adds chlorine atoms to the lignin degradation products, thus producing significant amounts of chlorinated organic material.

$$\textbf{Consistency} = \frac{\textbf{Weight of Pulp}}{\textbf{Weight of bleching solution}} \qquad \textbf{Eq. 2.4}$$

Different ratio of Jefft to chlorine-water solution were evaluated, the best results was obtained when pulp to chlorine ratio was 1:2 (33.3 consistency). As shown in Table 3.6 samples 3, 7, 8, 11 bleached at consistency of 33.3% showed higher percentage yield and lower Kappa number than sample 9, 10 which were treated with chlorine at a consistency of 50% and 25%, respectively.

In the second stage of bleaching sequence, pulp was subjected to treatment with sodium hydroxide at concentration of 5% (E-stage) and a consistency of about 10%. At this stage usually colored components from partially bleached pulp that are insoluble in water are removed. As shown in Figure 2.4, sodium hydroxide increases number of hydroxyl groups on lignin monomers rendering it more water soluble.

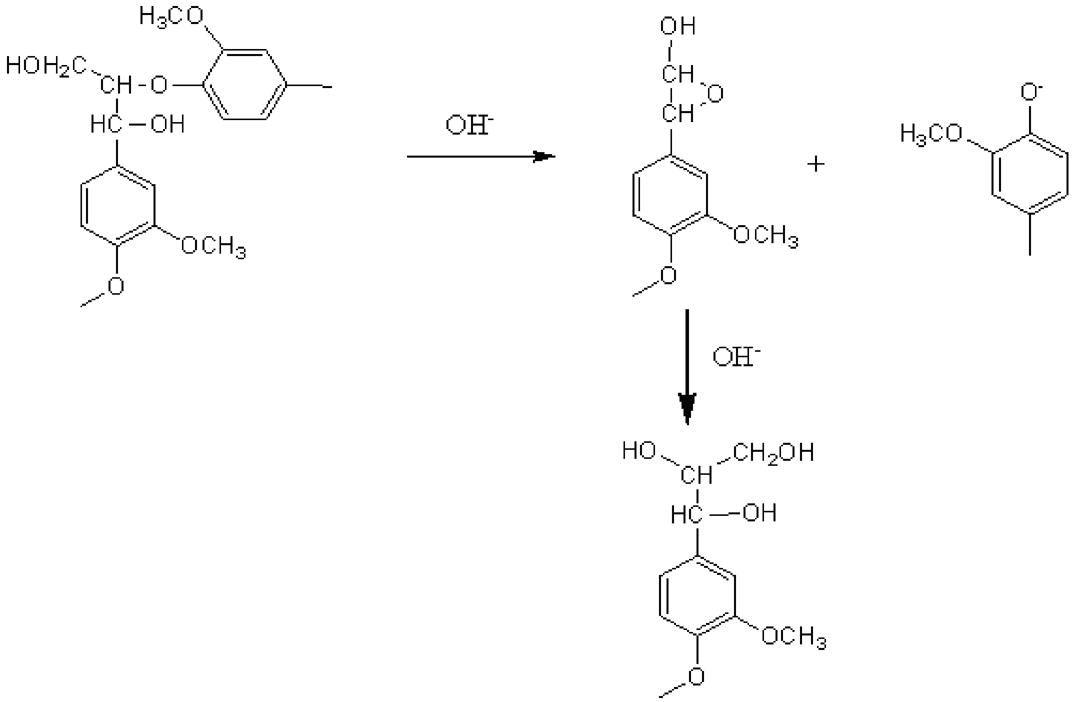


Figure 2.4(An example of a degrading process of lignin into smaller units)

In the third stage pulp was subjected to treatment with sodium hypochlorite H-stage (5%) and a consistency of about 10%. Hypochlorite is an important and versatile bleaching agent for pulp. It can be used in two different stages during a sequence of bleaching to accomplish two things: high brightness and high delignification (residual lignin removal). During treatment with hypochlorite, alcohol on lignin oxidized to acid functional groups making lignin more soluble in bleaching solution.

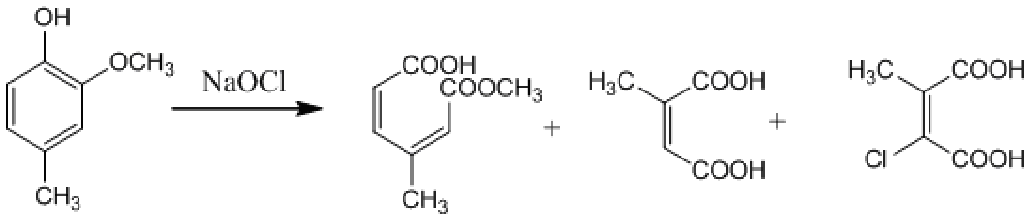


Figure 2.5(oxidation of alcohol on lignin to acid functional group)

Then again E-stage performed for another time on the same pulp followed by the final H-stage.

The second sequence was (CEHP). In this sequence, pulp was first treated with chlorine water at a concentration of 10 % (C-stage) and a consistency of 10 %. Then it was subjected to treatment with sodium hydroxide at a concentration 5 % (E-stage). After that it was subjected to treatment with sodium hypochlorite (H-stage) at a concentration of 5 %and a consistency of 10%. In the final stage, hydrogen peroxide (P-stage) was used at a concentration of about 2 % (P-stage). Hydrogen peroxide is one of the more widely used oxygen-based bleaching chemicals in the pulp and paper industry.

The use of hydrogen peroxide started from its introduction for mechanical pulp, and it is now the most popular oxidative agent in chemi-mechanical pulp bleaching. [27-31] Nowadays, the peroxide bleaching stage (or stages) is an integral part of all TCF (total chlorine free) chemical pulp bleaching sequences.

Hydrogen peroxide can be applied in combination with sodium hydroxide to reinforce an extraction stage, or as a primary delignification and bleaching agent to decrease Kappa number and to increase brightness and brightness stability.

As mentioned earlier hydrogen peroxide (H_2O_2) is often used at the end of a conventional bleaching sequence to prevent the pulp from losing brightness over time. Pulp bleaching with a mixture of the two reagents NaOH and H_2O_2 appeared as the most effective way to decompose lignin. Their synergistic activities combined with the function of NaOH in primarily hydrolyzing chlorinated lignin formed during treatment with chlorine and H_2O_2 helped in further oxidizing the lignin structure .[32] As shown previously NaOH is the nucleophiles pulping chemical that involved in reaction with lignin, leading to the fragmentation and dissolution of lignin. The modification of lignin structure occurred in two ways to enhance its dissolution. The first is by cleaving inter unit linkages to degrade lignin to become smaller units.

The second, is by introducing hydrophilic groups into both polymer and the cleaved fragments which makes the lignin to be more soluble.

Sample bleached with sequence contains hydrogen peroxide showed the lowest Kappa number with lower number of bleaching stages,(CEHP) compared with the first sequence (CEHEH).

These bleaching stages were performed on several samples after each of the bleaching process, the quality of the pulp was assessed in terms of (1) the extent of delignification (Kappa number), (2) the degree of cellulose polymerization as measured by pulp viscosity, (3) and viscosity. The Kappa number is an indicator of the residual lignin content of the pulp and is an important quality parameter. The higher Kappa number gives higher lignin content. Consequently, low Kappa numbers should be targeted if the pulp is to be bleached. The Kappa number is determined using a standard TAPPI method (TAPPI, 1985) and is commonly used in the pulp industry.

The results of bleaching sequences are summarized in Table 2.4.

The result of kappa number and lignin content of some bleached pulped are also shown in Table 2.4 As shown in Table 3.6, Kappa number decreases by increasing number of bleaching stages in the sequence, for instance sample 9B showed lower Kappa number (4.9) than sample 9A (5.3). Sample 5 which was bleached with 5 stages sequence showed a Kappa number of 1.4. Cellulose with highest purity was obtained using peroxide (P) as one of the sequence stage. Sample 12 which was bleached with 4 stages sequence where peroxide involved in the sequence gave the lowest Kappa number (lowest lignin contents).

These results indicate that peroxide is the most effective bleaching agent in this study.

A summary of Kappa number, bleaching sequence and lignin contents of cellulose samples treated with various bleaching sequencesis presented in Table 2.4

Table (2.4): bleaching sequences

Sample number	Bleaching sequence	Kappa number	Lignin content
5	CEHEH	1.4	0.225
7	CEH	6.1	
9A	CEH	5.3	0.795
9B	CEHE	4.88	0.732
9C	CEHEH	1.5	0.225
10A	CEH	2.16	0.174
11	CEH	4	0.6
11	CEHE	2	0.3
12	CEHP	1.3	0.195

Another important factor in determining pulp physical properties is viscosity. Pulp viscosity is related to degree of polymerization and it is directly proportional to degree of polymerization (Molar mass). Degree of polymerization of celluose usually depends on cellulose source. For instance, cotton linter (residual fiber on cotton seeds) has a degree of polymerization of about 3500, however for wood fiber it is about 1000.

Cellulose viscosity obtained form Jefft was determined according to a standard TAPPI method (TAPPI, 1989).

Determined viscosity was then used to calculate molar mass and degree of polymerization (Dp) of produced cellulose according to **Equation (2.5)**.

$$\eta = KM^{\alpha} \qquad \textbf{Eq. 2.5}$$

Where : **η is intrinsic Viscosity**

K is constant = 9.8 X 10^{-5}

ά = constant for it has a value of 0.9

Dp = M/162(MM of glucose repeat unit).

The viscosity for sample (4) was determined to be **1.767 cP. From the viscosity** Mn value was calculated using **equation 2.5** to be 50828.

Mn value was then divided by 162 which is the molar mass of glucose to 313.76. These results shows that Dp of cellulose obtained form Jefft is close to that off microcrystalline cellulose (Dp = 300). These results indicate that cellulose extracted form Jefft could have morphology (surface structure) close to that to that for microcrystalline cellulose.[33]

Figure 2.6 shows scanning microscopy pictures of microcrystalline cellulose with Dp of about 300.

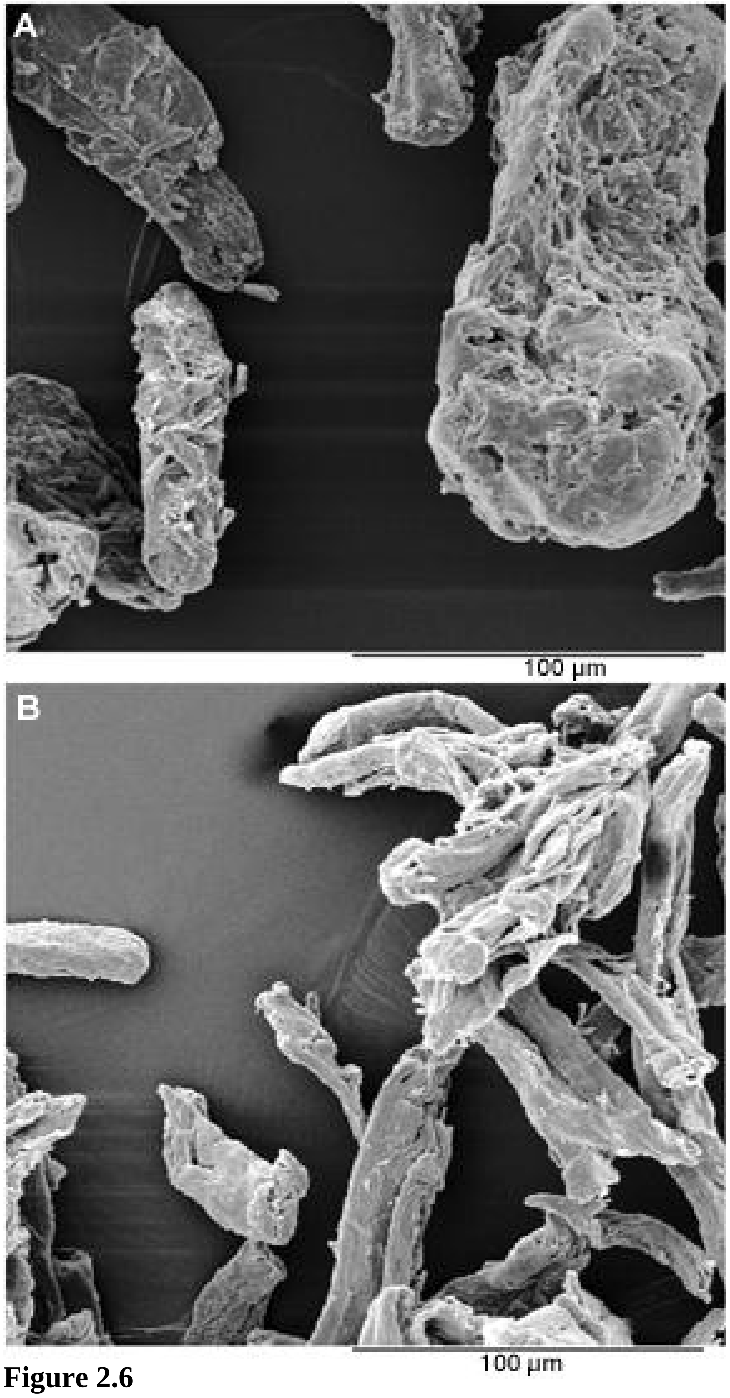


Figure 2.6

Morphology for (microcrystalline cellulose (Dp = 300)

As shown in the introduction, microcrystalline cellulose besides being a source for ethanol, has unlimited number of applications: food, drugs, paints, construction and others.

Chapter III

EXPERIMENTAL

General Experimental

All reagents were purchased from Aldrich Chemical Company and used without any further purification unless otherwise specified. Kraft pulping was performed in a high Parr Reactor purchased from (model: büchiglasuster, bmd 300). Fresh Jefft was obtained from an olive factory in palestaine and stored in a freezer at about 0 to -5 ^{o}C .

Cellulose was extracted from all samples of Jefft using the following methods combined or separate:

1. Extraction of residual materials
2. Pre-Hydrolysis
3. Pulping
4. Bleaching

3.1 Extraction of Residual Materials of Jefft

Residual materials were removed using soxhlet extraction. Jefft (100.0 g OD weight) was loaded in a soxhlet extractor and subjected to extraction with ethyl acetate (250 mL). The extraction was continued for about 6 hr. Then solvent was removed under reduced pressure to afford 5.0 g (10% based on Jefft weight) of pale yellow residual consisting mostly of olive oil.

3.2 Pre-hydrolysis

3.2.1 Pre-Hydrolysis of Jefft with Acid:

An aqueous solution of sulfuric acid (0.5% sulfuric acid) was introduced in a stainless-steel mini-high Parr reactor (batch reactor) that was heated by an outer jacket containing electrical wires. The reactor contents were stirred by rotating 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 Jefft was placed in the reactor together with the aqueous solution of sulfuric acid at ratio 4:1 to ensure a homogeneous mixture and an appropriate efficient agitation within the reactor. The temperature was increased gradually for 30 min, to reach a maximum of 160 ^{o}C under 5.0 psi of absolute pressure for 2hr. At the end of the pre-hydrolysis stage, the Jefft was washed with tap water, disintegrated in a laboratory blender, air dried at room temperature, and stored in plastic bags for further use. Yield was calculated by dividing the dry weight of the treated pulp produced by the dry weight of the starting Jefft.

Result of Pre-Hydrolysis with acid :

Pre-hydrolysis was performed on several samples and consistent results regarding yield and Kappa No. were obtained. The results are shown below.

Percentage yield =76%

Kappa no.= 15.4

Lignin Contents: 2.31

3.2.2 Pre-Hydrolysis of Jefft with base:

It was performed in a similar fashion to that used in pre-hydrolysis with acid, except for using 2% of NaOH was used.

Results:

Percentage yield =74%

Kappa no.=19

Lignin Contents: 2.85

3.3 Pulping

Pulping was performed in two different methods:

a. Organic acid pulping

b. Kraft pulping (Na_2S)

3.3.1 Organic acid pulping

General Procedure for Organic Acid Pulping:

Organic solvent pulping includes treating Jefft with high concentration of acetic acid (>80%) in the presence of HCl as a catalyst. The Jefft to acid solvent ratio was about 1:14 (w/v) , consistency = 10%. In a round- bottomed flask, (1.0 L) Jefft was suspended in a solution of HCl in acetic acid. The flask was fitted with a condenser and a magnet stir bar. The flask contents were refluxed for about 2.0 hr then the reaction mixture was allowed to cool to room temperature. The product (mostly cellulose) was collected by suction filtration, then washed thoroughly with water to neutral pH. The procedure was performed on several samples to study the effect of acetic acid concentration and reaction time on Kappa no. and % yield. The results are summarized in Table 3.1.

Table (3.1): Organic Acid Pulping

Number of sample	**Jefft Weight (g)**	**Reaction Time (hr)**	**Acid Content**		**Yield (%)**
			HCl %	**HOAc %**	
1	16	2	7	93	15.2
2	16	2	14	86	19.3
3	21.4	4	14	86	23
4	32	4	14	86	22.2
5	42.8	4	14	86	23

3.3.2 Kraft pulping

General Procedure for Kraft Pulping:

Pulping was conducted in a high Parr reactor (described previously) of one Liter capacity . Jefft (100 g) was placed in the reactor together with the liquor. At a ratio of 4:1 (consistency =20%) to ensure a homogeneous mixture and an appropriate efficient agitation within the reactor. The liquor is an aqueous solution of sodium sulfide (Na_2S) and sodium hydroxide (NaOH) at various concentrations. The temperature was increased gradually for 30 min, to reach of 140-150 ^oC under 5.0 psi of absolute pressure for 2hr. At the end of the pulping process, the pulp was removed from the reaction mixture by suction filtration, washed with tap water, air dried at room temperature, and then stored in plastic bags for further use. Yield was calculated by dividing the oven dried weight (OD weight) of the produced pulp by the original weight of the starting Jeff.

In order to determine optimum cooking conditions, several different experiments were conducted by Kraft pulping methods. The conditions and the results are summarized in Table 3.2.

Table (3.2a): Kraft Pulping Conditions

Sample	Weight of Jefft (g)	Pulping Chemicals		Pressure (psi)	Time of reaction (hour)	Percentage yield (%)
		NaOH (%)	Na_2S (%)			
6	50	21	7	--------	2	40
7	100	21	7	50	2	42
8	100	28	9	50	2	45
9	100	21	7	50	2	44
10	100	28	9	50	3	46

Table (3.2b): Kraft Pulping of Pre-Hydrolyzed Jefft

Sample	Weight of Jefft (g)	Pre-Hydrolysis	Pulping Chemicals		Pressure (psi)	Time of reaction (hour)	Percentage yield (%)
			NaOH (%)	Na_2S (%)			
11	175	0.5% sulfuric acid	15	6	45	2	48.5
12	175	2 % NaOH	16	6	45	2	48

3.4 Pulp Analysis

Produced pulp samples were evaluated before and after bleaching by subjecting them to testing by various test methods:

3.4.1 K-Number

3.4.2 Swelling

3.4.3Viscosity

3.4.1 K-Number

a. Preparation of reagents

1) **Potassium permanganate ($KMnO_4$) standard solution**:

A solution of $KMnO_4$ (0.02±0.001 mol /L). was prepared by dissolving 3.161g $KMnO_4$ in 1 Liter water .

2) **Sodium hydrosulfite ($Na_2S_2O_3$) standard solution**

A solution of ($Na_2S_2O_3$) (0.02±0.001 mol /L). was prepared by dissolving 24.82 g $Na_2S_2O_3$. $5H_2O$ in 1 liter water .

3) **Potassium iodide (KI) solution**, C= 1mol/L (KI).

A solution of KI (1.0 mol/L) was prepared by dissolving potassium iodide (166.0 g) in 1L water.

4) **Sulphuric acid (H_2SO_4) solution**, a solution of sulfuric acid, 2.0 M, was prepared.

5) Distilled water .

6) Starch solution with a concentration of 5g/L was prepared and used as an indicator. It was prepared by dissolving 0.5 g starch in 100 mL of boiling water.

b. General Procedure:

1. Oven dried pulp (1.00 g) was weighted and placed in a blender (scatter machine)
2. To the pulp, 400 mL distilled water were added and the machine was run for 3 min. The purpose of this step was to disintegrate the pulp..
3. The blender contents were added to a flask, then 50 mL of 0.02 mol/L of potassium permanganate was added using pipett. The pulp was left in contact with $KMnO_4$ for about 10 min at room temperature.

4. When the 10 min reaction time was over, 10 mL of potassium iodide was added to the mixture.

5. The produced mixture was titrated immediately with a standard solution of sodium hydrosulfite . The titration was continued until a light purple –yellow color appeared. Then 2-3 mL starch solution was added to the flask contents and at this point a blue color appeared, the titration continued with sodium hydrosulfite until the blue color disappeared.

7) The above procedure was performed on a blank solution. Exactly same steps were followed(except that no pulp was used in the blank solution).

3.4.2 Swelling

In this test, we can determine the amount of liquid absorbed by cellulose extracted form Jefft.

Procedure:

Cellulose (1. 0 g) was placed in an empty pre-weighed tea bag., The tea bag was placed in tap water for one hour. Then removed from water and hanged for about 5 min, to remove excess water that is not absorbed by pulp. Tea bag and contents were weighed and amount of liquid, absorbed by cellulose, was calculated according to the following equation . Swelling results for some of the produced cellulose and Jefft are summarized in Table3.3

Table (3.3): Swelling of Water

Sample Number	Swelling (g water/g Fiber)
3	6.16
9	9.71
4	8.69
5	9.1
10	7.05

Conditions used in determining Kappa number are summarized in Table 3.4 below

Table (3.4): kappa number determination conditions

Chemicals	Concentration (mol/L) and Volumes (mL)
Volume of 0.02mol/L $KMnO_4$ Standard Solution.(mL)	50
Volume of 2mol /L H_2SO_4 Solution (mL)	50
Volume of Total Liquor	400
Volume of 1mol/L(KI).Ml	10
Concentration of $Na_2S_2O_3$ Standard Solution .(mol/L)	0.1-0.2
The Maximum Mass of Absolute-dry Pulp.(g)	1.0 -2

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3.4.3 Viscosity

The following procedure describes the techniques for dissolving the pulp and measuring the viscosity of the pulp solution. The technique involves mechanical shaking of the sample-solvent mixture in a closed bottle containing glass beeds , pulp, and cuene.

Apparatus

1. *Cylinder of nitrogen gas,* purity 99.998%, was fitted with a pressure reducing valve to give 14 to 21 KPa (2 to 3 psi) pressure.

2.Constant temperature bath, capable of being maintained at 25.0 ± 0.1°C and equipped with clamps to support the viscometers in the thermostating fluid.

3.Viscometer, capillary type, size number 100 was chosen based on efflux time of 100 sec to 800 sec. .

4.Stopwatch or electric timer, readable to 0.1 s.

5. Burette, 25 mL, automatic gravity fill, all openings sealed to air; for solvent.

6.Burette or pipet, 25 mL; for water.

7.Büchner funnels, for forming slush pulps into pads.

8.Glass filter, coarse, small diameter; and vacuum flask

9.Vacuum, source and tubing.

10. Drying oven, 105 ± 2°C

11.Dissolving bottles, 118-mL (4-oz) flat medicine bottles with plastic screw cap and polyethylene liner or rubber septa caps.

12.Glass beads, approximately 6 mm diameter.

13.Mechanical shaker,

14.Suction device, such as a pipet bulb.

General Procedure:

Cupriethylenediamine solution, 1.0 ± 0.02*M* in cupric ion and 2.0*M* in ethylenediamine was used. This solution can be purchased commercially1 or prepared according to the procedure given in Appendix B. Cupriethylenediamine solutions must be stored under nitrogen at all times.

1. A sample moisture free pulp was weighed (0.2500 g) and placed in a plastic bottle and to it was added eight 6-mm glass beads.
2. To the plastic bottle was then added exactly 25.00 mL of distilled water (from burette), then capped.
3. The bottle was then shaked and allowed to stand for about 2 min.
4. To the bottle was added exactly 25.00 mL of the cupriethylenediamine (1.0 ± 0.02M in cupric ion and 2.0M in ethylenediamine), the bottle was purged with nitrogen for 1 min, capped and placed on a mechanical shaker until the fiber is completely dissolved (15 min).
5. The viscometer was filled with the pulp solution by immersing its small-diameter side into the solution and drawing the liquid into the viscometer by applying suction to the other end of the viscometer.

The viscometer was then placed in constant temperature bath at 25.0 ± 0.1°C and allowed at least 5 min to reach the bath temperature.

6. The solution in the viscometer was drawn up into the measuring side of the viscometer with a suction bulb, then allowed to drain down to wet the inner surfaces of the viscometer. The efflux time was determined by drawing the liquid above the upper mark, the time required for the meniscus to pass between the two marks is the efflux time.

Calculation:

The viscosity, V, was calculated using the following formula:

$V = Ctd$

Where :V = viscosity of cupriethylenediamine solution at 25.0°C, mPa•s (cP)

C = viscometer constant found by calibration using oil

t = average efflux time(s)

d = density of the pulp solution, g/cm^3.

The viscosity measurement was performed on the sample 4 , and results are summarized in Table 3.5

Table (3.5): viscosity result

Item	Value
Efflux time (s)	310
Viscometer constant	0.015
Pulp density	0.38 g/cc
Viscosity	1.767 cP

3.5 Bleaching:

Bleaching of all samples (pre-hydrolysis/organic pulp and Kraft pulp) was performed using the following chemicals

C: Chlorine in water

E: Extraction with NaOH (aq)

H: Sodium hypochlorite

P: Hydrogen peroxide

Ep: Alkaline/Hydrogen peroxide

3.5.1 Chlorine Stage (C-stage):

Elemental chlorine (Cl_2)/ breaks lignin bonds, it adds chlorine atoms to the lignin degradation products, thus producing significant amounts of chlorinated organic material, which is unstable in alkaline solution

Procedure:

Olive pulp was treated with chlorine water solution at various pulp to solution ratios (30-40)% consistency. In all experiments Cl_2 concentration was (10%), bleaching was performed in a plastic bag and heated in a water bath at about 20-25 C for 40 min. At the end of the bleaching C-stage, the bleaching pulp was removed from the reaction mixture by suction filtration, washed with tap water 3 times, air dried at room temperature, and stored in plastic bag for further use. Yield was calculated by dividing the oven dry weight of the produced pulp by the oven- dried weight of Jefft.

The conditions and the results are summarized in Table 3.6. various pulp to Cl2⁄ water solution were evaluated.

Table (3.6): Results of Chlorine Bleaching

Number of Sample	Weight of Pulp (g)	Jefft /($Cl_{2/}H_2O$) Ratio	Percentage Yield (%)
3	6	1:2	75
4	23	1:2	52
5	21	1:2	85
7	40	1:2	82
8	34	1:2	88
9	10	1:1	70
10	10	3:1	60
11	75	1:2	88
12	75	1:2	86

3.5.2 Extraction with sodium hydroxide Stage (E-stage):

Extraction with NaOH (aq) was performed to remove colored components from partially bleached pulps that have been rendered soluble in dilute warm alkali solution such as chlorinated lignin.

Procedure:

Olive pulp from C-stage was treated with 5% sodium hydroxide at ratio of about 1:10 (about 10 % consistency)., bleaching was performed in a plastic bag and heated in a water bath at about 60 C for 2 hour. At the end of the bleaching E-stage, the product was removed from the reaction mixture by suction filtration, washed with tap water 3 times, air dried at room temperature, and stored in plastic bags for further use. Yield was calculated by dividing the dry weight of the treated bleaching pulp produced by the dry weight of the starting Jefft based on the oven-dried bleaching pulp and Jefft.

The conditions and the results are summarized in Table 3.7.

Table (3.7): Sodium hydroxide Bleaching

Number of Sample	Weight of Pulp (g)	Amount of Sodium Hydroxide (Ml)	Percentage Yield (%)
4	4.5	50	53
5	18	180	66
7	18	220	72
9	24	240	83
10	30	288	96
11	50	480	85
12	50	480	87

3.5.3 Hydrogen Peroxide Stage (P-Stage):

Hydrogen peroxide (H_2O_2) is mainly used to brighten pulps in the final bleaching stages. Peroxide is often used at the end of a conventional bleaching sequence to prevent the pulp from losing brightness over time

Procedure:

Olive pulp E stage was treated with 2 % of hydrogen peroxide at a pH range (9-10) pH was adjusted using NaOH solution (5%) and a consistency of about 33%, Bleaching was performed in a plastic bag and heated in a water bath at about 70 C for 1 hour . At the end of the bleaching p-stage, the product was removed from the reaction mixture by suction filtration, washed with tap water until filtrate was neutral, air dried at room temperature, and stored in plastic bags for further use.

Yield was calculated by dividing the dry weight of the treated bleaching pulp produced by the dry weight of the starting Jefft based on the oven-dried bleaching pulp and Jefft.

The conditions and the results are summarized in Table 3.8 In all experiments bleaching pulp Jefft(dry weight) was used and the chemicals are solution of hydrogen peroxide. The conditions and the results are summarized in Table 3.8

Table (3.8): Hydrogen peroxide bleaching

Number of the Sample	**Percentage yield (%)**	**Amount of Hydrogen peroxide Solution (2%)**	**Weight of Olive pulp (g)**
11	88	100	50

3.5.4 Sodium hypochlorite stage (H-stage):

Hypochlorite is an important and versatile bleaching agent for pulp. It can be used in two different stages during a sequence of bleaching to accomplish two things: high brightness and high delignification (residual lignin removal).

Procedure:

Olive pulp from last stage was treated with 2 % of sodium hypochlorite, bleaching was performed in a plastic bag and heated in a water bath at about 50 C for 1 hour . At the end of the bleaching H-stage, the product was removed from the reaction mixture by suction filtration, washed with tap water 3 times. air dried at room temperature, and stored in plastic bags for further use. Yield was calculated by dividing the dry weight of the treated bleaching pulp produced by the dry weight of the starting Jefft based on the oven-dried bleaching pulp and Jefft.

The conditions and the results are summarized in Table 3.9 In all experiments bleaching pulp Jeffts (dry weight) was used the chemicals are solutions of sodium hypochlorite. The conditions and the results are summarized in Table 3.9

Table (3.9): Sodium Hypochlorite Bleaching

Number of Sample	Weight of Olive Pulp (g)	Amount of Sodium Hypochlorite (Ml)	Percentage Yield (%)
4	2	25	80
5	10	125	54
7	25	260	92
9	20	120	95
10	29	300	86
11	25	260	95
12	25	260	93

3.5.5 Extraction with sodium hydroxide Stage (Repeat E-stage):

It was performed in a similar fashion to that used in last E-stage, and in this experiment 5% NaOH was used. The conditions and the results are summarized in Table 3.10.

Table (3.10): Sodium hydroxide bleaching

Number of Sample	Weight of Pulp (g)	Amount of Sodium Hydroxide (Ml)	Percentage Yield (%)
5	5	50	62.8
9	18	180	73
12	20	200	80

3.5.6 Sodium hypochlorite stage (Repeat H-stage):

It was performed in a similar fashion to that used in last H-stage, this experiment 2% sodium hypochlorite was used. The conditions and the results are summarized in Table 3.11.

Table (3.11):Sodium hypochlorite bleaching

Number of Sample	Weight of Pulp (g)	Amount of Sodium Hypochlorite (Ml)	Percentage Yield (%)
5	3	40	40
9	13	160	50
12	15	100	70

Summary of all results of various bleaching sequences performed in this work are summarized in the following Table 3.12

Table (3.12): bleaching sequence

Sample Number	Bleaching Sequence	Kappa Number	Lignin Content
3	Without Bleaching	25	3.75
5	C-E-H-E-H	1.4	0.225
7	C-E-H	47.8	
8	Without Bleaching	19	2.85
9	C-E-H	5.3	0.795
9	C-E-H-E	4.88	0.732
9	C-E-H-E-H	1.5	0.225
10	C-E-H	1.16	0.174
11	Without Bleaching	19	2.85
11	C-E-H	4	0.6
11	C-E-H-E	2	0.3
12	Without Bleaching	15.4	2.31
12	C-E-H-P	1.3	0.195

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كلية الدراسات العليا

طرق استخراج السليلوز من جفت الزيتون

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قدمت هذه الرسالة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.
2009م

طرق استخراج السليلوز من جفت الزيتون

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الملخص

الجفت من اهم النواتج الفرعية التي تصاحب عملية عصر الزيتون. وينتج الجفت بكميات هائلة وبدون فائدة تذكر. ويعتبر الجفت كمادة "ليجنو سليلوزية" حيث انه يتكون من مواد مشابهة لتلك التي توجد في مادة الخشب مثل السليلوز والليجنين , وشبه السيليولوز. تم في هذة الدراسة استخلاص 30% من السليلوز النقي من الجفت. هذا وقد تمت عملية الاستخلاص لمادة السيليلوز في اربع خطوات وهي على التوالي : استخلاص , التشخيص الأولي, Pulping, والتبييض.

وتشير النتائج انه يمكن باستخدام خطوتين فقط هما Pulping, والتبييض , الحصول على نفس النتائج الم . وتشير النتائج الى أنه يمكن الحصول على نفس النتائج باتباع خطوتين رئيستين فقط هما pulping والتبييض.

في خطوة الأستخلاص أزيلت المواد القابلة للاستخراج مثل زيت الزيتون المتبقي , ثم عومل ذلك الناتج في الخطوة الثانية بمحلول مخفف من حامض الكبريتيك (5%) أو محلول مخفف من هيدروكسيد الصوديوم (5%) وتحت تأثير ضغط 5 psi . وقد كان

للخطوة الثانية الأثر الفعال على الجفت، حيث فتحت تركيب الجفت وجعلتة قابلا للمعالجة بالمواد الكيميائية المستعملة في عمليتي Pulping, والتبييض .

بعد ذلك تعرضت مادة الجفت لعملية Pulping باستخدام الحامض او بطريقة Kraft.

وقد اشارت النتائج الى ان طريقة كرافت (Kraft) قد أدت الى ارتفاع الناتج من مادة السليلوز اضافة الى امكانية اعادة استخدام المادة الكيميائية التي سبق استخدامها بطريقة كرافت(Kraft) . هذا وقد كان لأثر اعادة استخدام هذه المواد مرة اخرى سببا رئيسا لاجراء هذة الدراسة، حيث أن هذا الهدف الأبعد والأهم لتطبيق هذة الدراسة يكمن على النطاق الصناعي.

لقد عومل الجفت بواسطة طريقة كرافت مع محلول هيدروكسيد الصوديوم وكبريتيد الصوديوم وتحت ضغط _(5 psi).

أما السليلوز الناتج فقد عومل مع عدة عوامل مؤكسدة وذلك اثناء عملية التبييض . ثم قمنا بدراسة عوامل مؤكسدة من خلال استخدامها في عملية التبييض وكان افضل النتائج هي تلك التي استخدم فيها CEHP الذي يتالف من أربعة عوامل مؤكسدة وهي : الكلور، هيدروكسيد الصوديوم، هيبوكلورايت، بيروكسيد الصوديوم .

لقد اظهر السليلوز الناتج وباستخدام هذة العوامل المؤكسدة وجود محتويات قليلة من مادة lignin بواسطة طريقة .Kappa no .

أما بالنسبة للزوجة السليلوز الناتج وباستخدام طريقة التبييض التتابعي بمحاليل CEHP، فقد وجد من النتائج أن السيليلوز المستخلص من الجفت له نفس المواصفات للسيليلوز ذي الصفات المايكروبلورية.

وبناء على النتائج فقد نجحت الدراسة في تحويل في الجفت الصلب عديم الفائدة الى مادة ذات فوائد صناعية مهمة الا وهي مادة السيليلوزوالذي يستعمل في مجالات صناعية مثل الاغذية والطب والبناء وغير ذلك.