An-Najah National University

Faculty of Graduate Studies

Synthesis of Specialty Polymer from Cellulose Extracted from Olive Industry Solid Waste

By

Nisreen Riyad As'ad Yousef Alhaj

Supervisor

Dr. Othman Hamed

Dr. Shehdeh Jodeh

This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry, Faculty of Graduate Studies, An-Najah National University, Nablus, Palestine.

2013

Synthesis of Specialty Polymer from Cellulose Extracted from Olive Industry Solid Waste

By

Nisreen Riyad As'ad yousef Alhaj

This thesis was defended successfully on 17/1 /2013, and approved by:

Defense Committee Members		signature
1. Dr. Othman Hamed.	(Supervisor)	.....
2. Dr. Shehdeh Jodeh	(co-Supervisor)	.....
3. Dr. Orwah Jaber Hoosheyeh	(External Examiner)	.....
4. Prof. Mohamad Al- Nuri	(Internal Examiner)	.....

Dedication

I humbly dedicate this thesis to: My parents for their love, guidance, endless support and extraordinary encouragement. And also I would dedicate it to all my family members: Mahmoud, Azmi, Asma, and Rasha.

Acknowledgement

First of all I am grateful to The Almighty Allah for helping me to complete this thesis, Praise and thanks to Allah.

I would like to express my sincere thanks to my Adviser Dr. Othman Hamed for his enthusiasm, patience, motivation, and immense knowledge. His guidance helped me throughout the research and writing of this thesis, he provided me with his encouragement, advice, valuable directions and good ideas.

Besides my advisor, I would like to thank Dr. Shehdeh Jodeh (co-Supervisor) and the rest of my thesis committee: Dr. Orwah Hoosheyeh and Prof. Mohamad Al-Nuri for their encouragement, insightful comments, and questions.

I want to thank Mr. Omair Nabulsi, the chemistry labs supervisor at An-Najah National University, for his cooperation and support during this work. Many thanks for all lab technicians (specially Mr Nafed Dwekat, Eisa Abu Al'ez, Tareq Draidi, Mohammed Almasri, Ameed Amireh, Motasem Jamous, Ashraf Salman, and Motaz Laham), Mr Derar Smadi and Dr Ahed Zyood, for their help.

Finally, Thanks to all my friends: Tahreer, Sumoud, Khuloud, Shurooq, Sondos, Hiba, Mai, Kawthar, Aya, Hanan, Sana' and Reem. And special thanks for every person who supported, and helped me.

الاقرار

أنا الموقع أدناه مقدم الرسالة التي تحت عنوان:

Synthesis of Specialty Polymer from Cellulose Extracted from Olive Industry Solid Waste

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 بحثية لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

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

Student's name: **اسم الطالب:**

Signature: **التوقيع:**

Date: **التاريخ:**

List of contents

No.	Subject	Page
	Dedication	iii
	Acknowledgment	iv
	Declaration	v
	List of Contents	vi
	List of Tables	ix
	List of Abbreviations	xii
	Abstract	xiii
	Chapter One: Introduction	**1**
1.1	Background	1
1.2	Cellulose	6
1.3	Cellulose extraction from sources	10
1.3.1	Pulping process	11
1.3.2	Bleaching	13
1.4	Cellulose derivatives and applications	14
1.5	Cellulose acetate	18
1.6	Aims of the study	21
	Chapter Two: Experimental	23
	General experimental	23
2.1	Extraction of residual materials from Jeft	25
2.2	Pulping	26
2.3	Pulp Analysis	28
2.3.1	K-Number	28
2.3.1.1	Preparation of reagents	28
2.3.1.2	General procedure	29
2.3.2	Viscosity	30
2.3.2.1	Apparatus	30
2.3.2.2	General procedure	31
2.3.2.3	Calculation of intrinsic viscosity	32
2.4	Bleaching	33
2.5	Preparation of cellulose acetate from cellulose extracted form jeft	38
2.5.1	Apparatus	38

2.5.2	Procedure	38
2.5.2.1	Heterogeneous method	38
2.5.2.2	FTIR of selected samples of prepared cellulose acetate	39
2.5.2.3	Homogeneous method	41
	Chapter Three: Results and Discussion	43
	General experimental	43
3.1	Extraction of residual materials from Jeft	43
3.2	Pulping of olive industry solid waste	45
3.3	Bleaching	50
3.4.1	Analysis of extracted cellulose by FTIR	53
3.4.2	Differential Scanning Calorimetry (DSC) analysis of extracted cellulose	55
3.5	Preparation of cellulose acetate from cellulose extracted form jeft	57
3.5.1	Homogeneous method	57
3.5.2	Analysis of cellulose acetate prepared under homogeneous conditions	60
3.5.2.1	Analysis of cellulose acetate prepared under homogeneous conditions by FTIR	61
3.5.2.2	Scanning Electron Microscopy (SEM) and X-ray of cellulose acetate prepared under homogeneous conditions	62
3.5.2.3	Size exclusion chromatography of cellulose acetate prepared under homogeneous conditions	66
3.5.2.4	Differential Scanning Calorimetry (DSC) analysis of prepared cellulose acetate prepared under homogeneous conditions	69
3.5.3	Heterogeneous method of preparation of cellulose acetate	70
3.5.4	Analysis of cellulose acetate prepared under heterogeneous conditions	71
3.5.4.1	Analysis of cellulose acetate prepared under heterogeneous conditions by FTIR	72
3.5.4.2	Scanning Electron Microscopy (SEM) and X-ray of cellulose acetate prepared under heterogeneous conditions	73
3.5.4.3	Size Exclusion Chromatography of cellulose acetate	75

	prepared under heterogeneous conditions	
3.5.4.4	Differential Scanning Calorimetry (DSC) analysis cellulose acetate prepared under heterogeneous conditions	79
	Conclusion	81
	Future work	82
	References	83
	الملخص	ب

List of Tables

No	Table	Page
1.1	Chemical composition of some typical cellulose-containing materials	7
1.2	Global production of cellulose acetate-based products	19
2.1	Pulping results	27
2.2	Intrinsic viscosity of extracted cellulose	33
2.3	Results of acid stage	34
2.4	Results of bleaching with E-stage	35
2.5	Results of bleaching with H -stage	36
2.6	Results of bleaching with P-stage	37
2.7	Summary of the analysis results on bleached samples of cellulose extracted from jeft	37
2.8	Heterogeneous method conditions	39
2.9	The main absorption bands of cellulose acetate	40
3.1	Results from pulping of jeft at various conditions	46
3.2	Summary of the analysis results on bleached samples of cellulose extracted for jeft	53
3.3	X-ray of cellulose acetate prepared under homogeneous conditions	64
3.4	X-ray of cellulose acetate prepared under homogeneous conditions	65
3.5	X-ray of cellulose acetate prepared under homogeneous conditions	65
3.6	X-ray of cellulose acetate prepared under heterogeneous conditions	74
3.7	X-ray of cellulose acetate prepared under heterogeneous conditions	75

List of Figures

No.	Subject	Page
1.1	Chemical structure of xylane	3
1.2	Chemical structure of lignin	**4**
1.3	Chemical structure of cellulose	**8**
1.4	Chemical structure of cellobiose	**9**
1.5	Reaction of CMC preparation	**17**
2.1	FTIR results for cellulose acetate samples number 6 and 9	**40**
2.2	FTIR results for cellulose acetate prepared by homogeneous method	**42**
3.1	GCMS chromatogram of jeft extractives	**45**
3.2	Fatty acids triglycerides present in olive oil	**44**
3.3	Linkages of lignin	**48**
3.4	a) linkage of β-O-4 b) linkage of α-O-4	**48**
3.5	Example of hydroxyl group and β-carbon reaction in kraft pulping	**49**
3.6	Example of hydroxyl group and β-carbon reaction in kraft pulping	**49**
3.7	IR spectrum of cellulose extracted from jeft	**54**
3.8	IR spectra of cellulose extracted from jeft and microcrystalline cellulose	**55**
3.9	DSC of cellulose extracted from jeft	**56**
3.10	Structures of tertiary amineoxide used in dissolution of cellulose**.**	**58**
3.11	Proposed interactions between cellulose and DMA/LiCl solvent system during the dissolution	**59**
3.12	Converting cellulose into cellulose acetate	**60**
3.13	IR spectra of cellulose acetate prepared from cellulose extracted from jeft	**61**
3.14	IR spectra of cellulose acetate made from cellulose extracted from jeft and cellulose acetate obtained from Aldrich Chemical Company	**62**
3.15	SEM images of cellulose acetate at three different	**63**

	magnifications; a) 300x, b) 500x, and c) 1000x	
3.16	X-ray of cellulose acetate prepared under homogeneous method- run 1	**64**
3.17	X-ray of cellulose acetate prepared under homogeneous method- run 2	**64**
3.18	X-ray of cellulose acetate prepared under homogeneous method- run 3	**65**
3.19 (a)	SEC of cellulose acetate made from cellulose extracted from jeft	**67**
3.19 (b)	SEC of cellulose acetate made from cellulose extracted from jeft	**68**
3.20	DSC of cellulose acetate made under homogeneous conditions	**70**
3.21	Reaction mechanism for acetylation of cellulose under heterogeneous conditions:	**71**
3.22	IR spectra of cellulose acetate prepared under heterogeneous conditions	**73**
3.23	SEC of cellulose acetate made from cellulose extracted from jeft under heterogeneous conditions-Run 1	**75**
3.24	X-ray of cellulose acetate prepared under heterogeneous conditions-Run 2	**74**
3.25 (a)	X-ray of cellulose acetate prepared under heterogeneous conditions	**76**
3.25 (b)	X-ray of cellulose acetate prepared under heterogeneous conditions	**77**
3.25 (c)	X-ray of cellulose acetate prepared under heterogeneous conditions	**78**
3.26	DSC of cellulose acetate made under heterogeneous conditions	**80**

List of abbreviations

OISW	Olive Industry Solid Waste
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope
DSC	Differential Scanning Calorimetry
MCC	MicroCrystalline Cellulose
CA	Cellulose Acetate
SEC	Size-Exclusion Chromatography
Mn	The Number Average Molecular Weight
Mw	Molecular Weight Distribution
OILW	Olive Industry Liquid Waste
MT	Metric Tons
DP	Degree of Polymerization
DMA	N,N-Dimethylacetamide
DS	The Degree of Substitution
CMC	Carboxymethyl Cellulose
OD weight	On Dry weight
GC MS	Gas Chromatography- Mass Spectrometry
K-Number	Kappa Number
AA	Active Alkali

Synthesis of Specialty Polymer from Cellulose Extracted from Olive Industry Solid Waste

By
Nisreen Riyad As'ad Yousef Alhaj
Supervisors
Dr. Othman Hamed
Dr. Shehdeh Jodeh

Abstract

In the present work a method for extracting cellulose from olive industry solid waste (OISW) has been developed. The method involves subjecting solid waste (about 0.5 Kg) to extraction with organic solvent ethylacetate, then to kraft pulping, followed by multistep bleaching processes. After bleaching an average cellulose yield of about 35% has been obtained. The extracted cellulose was extensively characterized using FTIR, SEM, HPLC, DSC, and viscometry. Our key finding in this study is that the extracted cellulose was found to have physio-chemical properties that are similar to those of conventional MCC. This is important, as our results show how lignocellulosic agricultural wastes can be utilized to produce high value cellulose powder. Extracted cellulose powder was then converted via two methods of homogeneous and heterogeneous conditions into commercially important product cellulose acetate (CA). Prepared cellulose acetates by the two above methods were extensively characterized using FTIR, SEM, HPLC, DSC, and SEC. The degree of substitution of CA prepared by the homogeneous method was about 3.0; however CA prepared by heterogeneous method showed degree of substitution of about 1.77. Analysis of CA by size exclusion chromatography showed that, CA

prepared by homogeneous method is monodisperse with Mw and Mn of about 50,520 g/mol and 46,730 g/mol, respectively. However CA prepared by the heterogeneous method is polydisperse that contain two fractions with low and high Mw. These findings show that olive industry solid waste is a valuable source for cellulose powder that could be used as a precursor of commercial valuable products with unlimited number of industrial applications such as cellulose triacetate and cellulose diacetate.

CHAPTER 1

Introduction

1.1 Background

Palestine is one of the Mediterranean countries, which has a history of olive tree cultivation. The majority of the olive oil in the world is produced in the Mediterranean region. Oil produced in mills from crushed olive which is pressed and centrifuged to separate water from oil, leaving waste of residual solid and liquid from this process.

Olive oil is the backbone of the Palestinian agricultural economy, but on the other hand, olive oil industry produces environmental wastes which make a serious disposal problem. The waste is composed of two parts; the liquid waste which will be termed in this work as Olive Industry Liquid Waste (OILW) and is known in Palestine as “Zubarr”; and the solid waste will be termed in this work as Olive Industry Solid Waste (OILW) which is known in Palestine as Jeft (OISW). Usually the jeft is left to rot or burned thus releasing CO_2 to the atmosphere, while zubarr tends to be disposed via the sewage system, and has implication for water quality.

The challenge is to utilize and convert the waste materials into useful and low-cost marketable products. Jeft components are similar to wood components. Jeft components are cellulose, hemicelluloses, lignin, and extractives. Hemicelluloses present in jeft at a percentage ranging from 25-35%, while lignin (polyphenols) present at percentage ranging from 18-

35%. The main component of jeft is carbohydrate (specifically cellulose) which present in about 40 to 50%. All jeft components are precursor for valuable commercial products.

The waste produced at the olive during olive pressing process could reach up to 66.0% of the total olive volume, as mentioned up to 40% of this waste is carbohydrate and mainly cellulose[1].

Palestine alone produces about 35,000 MT of Jeft every year. The waste of this volume of olive contains about 9,000 MT of carbohydrates. Carbohydrates present in jeft could be extracted and specific fractions converted into specialty polymers and fine chemicals such as ethanol, furfural, and 5-hydroxymethylfurfural. Potentially, the amount of cellulose that could be produced from Jeft is more than enough to supply the existing number of factories and research institutes in Palestine with their requirements for cellulose and a proportion (~35 %) of their requirements for fine chemicals.

The primary component of jeft is cellulose; a detailed literature survey shows the importance of cellulose is shown in this chapter.

The second main component of jeft is hemicelluloses. The hemicellulose comprises roughly one-fourth to one-third of most plant material [2] , it is an amorphous polymer with DP (50-300) [3]. It is usually composed of heteropolysaccharides; xylose, arabinose, galactose, glucose, mannose, and 4-O-methyl-D-glucuronic acid residues [4].

The hemicelluloses are potentially very useful. Properties of hemicelluloses are worth exploiting are their ability to serve as adhesives, thickeners, and stabilizers, and as film formers and emulsifiers, and their importance in chemical and the pharmaceutical industry such as production of cationic biopolymers and hydrogels [5, 6]. One of the most important compositions of hemicelluloses is xylane which has a wide range of applications. It can be used as surface active agents due to its ability to form oil in water emulsions with good stability. Xylanes have role in bread making that affect the properties of the dough and texture of endproduct quality of baked products. It has biological activity as part of dietary fibers. Xylanes have other potential applications such as “super gel” for wound dressing, micro and nanoparticles for controlled drug delivery. Oligosaccharides with novel functional food ingredients modifying food flavor and physicochemical characteristics model compounds for enzymatic assays [7, 8].

A possible structure of xylane is shown in **Figure** 1.1; it is usually hydrolyzed into its repeat unit's C5 sugars such as xylitol which then further processed to commercial products.

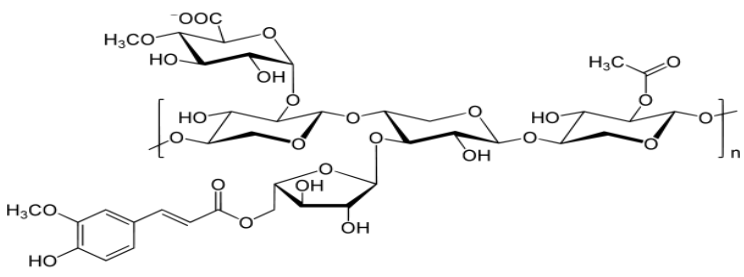


Figure 1.1: Chemical structure of xylane

Lignin is the third component of jeft, lignin is an amorphous, cross-linked poly-phenolic polymer (molecular mass over 10,000) [9], arising from an enzyme mediated dehydrogenative polymerization of three phenylpropanoid monomers, coniferyl, sinapyl and p-coumaryl alcohols. These phenyl-propanols are linked mainly by two types of linkages: condensed linkages (e.g., 5–5 and b-1 linkages) and ether linkages (e.g., ß -O-4 and α -O-4), while the ether linkages are the dominant linkages [10]. lignin is covalently linked to carbohydrates forming a lignin–carbohydrate network [11]. The possible chemical structure of lignin is shown in **Figure** 1.2.

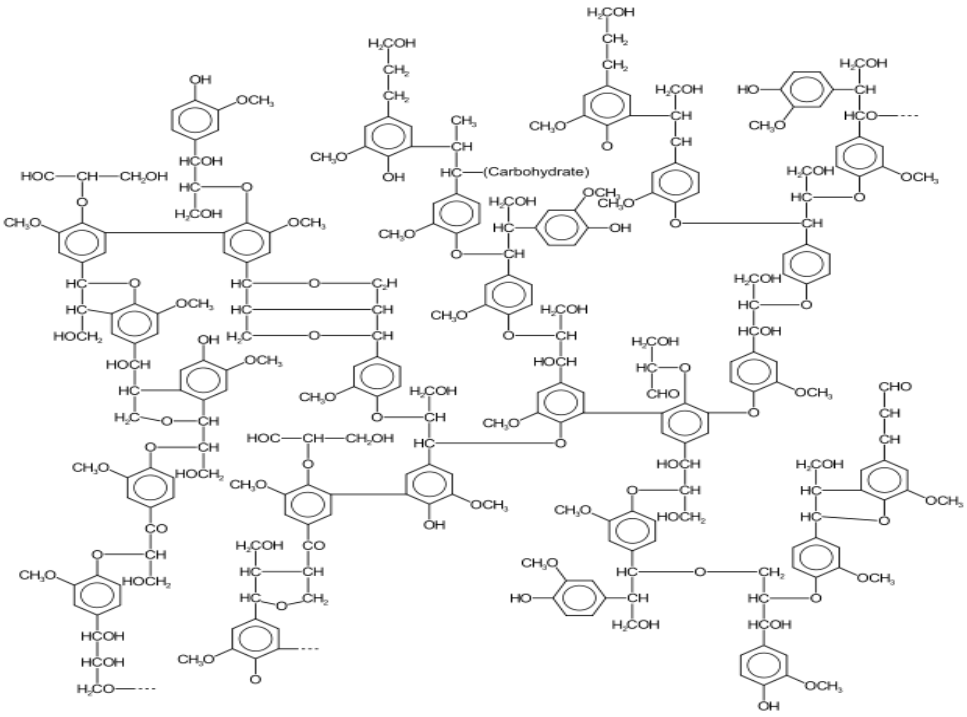


Figure 1.2: Chemical structure of lignin

It is found that the main chemical species causing the photo-discoloration of wood or high-yield pulps is lignin [12].

Wood extractives are defined as compounds that could be extracted from wood by means of both polar and non-polar solvents [13]. Extractives are soluble in non polar solvents, generally the extractive are few percent of wood mass ranging from 2.0 % and 5.0 % but in some cases it could reach up to 15%.

Extractives contribute merely a few percent to the entire wood composition; they have significant influence on its properties, such as mechanical strength or color quality and thermal stability of wood and wood–polymer composites. Extractives can even be toxic and harmful to the environment [14].

Extractives are varieties of organic compounds including fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, gums, resins, terpenes, starches, glycosides, saponins, and essential oils. These components function as intermediates in tree metabolism, and as energy reserves, or as part of the tree's defense mechanism against microbial attack. They contribute to wood properties such as color, odor, and decay resistance [15].

Some of these extractives such as the phenolic compounds tend to cause some difficulties and increase the consumption of chemicals during pulping and bleaching process and reduce pulp yield [16].

1.2 Cellulose

In this work we are interested in converting OISW into valuable commercial products by extracting cellulose from OISW. Then converting extracted cellulose into CA. Cellulose is the most abundant organic compound derived from biomass. The worldwide production of this biopolymer is estimated to be between 10^{10} and 10^{11} tons/year. Cellulose is a white fiber-like structure with no odor and has a bulk density of about 0.2-0.5 g/cm^3. Cellulose could be extracted from many sources of cellulose among these are plant (cotton, hemp, flax, etc.), marine animals (tunicate), or algae, fungi, invertebrates, and bacteria. Also it is present in the leaf (e.g., sisal), in the fruit (e.g. banana) or in the stalk or the rigid structure of plants (e.g., wood, flax) [17], and other sources as shown in **Table** 1.1. The primary occurrence of cellulose is the existing lignocellulosic material in forests, with wood as the most important source. Commercial cellulose production concentrates on harvested sources such as wood or on naturally highly pure sources such as cotton [18].

Table 1.1: Chemical composition of some typical cellulose- containing materials

	Composition (%)			
source	**cellulose**	**hemicellulose**	**lignin**	**extractives**
Hardwood	43-47	25-35	16-24	2-8
Softwood	40-44	25-29	25-31	1-5
Bagasse	40	30	20	10
Coir	32-43	10-20	43-49	4
Corn cobs	45	35	15	5
Corn stalks	35	25	35	5
Cotton	95	2	1	0.4
Flakes (retted)	71	21	2	6
Flakes (unretted)	63	12	3	13
Hemp	70	22	6	2
Henequen	78	4-8	13	4
Istle	73	4-8	17	2
Jute	71	14	13	2
Kenaf	36	21	18	2
Ramie	76	17	1	6
Sisal	73	14	11	2
Sunn	80	10	6	3
Wheat srtraw	30	50	15	5

Cellulose, it is a linear polymer made of the monomer D-glucose that are linked successively through ß-1,4-glycosidic bonds in the β-configuration

between carbon 1 and carbon 4 of adjacent unit to form a polymeric chain as shown in **Figure** 1.3.

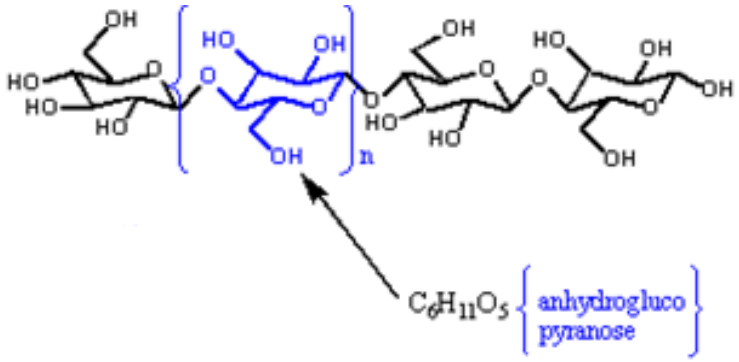


Figure 1.3: chemical structure of cellulose

As shown in **Figure** 1.3 cellulose has three hydroxyl groups, presence of these group gives cellulose the high tendency to form intra- and inter-molecular hydrogen bonds which stiffen the straight chain and promote aggregation into a crystalline structure and give cellulose a multitude of partially crystalline structures and morphologies. The degree of crystallinity depends on the cellulose source [19].

Cellulose is a glucan polymer consisting of linear chains of 1,4-ß-bonded anhydroglucose repeat units with different degree of polymerization (DP) which depends on cellulose source. Cotton is the source of the cellulose with the highest DP that could reach up 10,000. This represents the average number of repeat unit (glucose) in cellulose chain. Wood cellulose has a (DP) of at least 9,000-10,000, and possibly as high as 15,000, but after pulping and bleaching process the DP drops to about 300- 1700.

Native cellulose is partially amorphous, most of its structure is crystalline (crystalline region) which makes it resistant to all solvents; the unit cell contains eight cellobiose moieties. Cellobiose consists of two unhydroglucose repeat units as shown in **Figure** 1.4.

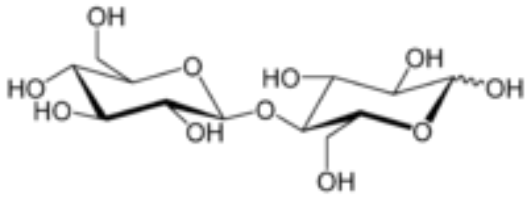


Figure 1.4: chemical structure of cellobiose

Cellulose consist of chains that are pack in layers and held together by weak van der Waals' forces. The layers consist of parallel chains of anhydroglucose repeat units, and the chains are held together by strong intermolecular hydrogen bonds. There are also intramolecular hydrogen bonds between the atoms of adjacent glucose units due to the presence of the three 3 hydroxyl groups as mentioned earlier on each monomer [20].

The molecular structure imparts cellulose with its characteristic properties: hydrophilicity, chirality, degradability, and broad chemical variability initiated by the high donor reactivity of the OH groups [21].

The presence of inter-molecular forces, intra-molecular forces and rigidity in cellulose chains make it a supramolecule that is insoluble in most common solvents, and difficult to dissociate without chemical modification

or derivatization. Solution systems were developed that could be used to dissolve cellulose such as, cuoxam, cuen, and cadoxen as well as lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) contain metal complexes Others including N_2O_4/N,N-dimethylformamide, NH_3/NH_4SCN , N-methylmorpholine-N-oxide monohydrate (NMMO) [22]. However, most of these systems are either expensive, toxic or require high concentration of chemicals leading to difficulties in recovery and reuse of the chemicals that raises environmental and health concerns [23].

The insolubility of cellulose in water and in most organic solvents caused by as mentioned above its supramolecular structure and the disadvantages in the cellulose solvent systems are the reasons behind the fact that all commercially available products made from cellulose are currently produced through heterogeneous reactions of cellulose in the solid phase, or more or less swollen state and other reagents [21].

Cellulose is considered thermal stable, it has a glass transition temperature is in the range of 200 to 230^{o}C, undergoes thermal decomposition at temperature of 260^{o}C [24].

1.3 Cellulose extraction from sources:

Wood is the most important source of cellulose. Other cellulose-containing materials include agriculture residues, water plants, grasses, and other plant substances. The primary occurrence of cellulose is the existing lignocellulosic material in forests with wood, and it is often combined with

other biopolymer. Also those are commercial cellulose production concentrates on harvested sources such as wood or on naturally highly pure sources such as cotton [18].

Several methods have been used to extract cellulose from its sources. The properties of cellulose depend on its raw material and pretreatment methods. In general extracting cellulose from wood contains two main processes; pulping and bleaching. Each process has different reagent that can be applied depending on the nature of cellulosic material.

1.3.1 Pulping process:

Pulping can be done either mechanically or chemically. Te Mechanical process leaves little or no waste but it requires high energy. It is two steps method that involves grinding in which wood are ground with revolving abrasive stone, and refining in which wood chips are fed between two metal discs, with one of them rotating. Mechanical pulping makes fines particles. These are smaller particles, such as broken fibers, giving the mechanical pulp its specific optical characteristics [25].

On the other hand, chemical pulping uses heat and chemicals to dissolve lignin, and only approximately half of the wood becomes pulp. Chemical pulping can be applied in several methods, such as steam explosion, kraft pulping (sulfate process), sulfite process and others [26].

Steam explosion depends on the treatment of cellulose source with high pressure for short period of time, followed by sudden explosion. During this process the raw material is exposed to pressurized steam followed by rapid reduction in pressure resulting in substantial break down of the lignocellulosic structure, hydrolysis of the hemicellulose fraction, depolymerization of the lignin components and defibrillization. This process leads to the cleavage of glycosidic links, ß-ether linkages of lignin, lignin–carbohydrate complex bonds.

Kraft pulping (sulfate method) is the most popular and is responsible for around 80% of world cellulose production. This process involves the digesting of wood chips at elevated temperature and pressure in white liquor (a mix of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), then digesting process that dissolves most of the lignin (90-95%) and only some of the hemicelluloses. Wood and white liquor (NaOH and Na_2S) are reacted in the digester at about 170 °C to produce kraft pulp and weak black liquor (the chemical mix left after the digesting process). Several by-products such as turpentine and non-condensable gases will be recovered from the digester also. Then Pulp is washed with water. Washing removes weak black liquor from the pulp [27].

Sulfite process uses bisulfites (HSO_3^-) or sulfites (SO_3^{2-}) as the active chemicals in pulping liquor, the counter ion can be sodium, calcium, potassium, magnesium or ammonium. The wood and the liquor are brought to a digester where the actual cooking takes place at elevated temperature

and pressure. Compared with the kraft pulping (sulfate process) sulfite pulping is not as versatile. On the other hand Sulfite pulps are more readily bleached and are obtained in higher yields [28].

In the final step, the pulp can be bleached to obtain a whiter product with lower amounts of impurities.

1.3.2 Bleaching:

Bleaching is decolorization of remaining colored lignin, or delignification process like pulping, but it is more selective and removes less lignin than pulp process. It removes colored residual lignin from pulp to increase its brightness, cleanliness, stability, and other desirable properties [25]. The bleached chemical pulps are composed mainly by cellulose (80–95%) and hemicelluloses (5–20%) though a small proportion of residual lignin (0.1–0.5%) is always present [29].

Oxidizing agents used in bleaching remove lignin in several ways; it break up the lignin molecule, and disrupt lignin carbohydrate bond allowing fragments to dissolve, or by introducing solubilizing groups into the fragments [28].

The residual lignin is a phenolic type. Many phenolic groups have a conjugated double bond on side chain forming stilbene, styrene and enol-groups. The bleaching agents can be classified in three different groups; The first group contains chlorine and ozone which react with any phenolic

and double bond, the second group is chlorine dioxide and oxygen which reacts with free phenolic group and double bond, and the third group contains sodium hypochlorite and hydrogen peroxide which react with carbonyl groups [30]. Chemically the pulp is treated with each chemical in separated stage. Bleaching processes use various combinations of chemical stages called bleaching sequences [31].

The bleached pulp yield and strength was determined by the degree of polysaccharides preservation during bleaching. The carbohydrate degradation and loss with bleaching are therefore the controlling factors for the potential usability of the bleached pulp and suitability of the bleaching process [32].

1.4 Cellulose derivatives and applications

Cellulose has been industrial feedstock to a large number of derivatives with unlimited number of commercial applications, and also an important source of ethanol when chemically or enzimatically hydrolyzed to glucose which then fermented to ethanol [33]. Surface modified cellulose also of great interest due to a wide range of potential applications [34]. Therefore, researchers are striving continuously to optimize hydrophobicity, wettability and adhesion properties of cellulose- through immobilization of suitable chemical functional species onto cellulose chains.

Cellulose occupies a unique place in the history of polymers. Cellulose is a precursor for chemical modifications that has been used even before its

polymeric nature was recognized and well understood, and most likely it will become the main chemical resource in the future. Moreover, numerous new functional materials from cellulose are being developed over a broad range of applications, because of the increasing demand for environmentally friendly and biocompatible products [35]. Since cellulose is natural product it is biodegradable, biocompatible due to the presence of the hydroxyl groups add advantage to this and make cellulose derivatizable.

In cellulose polymer each D-anhydroglucopyranose unit possesses hydroxyl groups; secondary OH at the C-2, secondary OH at the C-3, and primary OH at the C-6 position, capable of undergoing the typical reactions known for primary and secondary alcohols.

Production of cellulose derivatives was done by first dissolving cellulose in solvent system mentioned earlier, then reacting the free hydroxyl groups in the anhydroglucose units with various chemical substitution groups. The introduction of the substituent to hydroxyl groups disturb the inter and intramolecular hydrogen bonds between cellulose chains, which leads to liberation of the hydrophilic character of the numerous hydroxyl groups and restriction of the chains to closely associate. However, substitution with alkyl groups reduces the number of free hydroxyl groups, thus the hydrophilic characteristics of cellulose decreases [36].

The degree of substitution (DS) is defined as the average number of hydroxyl groups substituted per glucose monomer. And the maximum DS

is considered to be 3, because of the three hydroxyl groups. Physical properties such as swelling and solubility are strongly affected by the DS. It is difficult to get a complete substitution or an even distribution of substituents in a cellulose chain. The properties of cellulose derivatives, hence their applications, depend, entirely on the functional group introduced, the degree of substitution (DS), and the average degree of polymerization (DP) [37].

Cellulose is the most preferred raw material for the textile, paper and packaging industry. Water soluble cellulose derivatives are mostly used as biocompatible that are used as thickener, binding agents, emulsifiers, film formers, suspension aids, surfactants, lubricants and stabilizers, especially as additives in food, pharmaceutical, and cosmetic industries.

The most common cellulose derivatives are cellulose esters and cellulose ethers. Carboxymethyl cellulose (CMC) is the most important commercial water soluble cellulose ether, in which the hydroxyl group of anhydrous glucose is replaced by the carboxymethyl group under alkaline conditions **Figure** 1.5.It is usually used as its sodium salt (NaCMC). It's degree of substitution generally in the range 0.6–0.95 cabroxymethyl group per monomer unit depending on method of CMC preparation. CMC acts as an effective thickener, binder, stabilizer and film former. It thus finds applications in the cosmetics, food, pharmaceutical, textile, adhesives, oil drilling fluids and other industries [38].

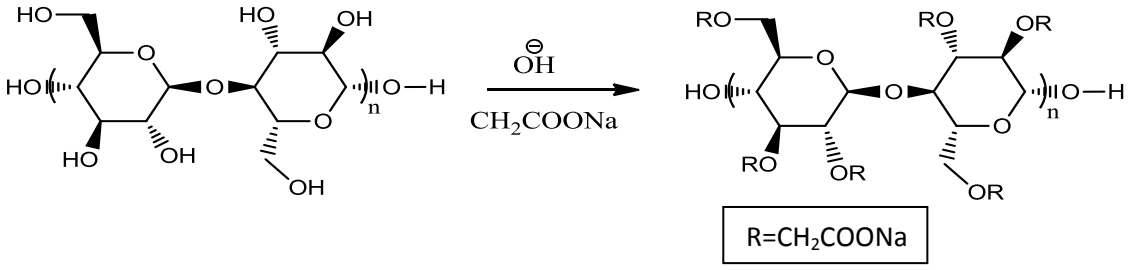


Figure 1.5: reaction equation for the preparation of CMC from cellulose

Some cellulose ether derivatives such as methyl cellulose (MC), hydroxypropyl cellulose (HPC), hydroxypropylmethyl cellulose (HPMC), and carboxymethyl cellulose (CMC) have been used to fabricate cellulose-based hydrogels derivatives, through physical and chemical cross-linking of hydrogels. Cellulose-based hydrogels have many favorable properties such as hydrophilicity, biodegradability, biocompatibility, transparency, low cost, and non-toxicity. Therefore, cellulose-based hydrogels have wide applications in tissue engineering, blood purification, agriculture, as well as water purification, and chromatographic supports [39].

Cellulose esters constitute a family of well-known commercial products include cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB). Cellulose acetate is used commercially in plastics (such as tool handles, face shields, eyeglass frames), tapes, textile fibers, cigarette filters and they have high glass transition temperature and produce tough and hard films). Cellulose acetate butyrate is used in printing inks, specialty coatings, toothbrushes, tool handles, and ophthalmic frames. Cellulose acetate butyrate is also used in plastics, such as brush and tool handles, automotive and furniture coatings, films and

sheets; they provide excellent color and color retention, toughness, flexibility, and good weather resistance [40].

Another important cellulose derivative is cellulose nitrate. Nitration of cellulose was discovered in 1832 by using equal parts of nitric acid and sulfuric acid. Commercial celluloid (cellulose nitrate solid plastic) was developed by in 1863. The first use of cellulose nitrate was in photography to create a light sensitive emulsion for the collodion in a Wet Plate process in 1851. It wasn't until 1889, that the process for creating a self-supporting plastic film was made commercial [41]. Cellulose nitrate refers to a family of transparent, light, flexible, and easy to handle film supports used for motion picture film and still photographic negatives. This material was most common between about 1910-1950 Other applications include blasting agents, propellants shooting agents, detonating agents, ignitions agents, and pyrotechnical agents [42].

1.5 **Cellulose acetate:**

Natural polymers such as cellulose or starch can be modified physically by plasticization, or chemically through the reaction of their active hydroxyl groups. Typical examples of such modifications are the benzylation of wood, the plasticization of starch, grafting of cellulose, and acetylation of acetate. The most common commercial process of neutral product modification is the acetylation of cellulose and formation of cellulose

acetate (CA). Considering that the global production for CA materials was over 800,000 metric tons per year in 2008 as shown in **Table** 1.2.

Table 1.2: Global production of cellulose acetate-based products

Cellulose diacetate material	Degree of substitution (DS)	2008 global production (metric tons)
Coating, plastics and films	**2.5**	**41,000**
Textile fiber	**2.5**	**49,000**
Filter tow	**2.5**	**690,000**
LCDs photo film, and textiles	**3.0**	**41,000**

The esterification reaction of the primary and secondary hydroxyl groups does not basically differ from that of other alcohol, but it lies in macromolecule structure of the cellulose molecule. Many esterification reagents can be used such as acids (like nitric acid, acid chlorides, and acid anhydrides. Numerous catalyses were suggested to accelerate the reaction such as mineral acids, zinc chloride, and the most important catalysts are sulfuric acid and perchloric acid [43].

Various methods have been developed for producing cellulose acetates. Because of the poor solubility cellulose, a number of cellulose derivatives are currently prepared under heterogeneous conditions which mostly used in industry. Cellulose esters are generally synthesized reaction cellulose with anhydrides in presence of catalytic amount of sulfuric acid with or

with acid chloride in the presence of a tertiary base. Problems arise such as poor uniformly of substitution; low yields and extensive by product formation. For a maximum conversion of cellulose to its derivatives, it is usually better to carry out the reaction in a homogeneous medium, using a suitable solvent system that dissolves cellulose and other reactants while inert toward cellulose or other reagents. The average number of acetyl groups per anhydroglucose repeat unit, can range from 0 in the case of cellulose, to 3 for the triacetate cellulose, the most common form cellulose acetate with 2-2.5 DS which is known as cellulose diacetate or acetate [44].

Depending on the way it has been processed cellulose acetate can be used in unlimited number of applications (e.g. for films, membranes or fibers). The properties of the applied cellulose acetates are very important for these applications [45]. Commercially cellulose acetates are available as white powder or flakes with amorphous structure. They are odorless, tasteless, nontoxic, resistant to weak acids, and largely stable to mineral and fatty oils. Its properties and application depends on viscosity of their solutions which indicates its degree of polymerization, and this influences the mechanical properties of the resulting films, fibers, or plastic masses. The degree of esterification also affects cellulose acetate properties; it affects the solubility, mechanical properties and compatibility with softeners, resins, varnish and others [43].

1.6 Aims of the Study

As previously dicussed, cellulose is a diverse polymer. Cellulose can be chemically modified to yield derivatives which are widely used in different industrial sectors in addition to conventional applications. As an example, in 2003, 3.2 million tons of cellulose was used as a raw material in the production of regenerated fibers and films in addition to cellulose derivatives [46].

In this study cellulose extracted from OISW will be converted into cellulose acetate using both methods available in the literature the homogeneous method and the heterogeneous method.

Homogeneous Method:

In this method cellulose will be dissolved in organic water-free solvent systems consist of two-component N,N-dimethylacetamide /lithium chloride (DMA/LiCl) [47]. The dissolution process could be achieved in a two step process:

1. A mixture of DMA containing the 2.5% (w/w) of cellulose is stirred at 130°C for two hours (activation step). When the cellulose concentration is higher 4.3% (w/w) the temperature is increased to 160°C.

2. After the activation step the temperature is decreased to 100°C at which dry LiCl is added in one portion. Then, the mixture is left to

cool to room temperature to obtain a clear solution. In order to remove the remaining water bound to cellulose [47, 48].

After the complete dissolution of cellulose excess acetic anhydride or acetyl chloride was added to the solution along with a base such as triethylamine which also acts as a catalyst.

Heterogeneous Process

In the heterogeneous process, cellulose will be mixed with acetic anhydride in presence of a catalytic amount of sulfuric acid in the absence of acetic acid. Both method homogeneous and heterogeneous will carried out and results will be compared regarding degree of substitution (DS), intrinsic viscosity (IV), and other physical properties.

CHAPTER 2

Experimental

Materials

All reagents were purchased from Aldrich Chemical Company, and used as received unless otherwise specified. Kraft pulping was performed using a high Parr Reactor model: Buchiglasuste, bmd 300. Fresh OISW was obtained from an olive factory near city of Tulkarm in the West Bank and stored in a freezer at about -5^{o}C to 0^{o}C.

Methods

The FTIR instrument used in this work was the Magna 6400 Spectrometer from Thermal Scientific. A Split Pea ATR accessory was used as the sample interface. The SEM (Scanning Electron Microscope) Hitachi S-3400N and EDS (Energy Dispersive Spectroscopy) Oxford SwiftED were used to obtain greater details of the sample morphology and determine basic elemental make-up. HPLC analysis was performed on an L-2400-2-Lachrom Flite HPLC System connected to a refractive index (RI) detractor and equipped with an Amino column with dimensions of 150 x 4.6 mm The mobile solvent used in the analysis was composed of acetonitrile and a buffer solution of NaH_2PO_4 (1.15 g) in water (1 L) at ratio of 80:20. Differential Scanning calorimetry was on performed on DSC Instrument: TA Instruments Q200 MDSC Cooling System: RCS, Purge Gas: Nitrogen at 50 mL/min , Calibration Standards: Indium for heat flow and sapphire

for heat capacity , Pan Type: Crimped Aluminum, approximately 23 mg , Sapphire Test Method: DSC @ 10 °C/min from 0 to 300 °C , Sample weight of 26.09 mg (disk.) .

Kraft pulping was performed in a high Parr Reactor purchased from (model: büchiglasuster, bmd 300). All reagents were purchased from Aldrich Chemical Company and used without any further purification unless otherwise specified.

Percent yield was calculated by dividing the dry weight of the produced pulp by the dry weight of the starting OISW. Moisture contents was determined according to the standard method ASTM D-13148, ash contents was determined using the standard method ASTM D-1107-8, and ASTMD D-111-84 and ASTM D-1107-87 standard methods were used to determine water and ether extracts. Pulp viscosity and degree of polymerization were determined according to standard process ISO 5351-1 which involves the dissolution of the pulp in an aqueous solution of copper ethylene diamine using a Cannon-Fenske viscometer. Kappa number was determined using the standard method T236 cm-85.

The Size Exclusion Chromatography (SEC) analysis was performed on HPLC system with a UV detector connected to other two detectors, 18-angle light scattering detector The DAWN® HELEOS® II for the measurement of absolute molecular weight, size, and conformation of macromolecules in solution and the Refractive Index detector Optilab® T-

rEX (refractometer with extended range. Both detectors are made by Wyatt technology. Three columns that are connected on a series were used in the analysis; the columns are 3 x PLgel 10 μm MIXED-B, 300 x 7.5 mm.

GC/MS analysis was performed on a GC. The GC measurements were performed on a gas chromatograph (HP 5890 Series II, Hewlett-Packard, Avondale, PA, USA) equipped with FID and a split–splitless injection port. The separation of the compounds was carried out on a DB-624 column (75m×0.53mm, 3 μm in film thickness, J&W Scientific Inc., Folsom, CA, USA). Data acquisition and processing were done using Qianpu chromatography workstation (Qianpu Software Inc., Nanjing, China).

The experimental section is divided into two parts: extraction of cellulose from Jeft and converting the extracted cellulose into cellulose acetate.

Cellulose was extracted from Jeft in a process consist of three stages. Each stage consists of one or more than one step. The three stages are: Extraction of residual materials, Pulping, and Bleaching. Then extracted cellulose converted into cellulose acetate.

2.1 Extraction of Residual Materials from Jeft

Residual materials were removed from Jeft using the soxhlet extraction method. Jeft (200.0 g, OD weight 80%) was added to a round bottomed

flask (1.0 L) of soxhlet extractor and subjected to extraction with ethyl acetate (500 mL). The extraction was continued for about 4 hr. Then ethyl acetate solvent was removed under reduced pressure using rotary evaporator to afford about 10.0 g (5.6% based on OD weight of OISW) of pale yellow residual liquid. The residue was subjected to analysis by GC/MS. The separation of the compounds was carried out on a DB-624 column (75m×0.53mm, 3 μm in film thickness, J&W Scientific Inc., Folsom, CA, USA). Data acquisition and processing were done using Qianpu chromatography workstation (Qianpu Software Inc., Nanjing, China). The GC oven temperature program was as follows: 50°C held for 3 min, rate at 5°C/min to 130°C and held for 2min. The carrier gas was highpurity nitrogen with a pressure of 20 psi in the injection port. The injection port and detector temperatures were set at 300 and 250°C, respectively. The pressure of the H_2 and air for the detector was 20 and 40 psi, respectively. Splitless mode was adopted

2.2 Pulping

Kraft pulping was conducted in a high Parr Reactor of one liter capacity. In all experiments, the liquor to Jeft ratio, cooking temperature, temperature rising time, holding time, and operation pressure were 4:1, 160^{o}C, 30 min, 90 min and 50 psi, respectively. Active alkali charge is defined as [NaOH+Na_2S], and sulfidity is defined as [Na_2S/(NaOH+Na_2S)], where the concentrations are expressed as g/L Na_2O. Active alkali and sulfidity levels ranging from 14% to 20% and from 10% to 25% (based on

the oven dried pulp), respectively, were investigated. At the end of pulping, the produced pulp (cellulose left over after the pulping process) was collected by suction filtration, washed several times with tap water, air dried at room temperature, and stored in plastic bags for further use. Various pulp properties were determined according to standard methods mentioned earlier. The pulping process was performed on 0.5 Kg of jeft

Several experiments were performed to reach the optimum cooking conditions with high yield, high purity, and least cost. The conditions and results obtained from pulping experiments are summarized in **Table** 2.1.

Table 2.1: Pulping results

Run	Pulping conditions		Reaction time (hr)	Pulp Yield (%)	Kappa Number	Viscosity (c.p.)
	Sulfidity (%)	Active alkali				
1	30.4	23	2	44.0	31.3	2.42
2	29.4	17	2	50.0	36.6	2.31
3	30.4	23	1	49.0	34.2	2.28
4	24.0	21	2	48.4	33.1	2.13
5	29.4	17	1	50.2	38.8	2.39
6	31.3	21	1	48.6	33.8	2.24

2.3 Pulp Analysis

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

K-Number

Viscosity

2.3.1 K-Number according to standard method T236 cm-85

2.3.1.1 Preparation of reagents

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 1L of water.

Sodium thiosulfite ($Na_2S_2O_3$) standard solution: A solution of (Na_2S2O_3) (0.02±0.001 mol /L) was prepared by dissolving 24.82 g $Na_2S_2O_3.5H_2O$ in 1liter of water.

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

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

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

2.3.1.2 General Procedure:

1. Oven dried pulp (1.00 g) was weighted and placed in a blender

2. To the pulp, 400 mL distilled water was added and the machine was run for 3 min. The purpose of this step was to disintegrate the pulp.

3. After disintegration pulp suspension was added to a flask, followed by 50 mL of 0.02 M potassium permanganate. The pulp was left in contact with $KMnO_4$ for about 10 min at room temperature.

4. After the 10 min, 10 mL of potassium iodide was added to the mixture.

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

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

2.3.2 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 beads, pulp, and cuene.

2.3.2.1 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. Syringe, 25.00 mL, for solvent.
6. Syringe, 25.00 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 pipett bulb.

2.3.2.2 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 commercially or prepared. 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. Eight 6-mm glass beads were added.

2. Exactly 25.00 mL of distilled water (from burette), was then added to the plastic bottle. The bottle was then capped.

3. The bottle was then shaken and allowed to stand for about 2 min.

4. Exactly 25.00 mL of the cupriethylenediamine (1.0 ± 0.02M in cupric ion and 2.0M in ethylenediamine) was added, and 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.

6. 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.

7. The solution in the viscometer was drawn up into the measuring side of the viscometer with a suction bulb, and 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.

2.3.2.3 Calculation of intrinsic viscosity:

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

$$V = Ctd$$

Where:

V = viscosity of pulp 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 some samples, results are shown below.

Table 2.2: Intrinsic viscosity of extracted cellulose

Run	Pulping conditions		Reaction time (hr)	Viscosity (c.p.)
	Sulfidity (%)	Active alkali		
1	30.4	23	2	2.42
2	29.4	17	2	2.31
3	30.4	23	1	2.28
4	24.0	21	2	2.13
5	29.4	17	1	2.39
6	31.3	21	1	2.24

2.4 Bleaching

Many chemicals were used in bleaching of olive pulp in different sequences to choose the best sequence of them. The following chemicals were used:

A: acid wash

E: Extraction with NaOH (aq).

H: Sodium hypochlorite.

P: Hydrogen peroxide.

Ep: Alkaline/Hydrogen peroxide.

Bleaching was performed in sequential stages, for instance the product of A-stage was performed on it E-stage, and the process continued until the bleaching sequence was completed. Sample number is related to run number; i.e. sample 1 was obtained from renumber 1 Table 1.

3.4.1 Acid wash (A-stage)

A-stage was performed in a beaker at 5% consistency for 30 min at room temperature; pulp was suspended in a 2% solution of sulfuric acid, then collected by suction filtration and washed with water until almost free of acid. The acid stage was performed on the samples listed in **Table** 2.3

Table 2.3: Results of acid stage

Sample	Pulp Weight(g)	Percentage Yield (%)
4	**44**	**96**
5	**62**	**97**
6	**45**	**88**

2.4.2 Extraction with sodium hydroxide stage (E-stage)

The E-stage was conducted in a plastic bag at 10% consistency for 90 min at 60°C and with 5% NaOH (5% based on pulp weight). After the completion of the treatment produced pulp was collected by suction filtration, and washed several times with water until neutral filtrate was obtained.

This stage was repeated more than one time for some samples. Results are summarized in **Table** 2.4.

Table 2.4: Results of bleaching with E-stage

Sample No	Pulp Weight Pulp (g)	Percentage Yield (%)
3	**50**	**93**
4	**56**	**89**
5	**46.5**	**87**
6	**52**	**88**

3.4.3 Sodium hypochlorite stage (H-stage)

The H-stage was conducted in a plastic bag at 10% consistency for 60 min at 60°C and a pH of 10. Hypochlorite charge was 2.5% based on pulp weight. NaClO was obtained from a stock solution that contained 5% of NaClO (5%). This stage was carried out on pulp obtained from H-stage.

At the end of the bleaching stage, produced pulp was collected by suction filtration, washed with tap water until neutralized, air dried and stored in plastic bag. Yield was calculated by dividing the treated bleaching pulp produced (OD weight) by the starting bleaching pulp (OD weight). Results are summarized in **Table** 2.5.

Table 2.5: Results of bleaching with H-stage

sample	Weight Of Pulp (g)	Percentage Yield (%)
3	**53**	**93**
4	**59**	**97**
5	**55**	**90**
6	**56**	**96**

2.4.4 Hydrogen peroxide stage (P-stage)

Olive pulp Obtained from H-stage was treated with a solution of 2% H_2O_2 0.5% $MgSO_4.7H_2O$ 3% NaOH of pH (9-11), at ratio of 10% consistency, at 60°C for 60 min in plastic bag. The product was collected by suction filtration, washed with tap water until neutralized, air dried and stored in plastic bag. Yield was calculated by dividing the treated bleaching pulp produced (OD weight) by the starting bleaching pulp (OD weight). Results are shown in **Table** 2.6.

Table 2.6: Results of bleaching with P-stage

sample	Weight Of Pulp (g)	Percentage Yield (%)
5	**45**	**93**
6	**43**	**89**
7	**36**	**95**
8	**44**	**96**
9	**60**	**96**
11	**39**	**91**

The following table summarizes the various bleaching sequences performed on each sample and analysis results:

Table 2.7: Summary of the analysis results on bleached samples of cellulose extracted for jeft

Sample No	Bleaching Sequence	Intrinsic Viscosity (c.p.)	Kappa Number	lignin Contents	Final Yield (%)
1	**H-E-P-H-E**	2.33	1.21	0.18	70
2	**H-E-P**	2.61	2.13	0.32	77
3	**H-E-P**	2.73	2.10	0.31	75
4	**H-E-A-P-E-P**	1.98	0.97	0.15	60
5	**A-P-E-P**	2.53	1.65	0.25	75
6	**A-P-E-P**	2.71	1.54	0.23	77

2.5 Preparation of cellulose acetate from cellulose extracted form jeft

2.5.1 Apparatus

1. Nitrogen gas, purity 99.998%, was fitted with a pressure reducing valve to give 14 to 21 KPa (2 to 3 psi) pressure.
2. Oil bath
3. Drying oven.
4. Büchner funnels.
5. Three necked round bottomed flask.
6. Condenser.
7. Addition funnel.
8. Oil bubbler (air trap).
9. Hot plate with magnetic stirrer.

2.5.2 Procedure:

2.5.2.1 Heterogeneous method:

Chemicals: Acetic acid, sulfuric acid and acetic anhydride

To a three necked round bottomed flask equipped with magnet stir bar, condenser, addition funnel, and connected to a trap was added exact mass of cellulose (**Table** 2.8). To cellulose in the round bottom flask was added

acetic acid and sulfuric acid. The flask and content was placed in an oil bath and stirred for about 10 minutes, and then known amount of acetic anhydride was added drop wise from addition funnel over a period of about 10 min. Several experiments were carried out under various conditions of reaction time, temperature, and amount of chemicals used. All variable are summarized in **Table** 2.8. After the completion of reaction, the reaction mixture was diluted with water and the produced precipitate was collected by suction filtration and washed with plenty amount of water to remove all acids.

Table 2.8: Heterogeneous method conditions

Run No	Cellulose acetate (g)	Time (Hr)	Temp (C°)	H_2SO_4 (drop)	Acetic anhydride (ml)	Acetic acid (ml)	Cellulose (g)	Yield (%)
1	**11.5**	**48**	**80-100**	**10**	**35**	**100**	**9.35**	**69**
2	**3.8**	**7**	**R.T**	**7**	**55**	**50**	**5**	**43**
3	**4.74**	**24**	**R.T**	**20**	**85**	**50**	**5**	**53**
4	**6**	**6**	**80**	**20**	**85**	**50**	**5**	**68**
6	**6**	**6**	**80-100**	**7**	**85**	**50**	**5**	**68**

2.5.2.2 FTIR of selected samples of prepared cellulose acetate

The IR spectrum of samples 3 and 6 are shown in **Figures** 3.1 and 3.2, they showed the following bands in **Table** 2.9.

Table 2.9: The main absorption bands of cellulose acetate

Wave number (cm^{-1})	Assignment
3500	v O-H
2950	v C-H (CH_3)
2890	v C-H (CH_2)
1750	v_{sym} C=O strong
1650	v_{assym} C=O
1430	δ CH_2
1370	δ C-H
1260	v C-O strong
1160	v_{assym} C-O-C
1040	δ C-O strong
900	δ C-H

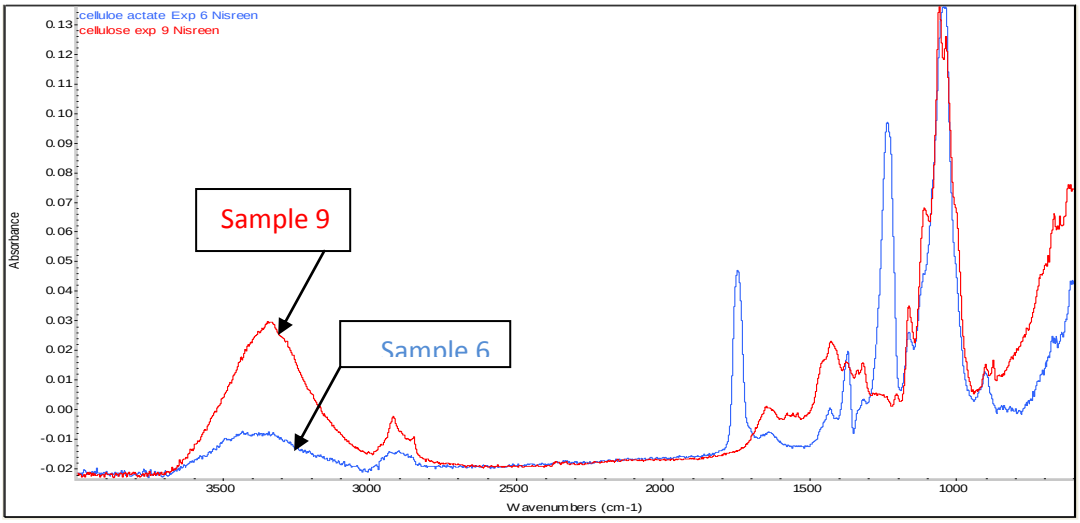


Figure 2.1: FTIR results for cellulose acetate samples number 6 and 9

2.5.2.3 Homogeneous method

Chemicals:

N,N dimethyl acetamide (DMA)**,** lithium chloride LiCl, acetic anhydride, triethylamine.

The reaction was carried out in a three-necked round bottomed flask equipped with magnet stir bar, condenser, addition funnel, and connected to a trap via the condenser. To the flask 13.0 g of LiCl, 200 ml N,N dimethyl acetamide (DMAc) and 5.0 g of cellulose were added. The mixture was heated under nitrogen gas in oil bath at 150°C for 1 hr with stirring, then temperature was reduced to 90 °C until cellulose dissolved and solution became clear. To the solution triethylamine (50.0 ml) through the addition funnel, after 5 minutes from the addition of triethylamine, acetic anhydride (30 ml) was added drop wise to the reaction mixture through addition funnel, and the reaction continued for about 6 hr. At the end of the reaction, the reaction mixture was cooled to room temperature, diluted with water, and product separated, washed with plenty of tap water, air dried, and stored in a plastic container. The FTIR spectrum of selected sample prepared by homogeneous method is shown **Figure** 2.2.

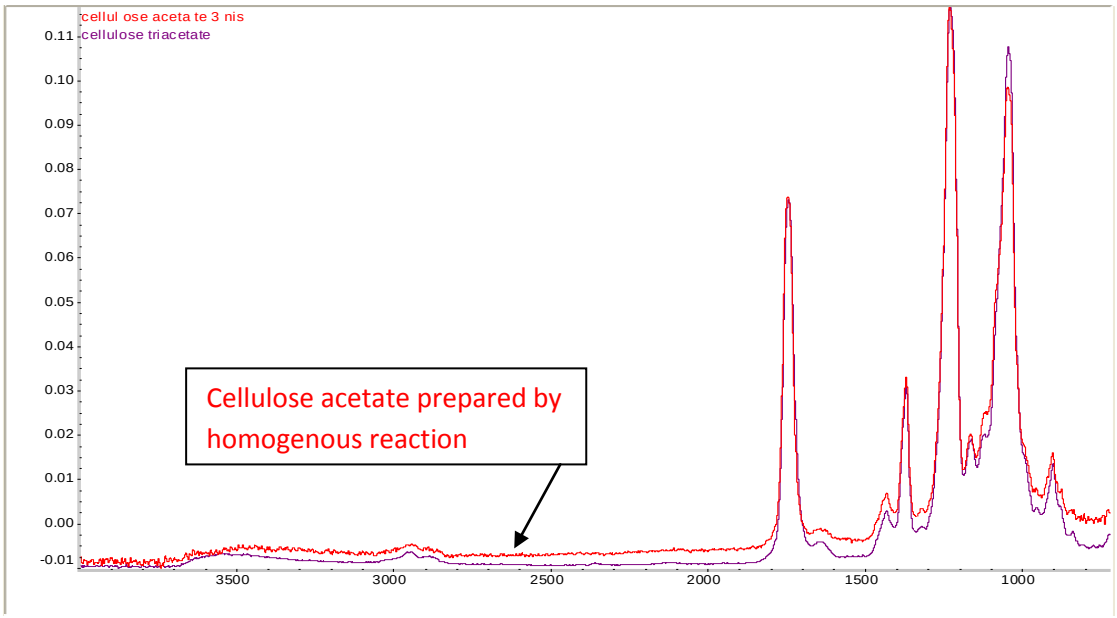


Figure 2.2 FTIR results for cellulose acetate prepared by homogeneous method

CHAPTER 3

Results and Discussion

Olive industry solid wastes (jeft) consist of four components: Cellulose, hemicelluloses, lignin, and extractives, the purpose of this study is to extract cellulose from jeft in high purity form and then convert the extracted cellulose in commercially valuable products such as cellulose acetate. The work shown in this thesis is a continuation of wok started with a previous MS student Yusra Fuad [33]. The process developed previously has been scaled up and modified to increase the yield and lower the cost. The developed process is now more suitable for commercial production. In addition, a method was developed for converting cellulose extracted from jeft into a new commercial material that has never been made from jeft. The prepared material is cellulose acetate that has unlimited number of industrial applications.

3.1 Extractives of OISW

Residual materials were extracted from jeft using the soxhlet extraction method as shown in the experimental section. Out of OISW (200.0 g, OD weight 80%) 10.0 g (5.6% based on OD weight of OISW) of pale yellow residual liquid was extracted using 0.5 L of ethyl acetate. The extractives were subjected to analysis by GC as is with any further purification. The produced chromatogram is shown in **Figure** 3.1. The extractives, from **Figure** 3.1 are a mixture of several components which are identified using

the MS library. Peak with a retention time of 7.42 min correlates well with MS spectrum of hexadecanoic acid (palmitic acid). MS results shows that peak with a retention of 8.94 min present at highest percentage, correlates well with the MS spectrum of (9Z)-octade-9-enoic acid (Oleic acid). Peak with a retention time of 9.09 was identified to be octadecanoic acid (Stearic acid), since its MS spectrum correlate well with the MS spectrum of octandecanoic acid present in the MS library. Peaks with retention times between 11.4 and 13.8 are silicon compounds. Most likely the source of these compounds is the column, since olive has known silicon materials. This phenomena know as column bleeding, which occurs usually with that are used for some time. The peak at 14.28 was identified to be (9*Z*, 12*Z*, 15*Z*)-9,12,15-Octadecatrienoic acid α-Linolenic acid by comparing its MS with that available in the MS library

The peak at 20.756 was identified to be lenolic acid by comparing its MS with that available in the MS library. From these results we could conclude that the jeft extractives are mostly olive oil. The identified fatty acids (shown above) are the ingredient of olive oil, which are present in olive in the form of triglycerides shown in **Figure** 3.2. [49].

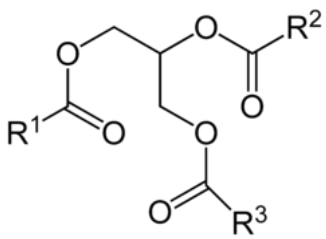


Figure 3.2: Fatty acids triglycerides present in olive oil

R^1, R^2, R^3 = fatty acids (hexadecanoic acid, octandecanoic acid, (9z)-octade-9-enoic acid, α-Linolenic acid and lenolic acid.

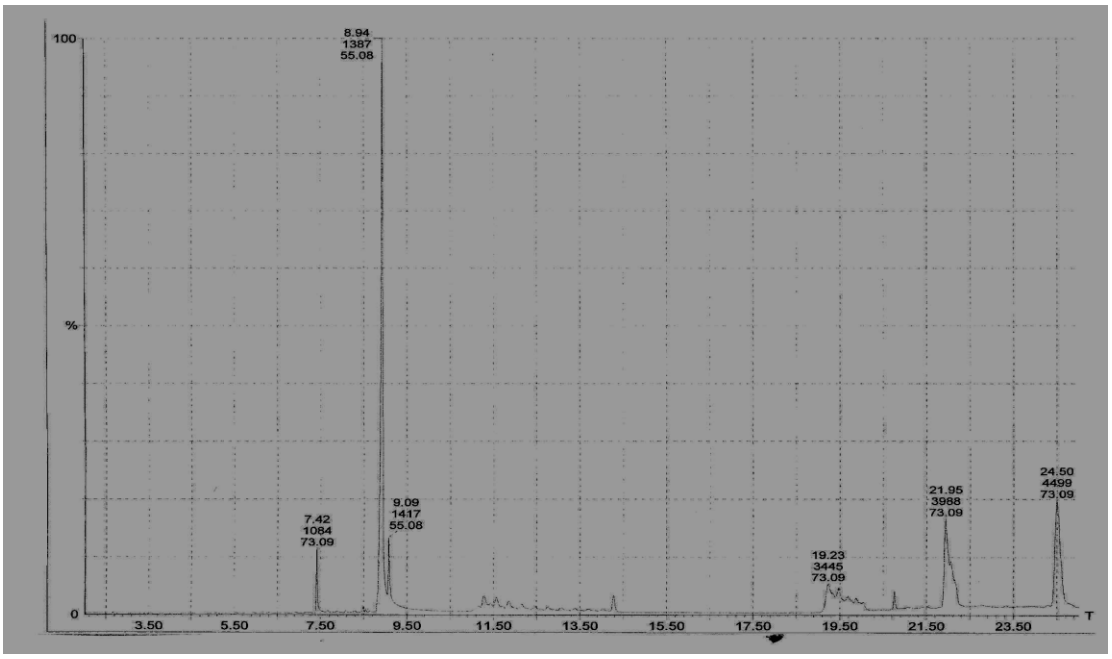


Figure 3.1: GC chromatogram of jeft extractives

3.2 Pulping of Olive Industry Solid Waste

Pulping was carried out at about 160^{o}C. Pulping below this temperature produces pulp with high contents of particles that are not totally delignified, so temperature below 160^{o}C is insufficient for the delignification of jeft. When the temperature was raised to about 160^{o}C, jeft was completely delignified into micro fibers. As shown in **Table** 3.1 kraft pulping was performed in an aqueous solution of sodium hydroxide and sodium sulfide, under high pressure and temperature as shown in experimental section. Various pulping conditions have been tried to determine conditions that produce highest yield and viscosity of cellulose.

Results of kraft pulping are summarized in **Table** 3.1.

Table 3.1: Results from pulping of jeft at various conditions

Run	Pulping conditions		Reaction time (hr)	Pulp Yield (%)	Kappa Number	Viscosity (c.p.)
	Sulfidity (%)	Active alkali				
1	30.4	23	2	44.0	31.3	2.42
2	29.4	17	2	50.0	36.6	2.31
3	30.4	23	1	49.0	34.2	2.28
4	24.0	21	2	48.4	33.1	2.13
5	29.4	17	1	50.2	38.8	2.39
6	31.3	21	1	48.6	33.8	2.24

All pulping runs were performed at about 160^{o}C (± 5.0)

As shown in **Table** 3.1, higher pulp yield with acceptable viscosity was obtained from run 5. Run 5 was performed under mild caustic condition if compared with other runs and shorter time. The developed pulping process is commercially feasible. Pulp obtained form run 5 was the highest about 50.2% and pulp viscosity was about 2.39 c.p.

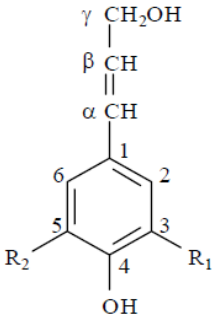
Fresh solution of sodium hudroxide and sodium sulfide is known in the field of pulping and bleaching as white liquor. The term active alkaline (AA) shown in **Table** 3.1 equal the sum (NaOH + Na_2S) in gram per liter liquid. In performed pulping process the white liquor was mixed with jeft and heated at about 155-160° C under a N_2 pressure of about 90 psi. During the pulping process the white liquor dissolves lignin and hemicelluloses,

since lignin is a large polymer with a black color, at the end of the pulping process the white liquor becomes black. The main reaction in between white liquor and lignin is shown in **Equation** 3.1

$$NaOH + Na_2S + jeft \longrightarrow Na\text{-org.} + S\text{-org.} + NaHS \qquad \textbf{Eq } 3.1$$

During the pulping process most of lignin is fragmented and dissolved in the white liquor. At the end of the pulping process produced pulp (cellulose extracted from jeft) has a dark brown color. The color could be attributed to the presence of lignin fragments: quinines, quinones, complexed catechols, chalcones and stilbenes, all of which are high unsaturated lignin monomer that absorb visible light and make the pulp brown [50].

In order to understand the reactions which break up lignin into soluble fractions, it is important that first understand lignin structure. The basic building block of lignin (the monomer) is a phenolic ring with a three carbon side chain. The lignin molecule is linked through a variety of linkages as shown in **Figure** 3.3 The most prominent linkage is an ether linkage which connects the β-carbon (2^{nd} carbon of the side chain) or the α-carbon (1^{st} carbon of the side chain) of one phenolic monomer the next monomer as shown in **Figure** 3.4 This linkage (β-O-4) makes up approximately ½ of the linkages, there are a large number of the units connected through carbon-carbon bonds which are difficult to cleave [51, 52].



R_1=OMe, R_2=H: Coniferyl alcohol/guaiacyl
R_1=R_2=OMe: Sinapyl alcohol/syringyl
R_1=R_2=H: *p*-Coumaryl alcohol

Figure 3.3: linkages of lignin

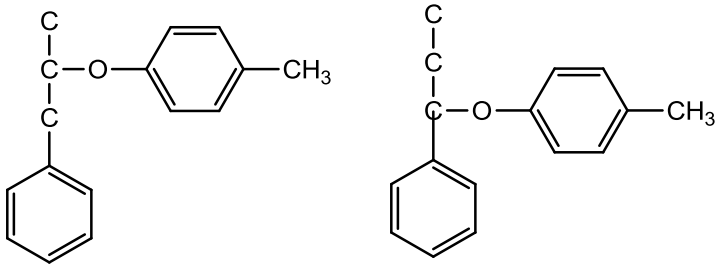


Figure 3.4: a) linkage of β-O-4 b) linkage of α-O-4

In kraft cooking (NaOH and Na_2S: OH^- and HS^-) both act as nucleophiles* and a base is shown in **Figures** 3.4 and 3.5. The OH^- abstract proton from the hydroxyl group at the β-carbon of the ether linkage, causing it to cleave into two fragments as shown in **Figure** 3.5.

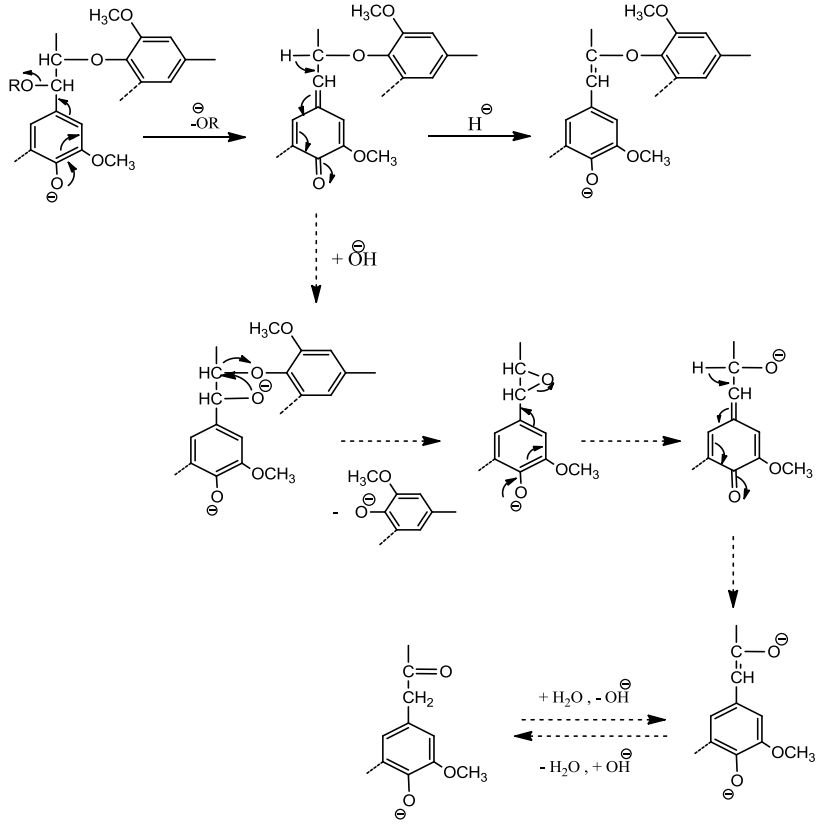


Figure 3.5: example of hydroxyl group and β-carbon reaction in kraft pulping

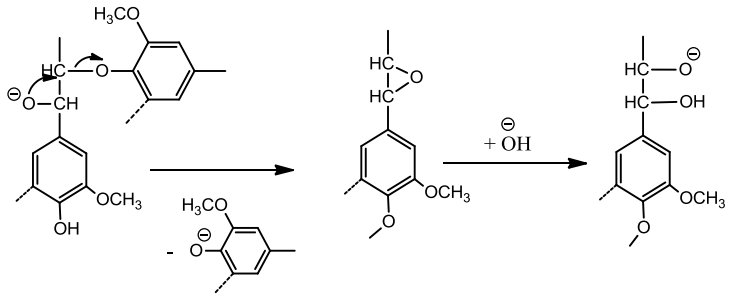


Figure 3.6: example of hydroxyl group and β-carbon reaction in kraft pulping

Sulfide ion plays a dual roles in the kraft process; it promotes and accelerates the cleavage of the ether links in phenolic units and is reduces

the extent of undesirable condensation [53]. The absence of sodium sulfide from the pulping process resulted in cellulose with high percentage of undelignified jeft. In addition, the color of the produced cellulose was very dark brown, which after bleaching did not go away completely, indicating that large portion of lignin still present in the produced cellulose.

3.3 Bleaching

Residual lignin stays on pulp after the pulping process usually removed by a bleaching process. In the bleaching process oxidizing agents are used to oxidize leftover lignin attached to cellulose chain. Various types of oxidizing agents could be used as bleaching agent in separate steps under suitable reaction conditions. So the bleaching process is a sequence of stages. After pulping obtained pulps were subjected to one of the following four bleaching sequences: HEPHE, HEP, HEAPEP, and APEP, a brief summary of individual stages is shown below:

E-stage: Conducted in a plastic bag at 10% consistency for 90 min at 60°C and with 5% NaOH (5% based on pulp weight). After the completion of the treatment the produced pulp was filtered and washed several times with water until neutral filtrate was obtained.

H-stage: Conducted in a plastic bag at 10% consistency for 60 min at 60°C and at a pH of 10. Hypochlorite charge of 2.5% based on pulp weight. NaClO was obtained from a stock solution that contained 5% of NaClO.

A-stage: Performed in a beaker at 5% consistency for 30 min at room temperature, pulp is suspended in a 2% solution of sulfuric acid, and then washed with water until almost neutralization.

P-stage: Conducted in a plastic bag at 10% consistency, for 60min, at 60 ^{o}C and a pH of 9 to 11 and with 2% H_2O_2, 0.5% $MgSO_4.7H_2O$, and 3.0% NaOH (based on pulp weight). The mixture was filtered, washed with water until neutralization, and air-dried [54, 55, 56].

The bleaching stages were performed in sealed plastic bags at suitable temperature in water bath. Samples were agitated from time to time. At the end of each stage pulp was separated by suction filtration, washed with water until neutralized, air dried, and yield calculated.

In the H-stage, the oxidizing agent sodium hypochlorite solution (NaClO) was used, to be an effective bleach, the hypochlorite solution was kept alkaline (pH > 9.0), in order to suppress the hydrolysis of OCl^- and prevent the formation of unstable HOCl. The OCl^- ion oxidizes chromophores in colored materials, and is itself reduced to chloride and hydroxide ions as shown in **Equation** 3.2.

$$OCl^- + H_2O + 2\,e^- \longrightarrow Cl^- + 2OH^- \qquad \textbf{Eq } 3.2$$

Alkaline extraction (E-stage) is an important stage in the bleaching process; the hydroxide ion undergoes nucleophilic substitution reaction chlorinated ligin rendering it more water soluble, thus improving the effectiveness of

oxidation stages to produce high brightness pulp [57]. E-stage is used to solubilize lignin degradation products. Also Under alkaline conditions, phenols (Ar-OH) become ionized to form phenolate anions ($Ar\text{-}O^-$) which are much more soluble in water than phenols [58].

One of the most powerful, satisfactory, and widely used bleaching agent in recent years is hydrogen peroxide. The active bleaching species in hydrogen peroxide is the perhydroxyl anion (OOH^-), formed through the ionization of H_2O_2 as shown in **Equation** 3.3

$$H_2O_2 + H_2O \longrightarrow H_3O^+ + OOH^- \qquad \textbf{Eq } 3.3$$

The acid ionization constant of hydrogen peroxide is very low ($K_a = 2 \times 10^{-12}$) with the result that solutions of H_2O_2 must be made alkaline in order to raise the concentration of OOH^-, for this reason bleaching with hydrogen peroxide usually carried out in a basic medium. In the absence of an alkaline medium, hydrogen peroxide is no longer effective as a bleaching agent. At the same time the pH must not rise above 11, as at this point, the decomposition of OOH^- begins to occur. Hydrogen peroxide usually used for brightening pulp as the last stage of bleaching sequence [59].

So the two components of sodium hydroxide and hydrogen peroxide are usually used in Ep-stage. If used by themselves they are ineffective but when mixed together, a strong oxidizing reaction is formed which is most effective in removing the natural color in wood.

Pulp obtained using the Kraft method was subjected to various bleaching sequences in an attempt to achieve high purity cellulose. The bleaching sequences and results are summarized in **Table 3.2**

Table 3.2: Summary of the analysis results on bleached samples of cellulose extracted for jeft

Sample No	Bleaching Sequence	Intrinsic Viscosity (c.p.)	Kappa Number	lignin Contents	Final Yield (%)
1	**H-E-P-H-E**	2.33	1.21	0.18	**70**
2	**H-E-P**	2.61	2.13	0.32	77
3	**H-E-P**	2.73	2.10	0.31	75
4	**H-E-A-P-E-P**	1.98	0.97	0.15	60
5	**A-P-E-P**	2.53	1.65	0.25	75
6	**A-P-E-P**	2.71	1.54	0.23	77

Sample 4 was chosen for analysis by various techniques, it was chosen because it has the lowest lignin content shown by its lowest K-number.

3.4.1 Analysis of extracted cellulose by FTIR

The IR spectrum of sample 5 is shown in **Figure** 3.7. The band at 3350 cm^{-1} could be attributed to hydrogen bonded hydroxyl group (OH) stretching vibration. The bands at 2920 and 2845 cm^{-1} correspond to the CH stretching vibration in CH and CH_2 in anhydroglucose units of cellulose. The 1430 cm^{-1} band could be attributed to CH_2 asymmetric bending. The band at 1380 cm^{-1} corresponds to the C-O stretching of ether and alcohol

groups. The band at 1160 cm^{-1} corresponds to C-O-C stretching of β-glycosidic linkage. The IR spectrum shows no peaks in the area of 1700 cm^{-1} that would be characteristics of carbonyl group in hemicelluloses. From this, we could conclude the absence of hemicelluloses in the extracted cellulose powder. Also the absence of 3070 and 1600 cm^{-1} band is an indication of the absence of lignin the two IR spectra are in almost in complete match. This could be an indication that the material extracted from OISW is actually high purity cellulose powder.

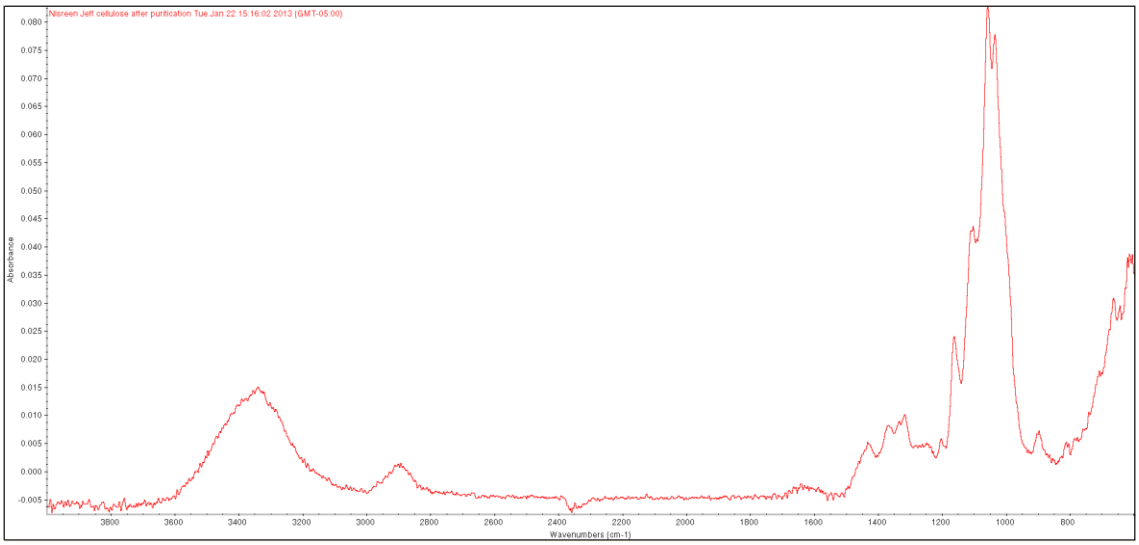


Figure 3.7: IR spectrum of cellulose extracted from jeft

Figure 3.8 shows a comparison between the IR spectrum of cellulose extracted form jeft and microcrystalline cellulose obtained from Aldrich chemical company. As can be seen in **Figure** 3.8, there is a good correlation between the two spectra.

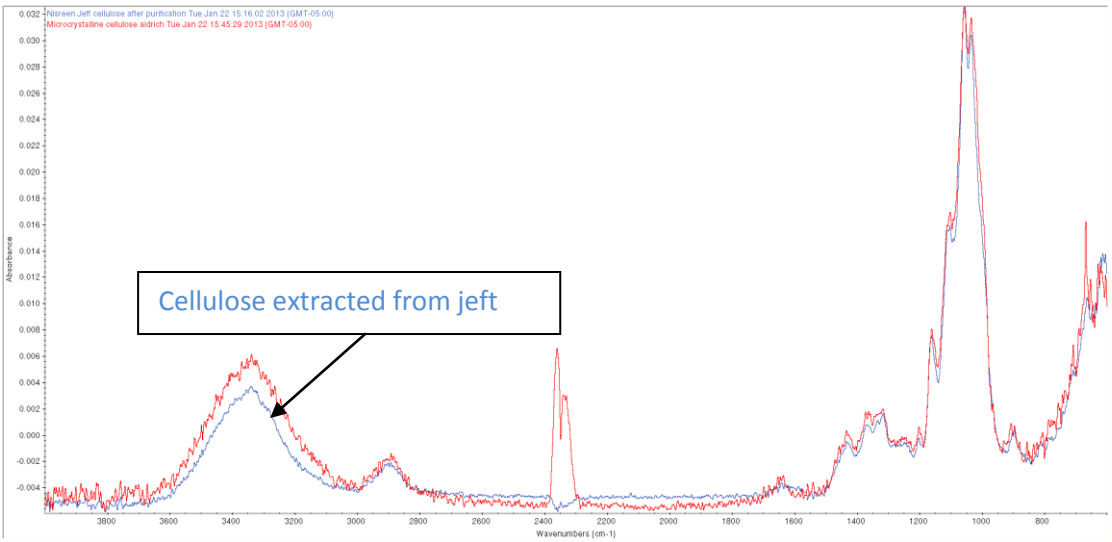


Figure 3.8: IR spectra of cellulose extracted from jeft and microcrystalline cellulose

3.4.2 Differential Scanning Calorimetry (DSC) analysis of extracted cellulose

The DSC of cellulose extracted from jeft (**Figure** 3.9) shows three endothermic peaks corresponding to enthalpies of dehydration and decomposition of cellulose. The first peak that shows at about 100^{o}C, is associated with the evaporation of water. The other two at 150^{o}C and at 224 ^{o}C are associated with the decomposition of cellulose. The lower one could be related to the decomposition of the amorphous area in the cellulose structure while the one at 224 could be attributed to the decomposition of the crystalline area of the cellulose structure. As can be seen form **Figure** 3.9 it takes about 30.55 J to decompose about one gram of cellulose or 5.07kJ/mol.

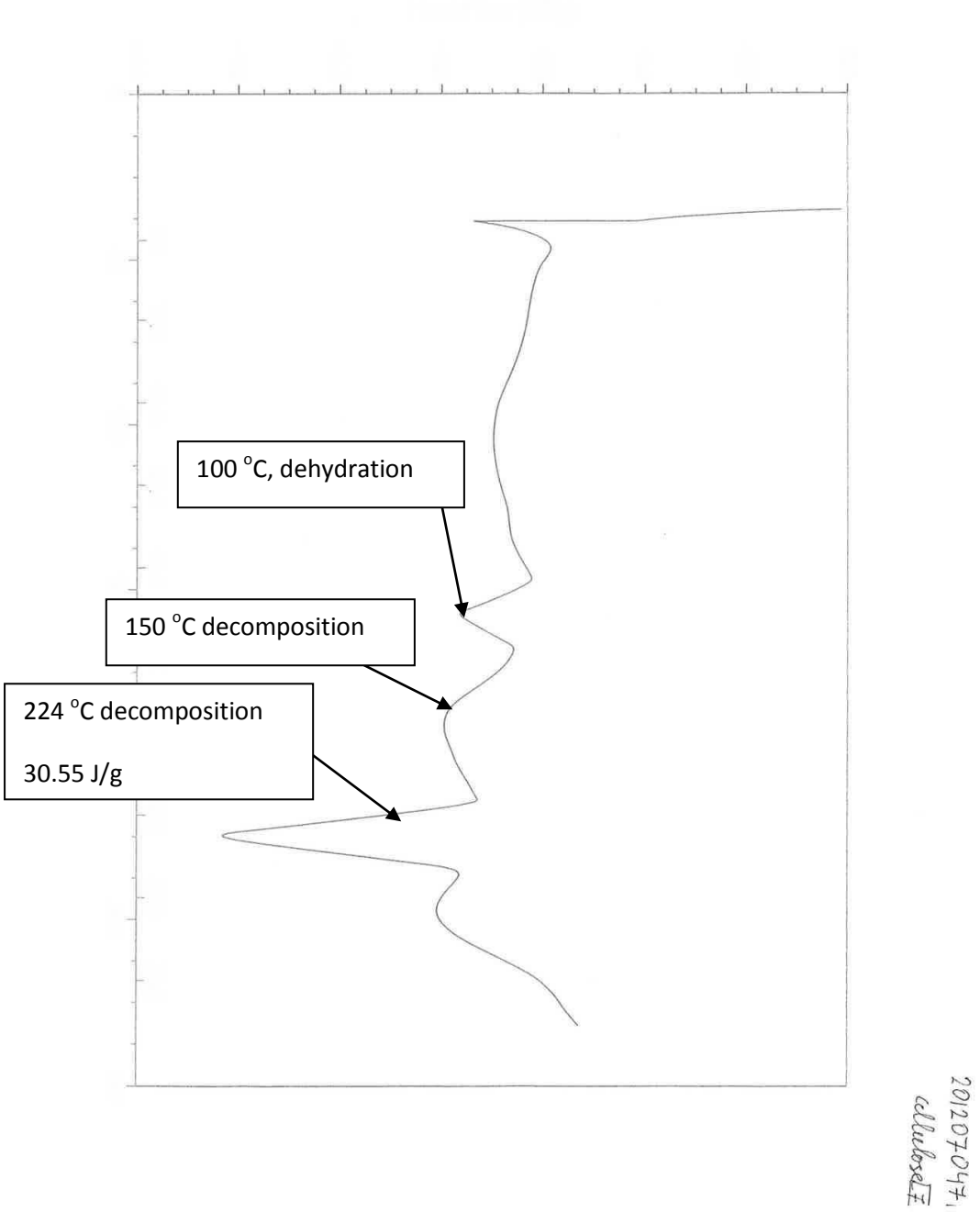


Figure 3.9: DSC of cellulose extracted from jeft

3.5 Preparation of Cellulose acetate form cellulose extracted from jeft

The esterification of primary and secondary hydroxyl groups of cellulose doesn't basically differ from that of other alcohols. The speed and completeness of the reaction is dependent on the quality of cellulose whereas the different reactivities of the primary and secondary hydroxyl groups. Cellulose acetates can be obtained by reaction of cellulose with acetic anhydride and acetic acid in the presence of sulfuric acid as a catalyst [46]. There are two method reported in the literature that could be used to convert cellulose into cellulose acetate homogeneous and heterogeneous. A modified version of these methods was used in this work.

3.5.1 Homogeneous method:

Cellulose is a large polymer consists of cellulose chains associated with each other by strong H-bonding as mentioned in the introduction. For this reason special process has to be used to dissolve it in solution**.** Cellulose is usually dissolved in an organic water-free solvent system consist of one to three component(s). A preactivation (swelling) of cellulose to a more soluble form is often a required step. Solvent systems of this kind include the frequently used two-component systems such as N,N-dimethylacetamide/lithium chloride (DMA/LiCl) and 1,3-dimethyl-2-

imidazolidinone/lithium chloride . Monohydrated N-methylmorpholine-N-oxide (NMMO) could also be used [47], [48].

In some cases one component system is used to dissolve cellulose as shown in **Figure** 3.10. N-methylmorpholine-N-Oxide (NMMO) is an example of the one-component tertiary amineoxide solvents used to dissolve cellulose.

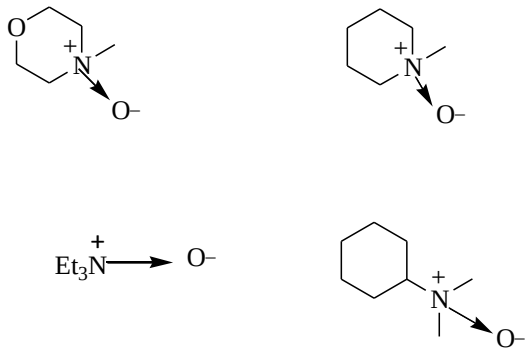


Figure 3.10: Structures of tertiary amineoxide used in dissolution of cellulose**.**

In the current work, the two-component DMAC/LiCl solvent system was used for the dissolution of cellulose and obtaining a homogeneous cellulose solution for preparation of cellulose acetate [46]. The dissolution process was achieved in a two step process:

1. A mixture of DMA containing the 2.5% (w/w) of cellulose was stirred at 130°C for two hours (activation step).

2. After the activation step, the temperature was decreased to about 100°C at which dry LiCl was added in one portion. Then, the

mixture was left to cool to room temperature. After few hours of stirring at room temperature a clear solution was obtained [47, 48].

The mechanism of cellulose dissolution is accompanied by the strong intermolecular interaction between cellulose and a strong N→ O dipole. The interaction may be interpreted as the formation of a hydrogen bond complex with a superimposed ionic interaction as shown in **Figure** 3.10 [59]

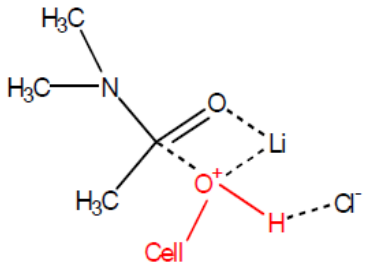


Figure 3.11: Proposed interactions between cellulose and DMA/LiCl solvent system during the dissolution

After the complete dissolution of cellulose, an excess amount of acetic anhydride was added to the solution along with a base such as triethylamine which also acts as a catalyst **Figure** 3.12. Triethylamine functions as a catalyst initiating the reaction by attacking the carbonyl group of acetic anhydride and thus produce a highly reactive intermediate which the hydroxyl group of cellulose can then attack producing the O-acetyl derivative along with ammonium acetate salt. Triethylamine is then released back to the catalytic cycle by de-protonation by acetate anion. A quantitative yield was obtained from the acetylation of cellulose under the homogeneous reaction conditions.

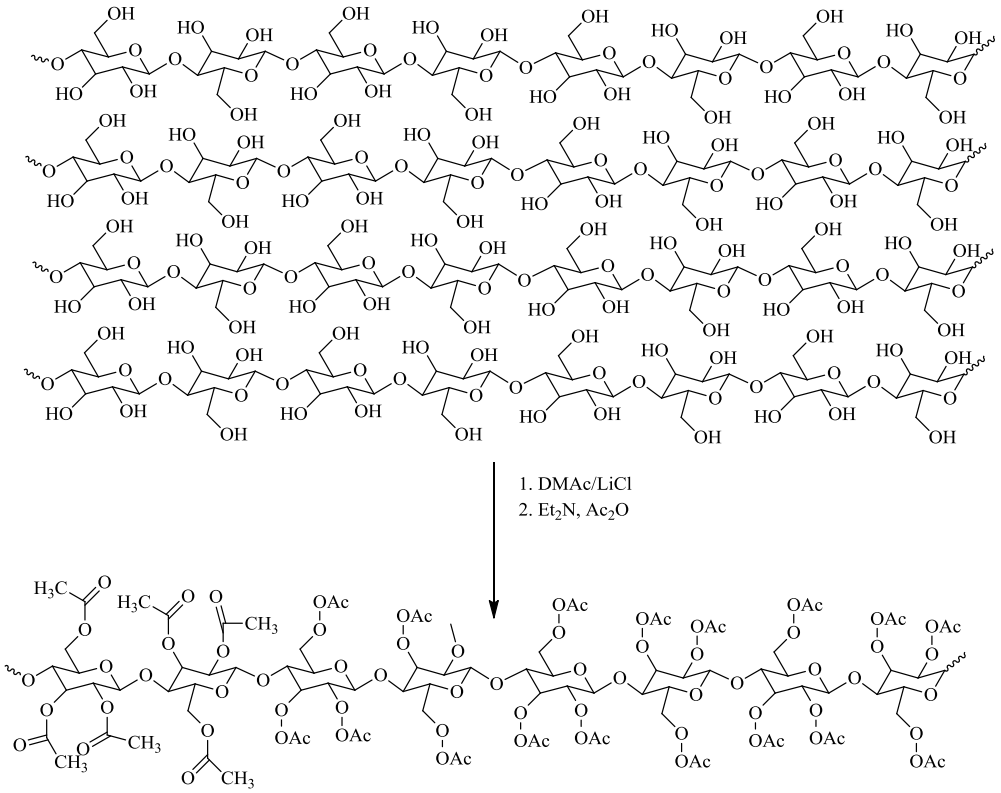


Figure 3.12: Converting cellulose into cellulose acetate

3.5.2 Analysis of cellulose acetate prepared under homogeneous conditions

Cellulose acetate prepared by reacting extracted cellulose from jeft with acetic anhydride in presence of triethyl amine in DMA/LiCl system. The acetate was subjected to analysis by various techniques such as FTIR, size exclusion chromatography (SEC), and scanning electronic microscope (SEM). The results are shown as follows.

3.5.2.1 Analysis of cellulose acetate prepared under homogeneous conditions by FTIR

The FTIR instrument used was the Magna 6400 Spectrometer from Thermal Scientific. A Split Pea ATR accessory was used as the sample interface. The IR spectrum was taken for a neat sample of celluloe acetate, results are shown in **Figure** 3.13 The IR spectrum shows no stretching band at about 3350 cm^{-1} which is for hydroxyl group present in cellulose, this is an indication that the three hydroxyl groups of cellulose are completely acetylated. The bands at 2920 and 2845 cm^{-1} correspond to the CH stretching vibration in CH and CH_2 in anhydroglucose repeat units of cellulose. The 1750 cm^{-1} that would be characteristics of carbonyl group of acetate. The 1430 cm^{-1} band could be attributed to CH_2 asymmetric bending. The band at 1380 cm^{-1} corresponds to the C-O stretching of ether and alcohol groups. The band at 1160 cm^{-1} corresponds to C-O-C stretching of β-glycosidic linkage.

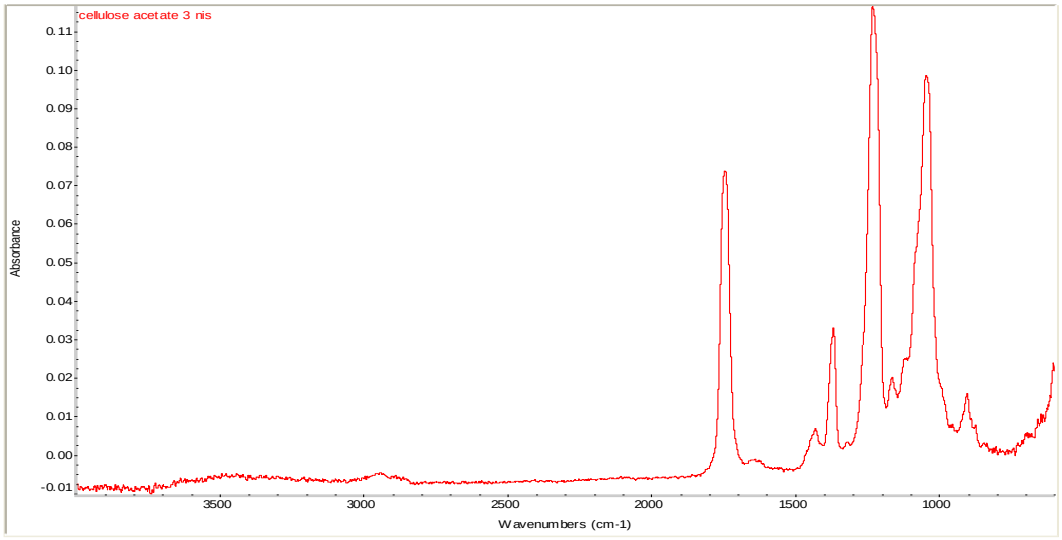


Figure 3.13: IR spectra of cellulose acetate prepared from cellulose extracted from jeft.

Figure 3.14 includes IR spectra of cellulose acetate made from cellulose extracted from jeft and cellulose acetate obtained from Aldrich Chemical Company. The Aldrich sample has acetyl contents of about 42% (about 2.8 degree of substitution). As shown from the **Figure** 3.14 there is an excellent correlation between the two spectra. This could be an indication that the material extracted from OISW is actually high purity cellulose powder cellulose and the cellulose made from it has about 2.8 degree of substitution.

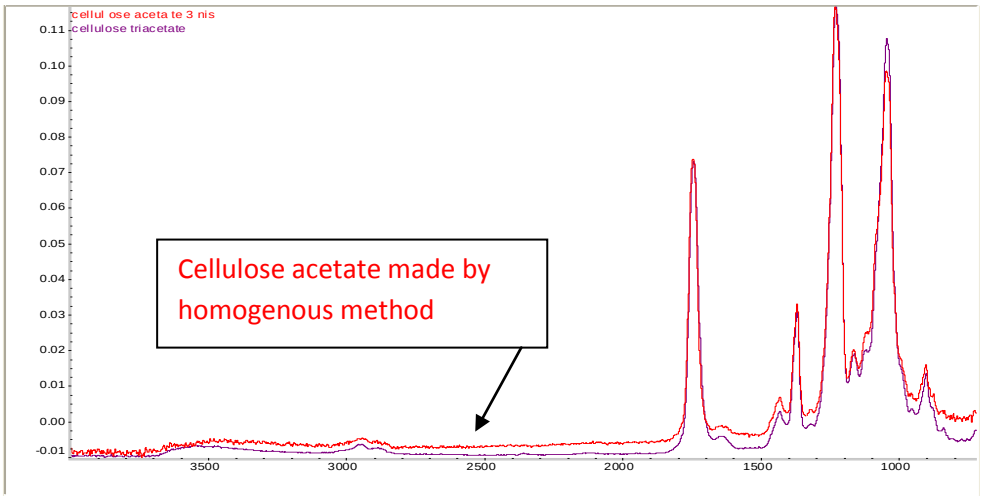


Figure 3.14: IR spectra of cellulose acetate made from cellulose extracted from jeft and cellulose acetate obtained from Aldrich Chemical Company

3.5.2.2 Scanning Electron Microscopy (SEM) and X-ray of cellulose acetate prepared under homogeneous conditions

Cellulose acetate prepared by the homogeneous method was also investigated by scanning electron microscope (SEM) and X-ray. **Figure** 3.15 shows the SEM images of cellulose powder at three different magnifications; a) 100x, b) 300x, and c) 1000x. These images clearly show that cellulose acetate particles are highly porous. **Figure** 3.16, 3.17 and

3.18 shows the x-ray analysis of three different spots in the images of cellulose acetate. The results of the x-ray analysis are shown in **Tables** 3.3 and 3.4 and 3.5 the x-ray results were used in computing the degree of substitution of cellulose acetate.

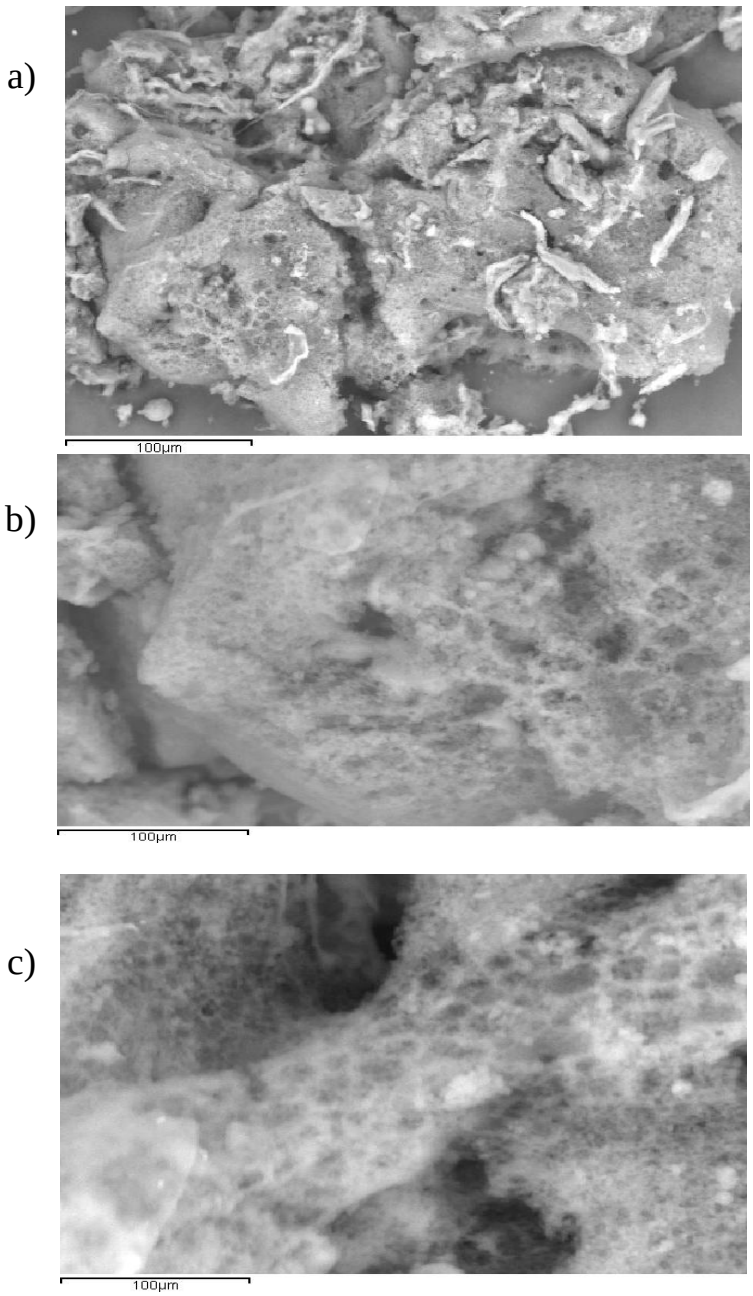


Figure 3.15: SEM images of cellulose acetate at three different magnifications; a) 300x, b) 500x, and c) 1000x

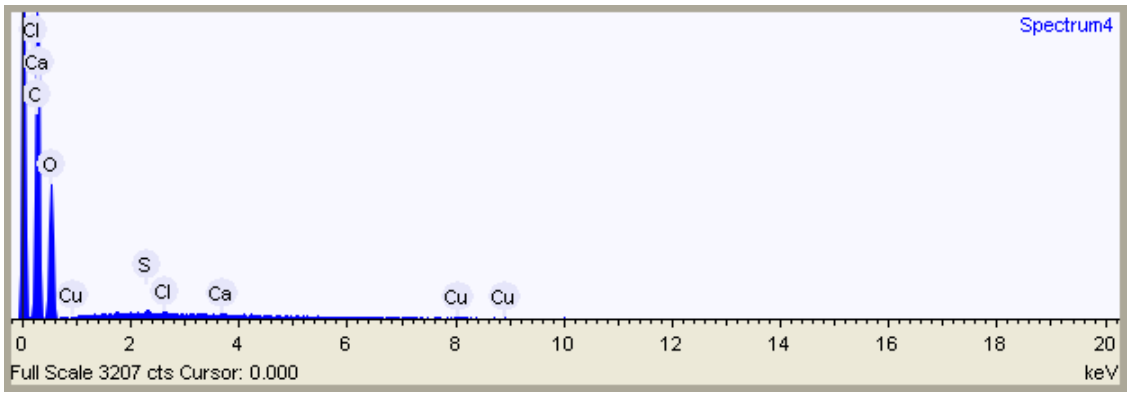


Figure 3.16 : X-ray of cellulose acetate prepared by homogeneous method-Run 1

Table 3.3: Elemetal analysis of cellulose acetate prepared by the homogeneous method-Run 1

Element	Weight %	Weight % σ	Atomic %
Carbon	54.038	0.548	61.153
Oxygen	45.507	0.549	38.662

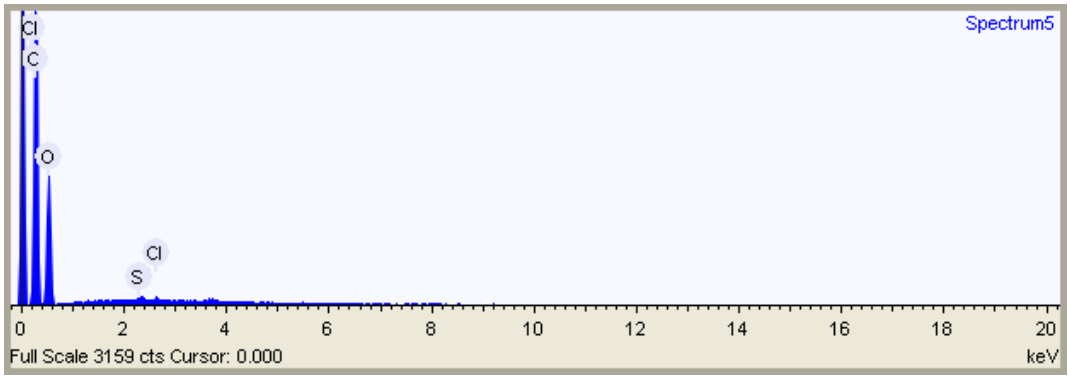


Figure 3.17: X-ray of cellulose acetate prepared by homogeneous method-Run 2

Table 3.4: **Elemetal analysis of cellulose acetate prepared by the homogeneous method-Run 2**

Element	Weight %	Weight % σ	Atomic %
Carbon	53.399	0.570	60.794
Oxygen	45.498	0.571	38.887

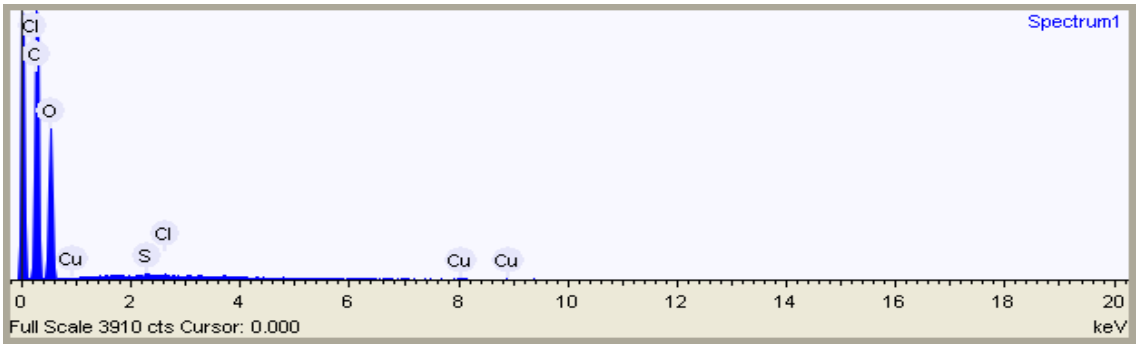


Figure 3.18: X-ray of cellulose acetate prepared by homogeneous method-Run 3

Table 3.5: Elemetal analysis of cellulose triacetate prepared by the homogeneous method-Run 3

Element	Weight %	Weight % σ	Atomic %
Carbon	50.741	0.458	58.078
Oxygen	48.527	0.458	41.698

Theoretically, the weight % of oxygen in cellulose triacetate could be calculated from the following **Equation** 3.4

$$\% \text{ weight of oxygen} = [(16^* X)/ 272]^*100\% \qquad \textbf{Eq } 3.4$$

X = no of oxygen atom in cellulose acetate

272 = molar mass of cellulose triacetate (based on carbon and oxygen atoms, hydrogen is not included)

In **Table** 3.3 x-ray shows the weight % of oxygen is 45.5%, by applying the above equation (**Equation** 3.4) number of oxygen atoms in the prepared cellulose acetate must equal to 8.0, since there are 5 oxygen already present in the anhydroglucose monomer, the results indicate that there are 3 new oxygen atom were added due to the actylation reaction, so the degree of substitution must be 3. These results are consistent with the IR results; **Tables** 3.4 and 3.5 show similar results.

3.5.2.3 Size exclusion chromatography (SEC) of cellulose acetate prepared under the homogeneous conditions

In this technique, the weight average molecular weight (Mw) and number average molecular weight (Mn) are determined. A solution of cellulose triacetate was prepared by dissolving 20.0 mg of cellulose triacetate in Dimethylacetamide (DMA, HPLC grade) containing 0.5% anhydrous lithium bromide, (Reagent Plus, ≥ 99%) were purchased from Sigma Aldrich. The absence of water was checked by solution IR spectroscopy

(Perkin Elmer Series 100) comparing the absorbance of water (at υ = 3500-4000 cm-1) against a fresh bottle of DMA (supposed to contain less than 0.2% of water). The mobile phase was also DMA containing 0.5% LiBr. The analysis was performed on a HPLC system with a UV detector connected to other two detector, 18-angle light scattering detector The DAWN® HELEOS® II for the measurement of absolute molecular weight, size, and conformation of macromolecules in solution and the Refractive Index detector Optilab® T-rEX (refractometer with extended range. Both detectors are made by Wyatt technology. Three columns that are connected on a series were used in the analysis; the columns are 3 x PLgel 10 μm MIXED-B, 300 x 7.5 mm. A 100 μL of the cellulose acetate solution was injected in the HPLC at a flow rate of 1.0 mL/min. Acquired chromatogram and the report that summarizes the results are shown in **Figure** 3.19 a and b.

a)

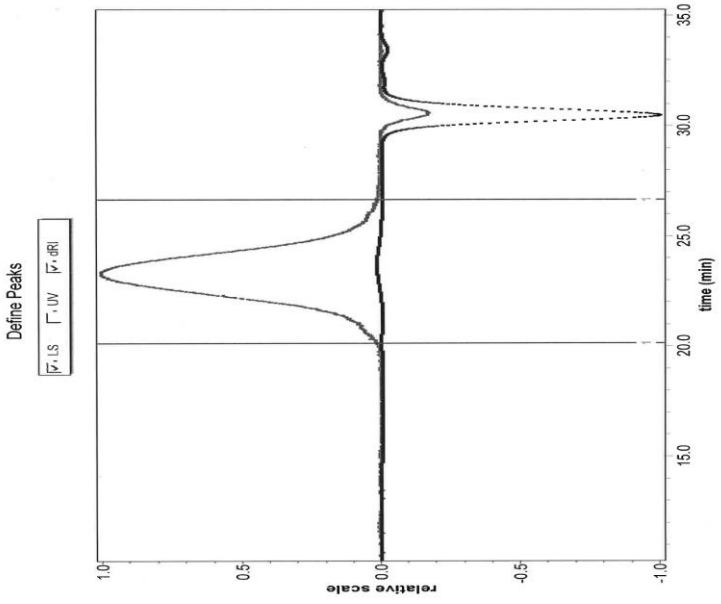


Figure 3.19 (a): SEC of cellulose acetate made from cellulose extracted from jeft

b)

untitled001(001)[CTA 4020-16-B]

ASTRA 5.3.4 Summary Report for untitled001(001)[CTA 4020-16-B]

Experiment name: D:\OAH\untitled001(001)[CTA 4020-16-B]
Sample: (CTA lab made sample in DMAc)
Processing Operator: Administrator
Collection Operator: Administrator
Collection Astra Version: 5.3.4.18

CONFIGURATION

Light scattering instrument: DAWN HELEOS
Cell type: Fused Silica
Laser wavelength: 658.0 nm
Calibration constant: 2.2966e-5 1/(V cm)
RI Instrument: Optilab rEX
UV Instrument: Generic UV instrument
Solvent: DMAc/LiBr
Refractive index: 1.430
Flow rate: 0.700 mL/min

PROCESSING

Processing time: Friday October 19, 2012 10:33 AM Eastern Daylight Time
Collection time: Thursday September 27, 2012 04:32 PM Eastern Daylight Time
Detectors used: 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Concentration detector: RI
Mass results fitting: none (fit degree: n/a)
Radius results fitting: none (fit degree: n/a)

	Peak 1
Peak limits (min)	21.495 - 24.999
dn/dc (mL/g)	0.087
A_2 (mol mL/g²)	0.000
UV ext. (mL/(g cm))	0.000
Model	Zimm
Fit degree	1
Injected mass (g)	1.0000e-5
Calc. mass (g)	3.4014e-5
Mass Recovery	340.1399 %
Mass Fraction	100.0000 %

RESULTS

	Peak 1
Polydispersity	
Mw/Mn	1.171(0.7%)
Mz/Mn	1.814(1%)
Molar mass moments (g/mol)	
Mn	5.052e+4(0.5%)
Mp	4.673e+4(0.4%)
Mv	n/a
Mw	5.914e+4(0.5%)

Figure 3.19 (b): SEC of cellulose acetate made from cellulose extracted from jeft

The Mw and Mn were determined to be 50,520 Dalton and 46730 Dalton, respectively. The polydespersity (Mw/Mn) is about 1.171, the number indicates that the polymer is monodisperse.

3.5.2.4 Differential Scanning Calorimetry (DSC) analysis of prepared cellulose acetate prepared under the homogeneous conditions

The DSC of cellulose acetate prepared from cellulose extracted from jeft is shown in **Figure** 3.20. Cellulose acetate shows two endothermic peaks corresponding to enthalpies of deacetylation and decomposition of cellulose. The first peak shows at about 153^{o}C, is associated with the decomposition of the acetate group of cellulose acetate, the energy cosumed for deacetylation is about 8.2 J/g (2.23 kJ/anyhydroglucose repeat unit). The other peak which shows at about 223^{o}C could be related to the decomposition of the cellulose structure. As can be seen form **Figure** 3.20 it takes about 29.6 J to decompose about one gram of cellulose or 8.51 kJ/anhydroglucose repeat unit.

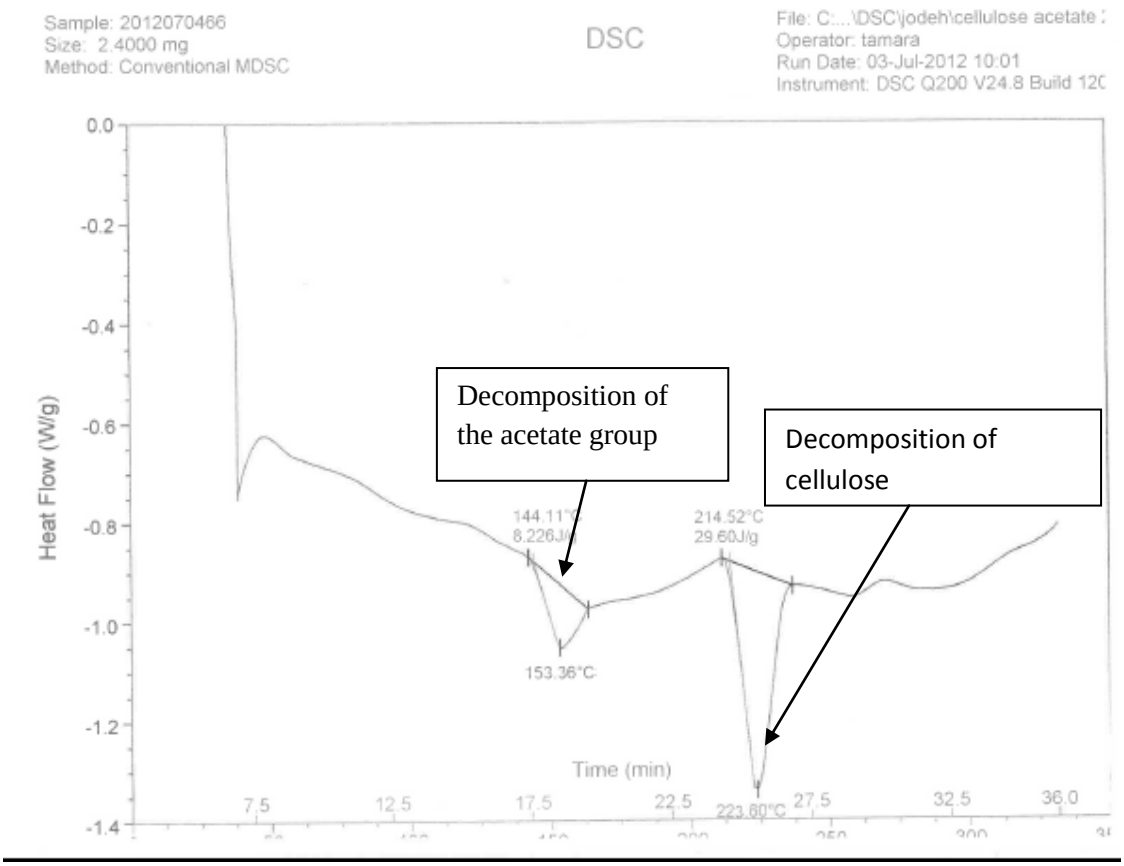


Figure 3.20: DSC of cellulose acetate made under homogeneous conditions

3.5.3 Heterogeneous method of preparation of cellulose acetate:

In the heterogeneous process, cellulose is suspended in acetic acid, then a catalytic amount of sulfuric acid is added followed by addition of excess acetic anhydride. The reaction usually carried at room temperature or at a temperature not higher than 50^{o}C to minimize the degradation of cellulose by sulfuric acid. After stirring the mixture for few hours, a clear solution produced, after which the reaction is quenched with water. After the addition of water, cellulose acetate participates out of solution, filtered and washed with excess water.

The mechanism of cellulose acetylation under heterogeneous conditions involves the following steps:

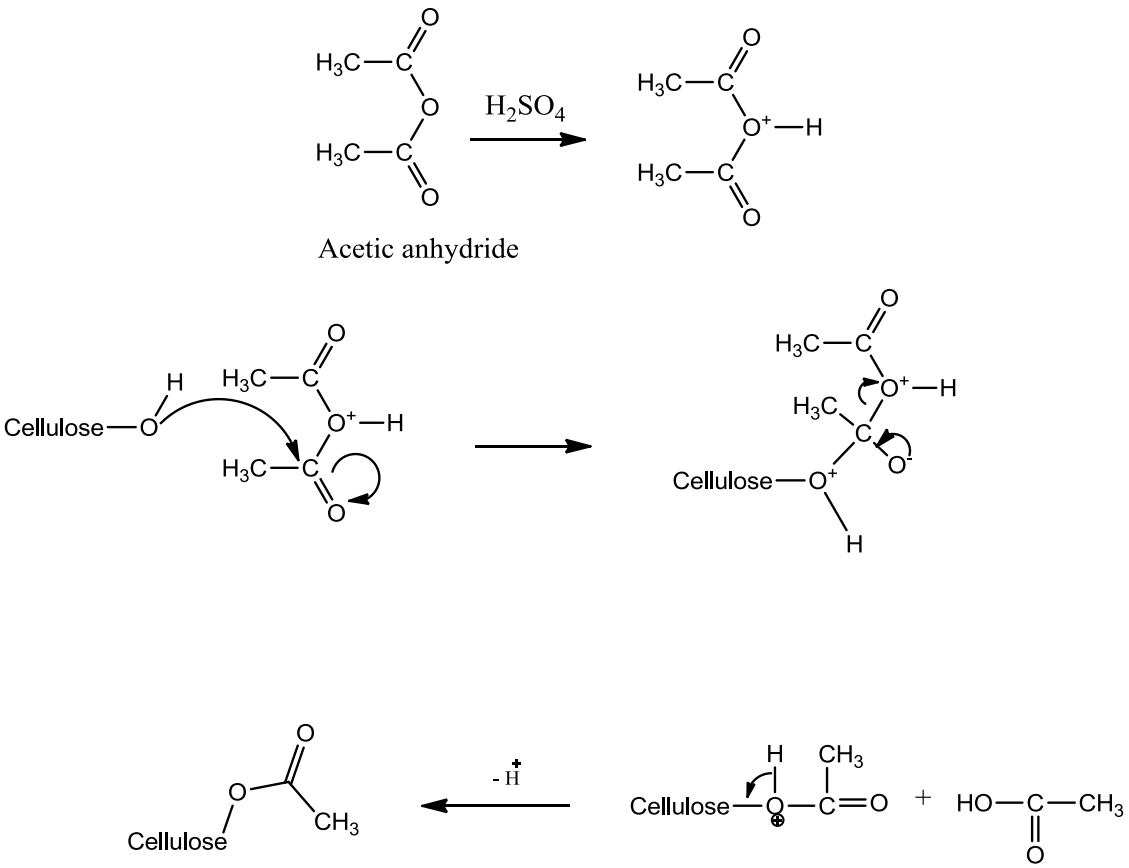


Figure 3.21: Reaction mechanism for acetylation of cellulose under heterogeneous conditions:

A quantitative yield was obtained from the acetylation of cellulose under the heterogeneous reaction conditions.

3.5.4 Analysis of cellulose acetate prepared under heterogeneous conditions

Cellulose acetate prepared by reacting extracted cellulose from jeft with acetic anhydride under heterogeneous condition, was subjected as before to analysis by various techniques such as FTIR, size exclusion

chromatography (SEC), scanning electronic microscope (SEM), and thermal gravimetric analysis (TGA), results are shown below

3.5.4.1 Analysis of cellulose acetate prepared under heterogeneous conditions by FTIR

The IR spectrum was taken for a neat sample of cellulose acetate. The results are shown in **Figure** 3.22 The IR spectrum shows weak stretching band at about 3350 cm^{-1} which is for hydroxyl group present in cellulose, this is an indication that the three hydroxyl groups of cellulose are not completely acetylated, partial acetylation under the heterogeneous conditions occurs. The bands at 2920 and 2845 cm^{-1} correspond to the CH stretching vibration in CH and CH_2 in anhydroglucose repeat units of cellulose. The 1750 cm^{-1} band could be characteristic of carbonyl of acetate group. The 1430 cm^{-1} band could be attributed to CH_2 asymmetric bending. The band at 1380 cm^{-1} corresponds to the C-O stretching of ether and alcohol groups. The band at 1160 cm^{-1} corresponds to C-O-C stretching of β-glycosidic linkage. **Figure** 3.22 shows a comparsion between the IR spectrum of cellulose acetate made under the heterogeneous conditions from cellulose extracted from jeft and cellulose acetate obtained from Aldrich Chemical Company. The Aldrich sample has acetyl contents of about 42% (about 2.8 degree of substitution). As shown from the Fig 3.22, the lab made sample has lower degree of substitution, due to the presence of OH stretching at about 3400 cm^{-1}. This could be an indication that the acetylation was incomplete under the heterogeneous conditions.

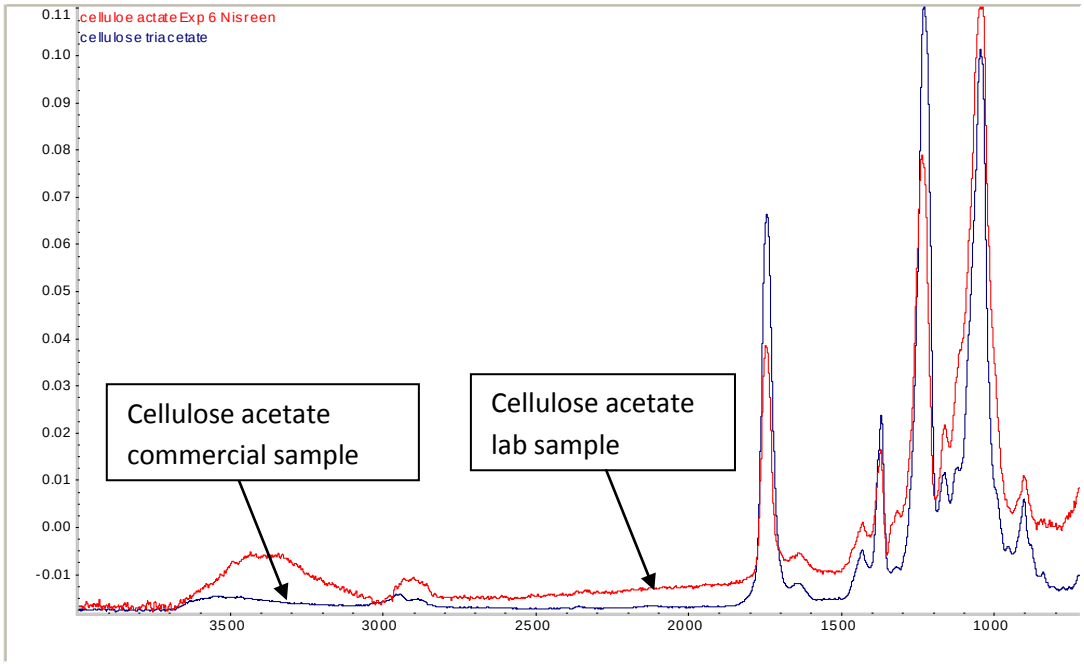


Figure 3.22: IR spectra of cellulose acetate prepared under heterogeneous conditions

3.5.4.2 Scanning Electron Microscopy (SEM) and X-ray of cellulose acetate prepared under heterogeneous conditions

Cellulose acetate prepared by the heterogeneous method was also was investigated by scanning electron microscope (SEM) and X-ray. No difference between the morphology of cellulose acetate prepared under both conditions was observed as shown in by SEM. X-ray analyses of two different spots in the images of cellulose acetate prepared by the heterogeneous method are shown in **Figures** 3.23 and 3.24. The results of the x-ray analysis are shown in **Tables** 3.6 and 3.7.

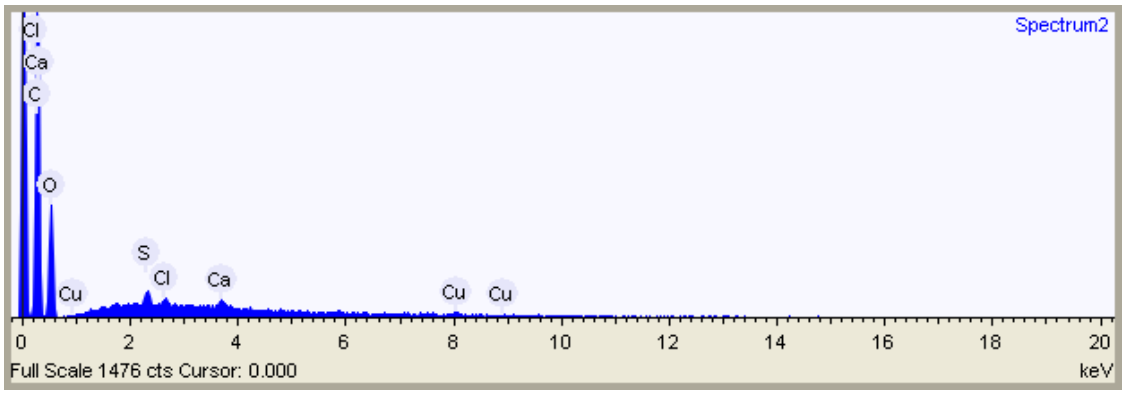


Figure 3.23: X-ray of cellulose acetate prepared under heterogeneous conditions-Run 1

Quantification Settings

Quantification method	All elements (normalized)
Coating element	None

Table 3.6: Elemental analysis of cellulose triacetate prepared by the heterogeneous method-Run 1

Element	Weight %	Weight % σ	Atomic %
Carbon	57.299	0.846	65.093
Oxygen	39.832	0.841	33.971

b)

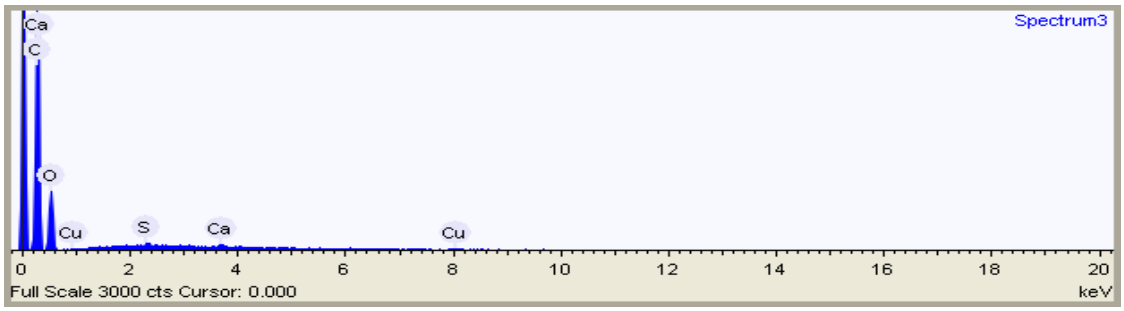


Figure 3.24: X-ray of cellulose acetate prepared under heterogeneous conditions-Run 2

Table 3.7: Elemental analysis of cellulose triacetate prepared by the heterogeneous method-Run 2

Element	Weight %	Weight % σ	Atomic %
Carbon	61.081	0.691	68.229
Oxygen	37.345	0.689	31.317

As before the equation was used to compute the degree of substitution of cellulose acetate made under the heterogeneous conditions:

% weight of oxygen = [(16* X)/ 272]*100% **Eq** 3.5

In **Table** 3.6 x-ray shows the weight % of oxygen is 39.8%, by applying the above equation (**Equation** 3.5.) number of oxygen atoms in the prepared cellulose acetate equal to 6.77, since there are 5 oxygen already present in the anhydroglucose monomer, the results indicate that there are 1.77 new oxygen atom were added due to the acetylation reaction, so the degree of substitution must be 1.77. The degree of substitution from **Table** 3.7 was calculated in the same manner to be 1.32.

3.5.4.3 Size exclusion chromatography (SEC) of cellulose acetate prepared under heterogeneous conditions

The SEC was performed as above produced a chromatogram and the report that summarizes the results are shown in **Figure** 3.25 a, b and c

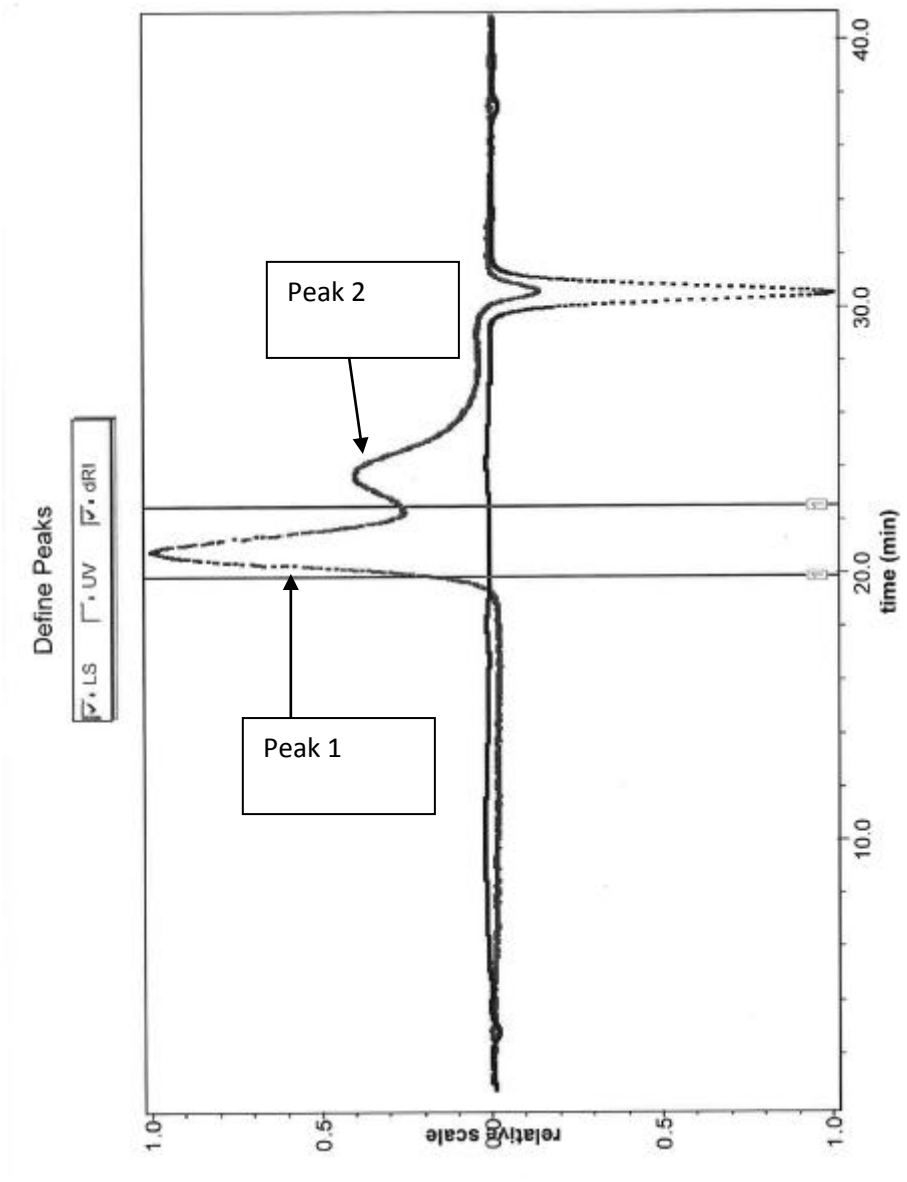


Figure 3.25 (a): SEC of cellulose acetate made from cellulose extracted from jeft under heterogeneous conditions

a) Report for the analysis of peak one

ASTRA 5.3.4 Summary Report for CA_NisR3[CA3_Nis R3]

Experiment name: D:\OAH\CA_NisR3[CA3_Nis R3]
Sample: CA_NisR3 []
Processing Operator: Administrator
Collection Operator: Administrator
Collection Astra Version: 5.3.4.18

CONFIGURATION

Light scattering instrument: DAWN HELEOS
Cell type: Fused Silica
Laser wavelength: 658.0 nm
Calibration constant: 2.2966e-5 1/(V cm)
RI Instrument: Optilab rEX
UV Instrument: Generic UV instrument
Solvent: DMAc/LiBr
Refractive index: 1.430
Flow rate: 0.700 mL/min

PROCESSING

Processing time: Friday October 19, 2012 10:24 AM Eastern Daylight Time
Collection time: Monday September 24, 2012 07:11 PM Eastern Daylight Time
Detectors used: 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Concentration detector: RI
Mass results fitting: none (fit degree: n/a)
Radius results fitting: none (fit degree: n/a)

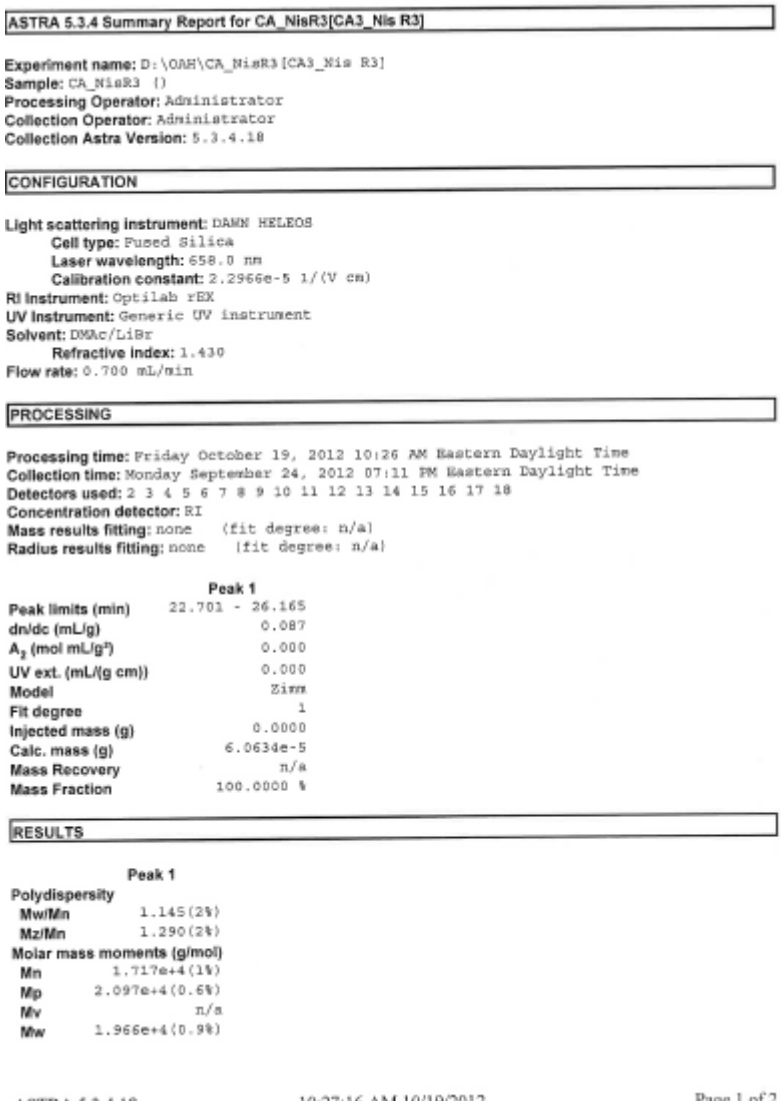
	Peak 1
Peak limits (min)	19.899 - 22.545
dn/dc (mL/g)	0.087
A_2 (mol mL/g^2)	0.000
UV ext. (mL/(g cm))	0.000
Model	Zimm
Fit degree	1
Injected mass (g)	0.0000
Calc. mass (g)	2.8610e-5
Mass Recovery	n/a
Mass Fraction	100.0000 %

RESULTS

	Peak 1
Polydispersity	
Mw/Mn	1.258(2%)
Mz/Mn	1.497(2%)
Molar mass moments (g/mol)	
Mn	6.249e+4(1%)
Mp	2.454e+4(2%)
Mv	n/a
Mw	7.858e+4(0.9%)

Figure 3.25 (b): SEC of cellulose acetate made from cellulose extracted from jeft under heterogeneous conditions

b) Report for the analysis of peak two



ASTRA 5.3.4 Summary Report for CA_NisR3[CA3_Nis R3]

Experiment name: D:\OAH\CA_NisR3[CA3_Nis R3]
Sample: CA_NisR3 ()
Processing Operator: Administrator
Collection Operator: Administrator
Collection Astra Version: 5.3.4.18

CONFIGURATION

Light scattering instrument: DAWN HELEOS
Cell type: Fused Silica
Laser wavelength: 658.0 nm
Calibration constant: 2.2966e-5 1/(V cm)
RI instrument: Optilab rEX
UV instrument: Generic UV instrument
Solvent: DMAc/LiBr
Refractive index: 1.430
Flow rate: 0.700 mL/min

PROCESSING

Processing time: Friday October 19, 2012 10:26 AM Eastern Daylight Time
Collection time: Monday September 24, 2012 07:11 PM Eastern Daylight Time
Detectors used: 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Concentration detector: RI
Mass results fitting: none (fit degree: n/a)
Radius results fitting: none (fit degree: n/a)

	Peak 1
Peak limits (min)	22.701 - 26.165
dn/dc (mL/g)	0.087
A_2 (mol mL/g^2)	0.000
UV ext. (mL/(g cm))	0.000
Model	Zimm
Fit degree	1
Injected mass (g)	0.0000
Calc. mass (g)	6.0634e-5
Mass Recovery	n/a
Mass Fraction	100.0000 %

RESULTS

	Peak 1
Polydispersity	
Mw/Mn	1.145(2%)
Mz/Mn	1.290(2%)
Molar mass moments (g/mol)	
Mn	1.717e+4(1%)
Mp	2.097e+4(0.6%)
Mv	n/a
Mw	1.966e+4(0.9%)

Figure 3.25 (c): SEC of cellulose acetate made from cellulose extracted from jeft under heterogeneous conditions

Two polymer fractions with different sizes were identified using SEC, the one with higher size eluted first (peak one), and the one with smaller size eluted last. The Mn and Mw for peak one was determined to be 52,490 Dalton and 78,580 Dalton, respectively. The polydespersity (Mw/Mn) is about 1.497, the number indicates that this fraction of the cellulose acetate

polymer is monodisperse. The two factions together make the cellulose acetate polymer prepared under the heterogeneous conditions polydisperse

3.5.4.4 Differential Scanning Calorimetry (DSC) analysis cellulose acetate prepared under heterogeneous conditions

The DSC of cellulose acetate prepared using the heterogeneous conditions are shown in **Figure** 3.26. The figure shows three endothermic peaks corresponding to enthalpies of deacetylation, decomposition of cellulose amorphous, and decomposition of cellulose acetate crystalline. The first peak that appears at about 174 ^{o}C, is associated with the associated with the deacetylation of cellulose acetate, the enthalpy of acetylation is about 2.56 J/g. The other two at 244^{o}C and at 297^{o}C could be related to the decomposition of cellulose chains. The one at lower temperature 244^{o}C could be related to the decomposition of the amorphous area in the cellulose structure while the one at 297^{o}C could be attributed to the decomposition of the crystalline area of the cellulose structure.

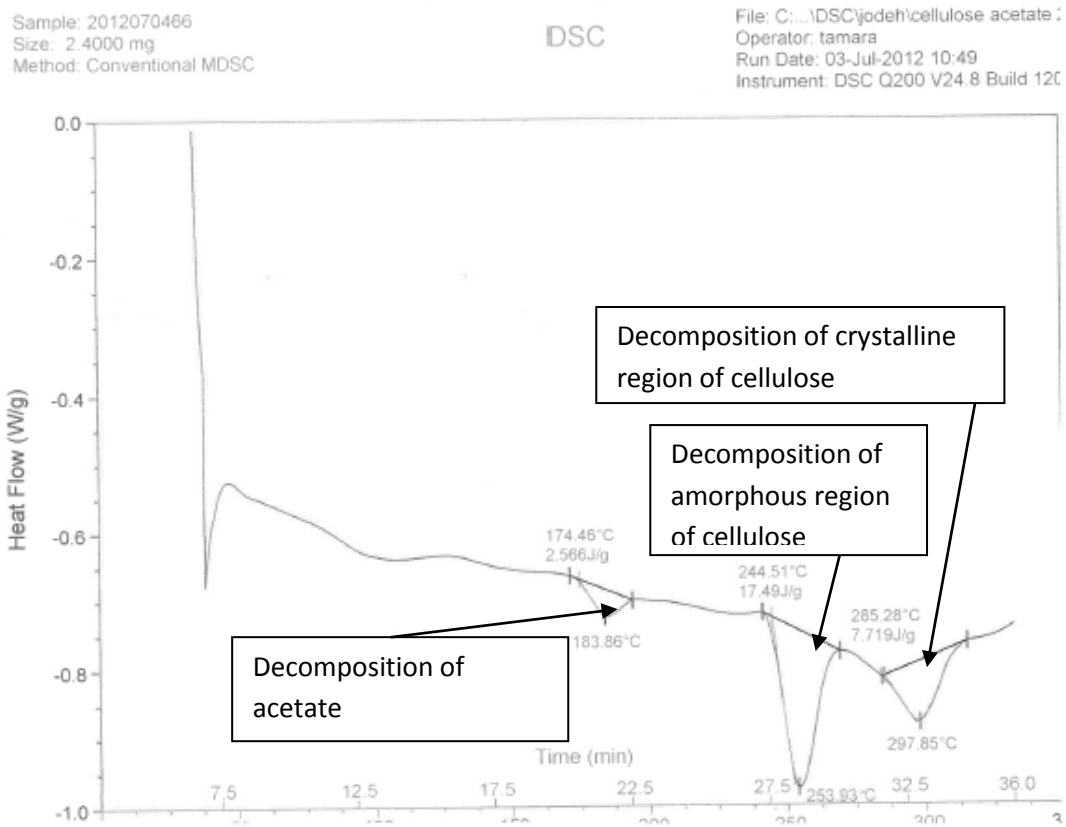


Figure 3.26: DSC of cellulose acetate made under heterogeneous conditions

Conclusion

1. Jeft is a valuable source for cellulose.

2. Cellulose extracted from jeft is suitable precursor of commercial products such as cellulose triacetate.

3. The pulping and bleaching lab scale process developed by the previous graduate student was scaled up to about 0.5 Kg [33].

4. Jeft extractives have been identified to be olive oil components

5. Acetylation of cellulose using homogeneous method produces cellulose acetate that is completely acetylated (Ds = 3.0) and monodisperse polymer.

6. Actylation of cellulose using heterogeneous method produces cellulose acetate that is partially acetylated (Ds = 1.3-1.7) and polydisperse polymer.

Future Work

1. Scale up the developed pulping from lab process into multi kilos process**.**

2. Develop method for converting extracted cellulose into other commercially valuable cellulose ester such as cellulose propionate.

3. Develop method for converting extracted cellulose into commercial valuable cellulose ethers such carboxymethyl cellulose and methylcellulose.

4. Develop a process for converting side products hemicelluloses into value added products such as fine chemical (example furfural).

5. Develop a process for converting side products lignin into value added products such as adhesives and fine chemical such free radical scavengers' phenolic compounds.

References

1. Wise, L. E.; Murphy, M.; D'addieco, A. A.; Trade, J. 122(2), 35-43, **1946**.

2. Sun, R.S.; Tomkinson, J. Characterization of Hemicelluloses Obtained by Classical and Ultrasonically Assisted Extractions from Wheat Straw. Carbohydrate Polymer, 50, 263-271, **2002**.

3. Mitikka, M.; Teeaar, R.; Tenkanene, M.; Laine, J.; Vuorinene, T. Sorption of Xylans on Cellulose Fibers, in 8th International Symposium on Wood and Pulping Chemistry, 231-236, **1995**.

4. Sun, J.X.; Sun, X.F.; Sun, R.C.; Su, Y.Q. Fractional Extraction and Structural Characterization of Sugarcane Bagasse Hemicelluloses. Carbohydrate Polymers, 56, 195–204, **2004**.

5. Suna, R.C.; Tomkinson, J.; Ma, P.L.; Liang, S.F. Comparative Study of Hemicelluloses From Rice Straw By Alkali And Hydrogen Peroxide Treatments. Carbohydrate Polymers, 42, 111, **2000**.

6. Junli, R.; Xinwen, P.; Linxin, Z.; Feng, P.; Runcang, S. Novel Hydrophobic Hemicelluloses: Synthesis and Characteristic. Carbohydrate Polymers, 89, 152– 157, **2012**.

7. Sissons, M. Role of Durum Wheat Composition on the Quality of Pasta And Bread. Global Science Books **2008**.

8. Ramsden, M.J.; Blake, F. S. R. A Kinetic Study of the Acetylation of Cellulose, Hemicellulose and Lignin Components in Wood. Wood Science and Technology, 3145-50, **1997**.

9. Modugno, F.; Ribechini, E.; Calderisi, M.; Giachi, G.; Colombini, M.P. Analysis of Lignin from Archaeological Waterlogged Wood by Direct Exposure Mass Spectrometry (DE-MS) and PCA Evaluation of Mass Spectral Data. Microchemical Journal, 88, 186–193, **2008**.

10. Wang, M.; Leitch, M.; Xu, C. Synthesis of Phenol–Formaldehyde Resol Resins Using Organosolv Pine Lignins. European Polymer Journal, 45, 3380–3388, **2009**.

11. Guerra, A.; Gaspar,A. R.; Contreras, S.; Lucia, L. A.; Crestini, C.; Argyropoulos, D.S. On The Propensity of Lignin to Associate: A Size Exclusion Chromatography Study with Lignin Derivatives Isolated From Different Plant Species. Phytochemistry, 68, 2570–2583, **2007**.

12. Chang, H.; Su, Y.; Chang, S. Studies on Photostability of Butyrylated, Milled Wood Lignin Using Spectroscopic Analyses. Polymer Degradation and Stability, 91, 816-822, **2006**.

13. Fernandez, M.P.; Watson, P.A.; Breuil, C. Gas Chromatography–Mass Spectrometry Method For The Simultaneous Determination of Wood Extractive Compounds in Quaking Aspen . Journal of Chromatography A, 922, 225–233, **2001**.

14. Shebani, A.N.; Van Reenen, A.J.; Meincken, M. The Effect of Wood Extractives On The Thermal Stability of Different Wood Species. Thermochimica Acta 471, 43–50, **2008**.

15. Rowe, J. W.; Conner, A. H. Extractives In Eastern Hardwoods A Review ; General Technical Report FPL 18, Forest Products Laboratory, Madison, WI, **1979**.

16. Yokoi , H.; Nakase, T.; Goto, K. Ishida, Y.; Ohtani, H.; Tsuge , S.; Sonoda, T. ; Ona, T. Rapid Characterization of Wood Extractives In Wood By Thermal Desorption-Gas Chromatography In The Presence of Tetramethylammonium Acetate . Journal of Analytical and Applied Pyrolysis, 67, 191–200, **2003**.

17. Lavoine, N.; Desloges, I.; Dufresne, A.; Bras, J. Microfibrillated Cellulose-Its Barrier Properties And Applications in cellulosic materials: A review, Carbohydrate Polymers, 90,735-64, **2010**.

18. Pe´rez, J.; Munoz-Dorado, J.de la Rubia, T.; Martı´nez, J. Biodegradation and Biological Treatments of Cellulose, Hemicellulose and Lignin: An Overview. Int Microbiol, 5, 53–63, **2002**.

19. Vail S.L; Crosslinkining of Cellulose, Chemistry and Its Applications (Nenell; J.P, Venell; S.H, edu.), Ellis Horwood, Chichester, **1985**.

20. Sjostrom, Eero "Wood Chemistry. Fundamentals and Applications"; Academic Press: New York, p: 56 –65, **1981**.

21. Klemm, D.; Heublein, B.; Fink, H.; Bohn, A. Cellulose: Fascinating Biopolymer and Sustainable Raw Material, Angew. Chem. Int. Ed, 44, 3358 – 3393, **2005**.

22. Zhang, S.; Li, F.; Yu, J.; Hsieh, Y. Dissolution Behaviour And Solubility of Cellulose In NaOH Complex Solution. Carbohydrate Polymers, 81,668–674, **2010**.

23. Xu, W.; Reddy, N.; Yang, Y. Extraction, Characterization and Potential Applications of Cellulose in Corn Kernels And Distillers' Dried Grains With Solubles (DDGS). Carbohydrate Polymers, 76, 521–527, **2009**.

24. Gardner, D. J.; Oporto, G. S.; Mills, R.; Samir, A. S. A. Adhesion and Surface Issues in Cellulose and Nanocellulose. Journal of Adhesion Science and Technology, 22, 545–56, **2008**.

25. Chandra, Y. Alkaline Pulping: Deadwood Reduction Studies in Chemical Recovery System. School of Chemical & Bimolecular Engineering Georgia Institute of Technology, **2004**.

26. Abdul Khalil, H.P.S.; Bhat, A.H.; Ireana Yusra, A.F. Green Composites from Sustainable Cellulose Nanofibrils: A Review, Carbohydrate Polymers, 87, 963– 979, **2012**.

27. U.S. Environmental Protection Agency. General Information Document for the Pulp and Paper Industry. Draft. Washington, D.C.: Office of Air Quality Planning and Standards, July **1991**.

28. Hakka, L. E.; Brown, D. J. Recovery and Recycling of SO_2 in A Sulfite Pulp Mill. “Sulphur 98”, 1-4, **1998**.

29. Loureiro, P.E.G.; Dominguesc, M. R. M.; Fernandesd, A. J.S.; Grac¸ M.; Carvalho, V.S.; Evtuguina, D. V. Discriminating The Brightness Stability of Cellulosic Pulp In Relation To The Final Bleaching Stage. Carbohydrate Polymers, 88, 726– 733, **2012**.

30. Gellerstedt, G.; Gustafsson, K.; Lindfors, E.L. Structural Changes In Lignin During Oxygen Bleaching Nordic Pulp and Paper Journal, 3, 14-17, **1986**.

31. Ragauskas, A. J. Basics of Bleaching Chemical Pulps. Institute of Paper Science and Technology Georgia Institute of Technology.

32. Shatalov, A. A.; Pereira, H. Polysaccharide Degradation During Ozone-Based TCF Bleaching of Non-Wood Organosolv Pulps. Carbohydrate Polymers, 67, 275–28, **2007**.

33. Salameh, Y. F. A. Methods of Extracting Cellulotic Material From Olive Pulp. An-Najah National University, Palestine, **2009**.

34. Duran, N.; Llemes, A. P.; Duran, M.; Freer’ J.; Baeza ,J. A Mini Review of Cellulose Nanocrystals and Its Potential Integration as Co-Product in Bioethanol Production. J. Chil. Chem. Soc. 56, 672-677, **2011**.

35. Chang, C.; Zhang, L. Cellulose-Based Hydrogels: Present Status And Application Prospects. Carbohydrate Polymers, 84, 40–53, **2011**.

36. Bono, A.; Ying, P.H; Yan, F.Y.; Muei, C.L.; Sarbatly, R.; Krishnaiah, D. Synthesis and Characterization of Carboxymethyl Cellulose from Palm Kernel Cake. Advances in Natural and Applied Sciences, 3, 5-11, **2009**.

37. Casaranoa, R. ; Fidalea, L. C.; Luchetia, C. M.; Heinzeb, T. ; El Seoud, O. A. Expedient, Accurate Methods For The Determination of The Degree of Substitution of Cellulose Carboxylic Esters: Application of UV–vis Spectroscopy (Dye Solvatochromism) And FTIR . Carbohydrate Polymers, 83, 1285–1292, **2011**.

38. Mishra, S.; Usha Rani, G.; Sen, G. Microwave Initiated Synthesis And Application of Polyacrylic Acid Grafted Carboxymethyl Cellulose. Carbohydrate Polymers, 87, 2255– 2262, **2012**.

39. Li, W.; Sun, B.; Wu, P. Study on Hydrogen Bonds of Carboxymethyl Cellulose Sodium Film With Two-Dimensional Correlation Infrared Spectroscopy. Carbohydrate Polymers, 78, 45–46, **2009**.

40. Chenga, H.N.; Dowda, M. K.; Shogrenb, R.L.; Biswasb, A. Conversion of Cotton Byproducts to Mixed Cellulose Esters. Carbohydrate Polymers, 86, 1130– 1136, **2011**.

41. Selwitz, C. Cellulose Nitrate in Conservation , United States of America , J. Paul Getty Trust, 67, **1988**.

42. Elidrissi, A.; El barkany, S.; Amhamdi, H.; Maaroufi, A.; Hammouti , B. New Approach to Predict the Solubility of Polymers Application:

Cellulose Acetate at various DS, prepared from Alfa "Stipa -tenassicima" of Eastern Morocco, J. Mater. Environ. Sci. 3,270-285, **2012**.

43. Fischer, S.; Thu¨mmler, K.; Volkert, B.; Hettrich, K.; Schmidt, I.; Fischer1, K. Properties And Applications of Cellulose Acetate, Macromol. Symp, 262, 89–96, **2008**.

44. Swatloski, R., Holbrey, J., Spear, S., Rogers, R. Electrochem. Soc. Proc. 19, 155, **2002**.

45. McCormick, C. US Patent 4278790, **1981.**

46. Takaragi, A., Minoda, M., Miyamoto, T. Cellulose, 6, 93, **1999**.

47. Johnson, D. US Patent 3447956 (Eastman Kodak Co.), **1969.**

48. Beltran, G.; Rio, C.; Nchez, S.; Martianez, L. "Influence of Harvest Date and Crop Yield on the Fatty Acid Composition of Virgin Olive Oils from Cv. Picual J. Agric. Food Chem, 52, 3434-3440, **2004**.

49. Dr David J. Saul (School of Biological Sciences, University of Auckland, Private Bag 90219, Auckland, New Zealand), Dr Moreland D. Gibbs and Professor Peter L. Bergquist (both of the School of Biological Sciences, University of Macquarie, Sydney, New South Wales 2109, Australia. Enzymatic Bleaching of Wood Pulp.

50. Adler, E.; Lignin - Past, Present and Future. Wood Science and Technology 11 (3), P: 169-218, **1977**.

51. Erikkson, O. and Lindgren, B.O.; About the Linkage between Lignin and Hemicelluloses in Wood. Svensk Papperstidning 80 (2), p. 59-63, **1977**.

52. Karlsson, O.; Westermark, U. The significance of glucomannan for the condensation of cellulose and lignin under kraft pulping conditions, NP&P Research J. 3,12,**1997**.

53. Browning, B. l.; Jogani, P. D. An Investigation of The Direct-Compression Characteristic of Compressed Lactose-Microcrystalline Cellulose Using Statistical Design. Pharm. Technol 23, 54, **1999**.

54. Browning, B. L. Methods of Wood Chemistry, Vol 2. Interscience/Wiley. New York, **1967**.

55. Shangraw, R. F.; Wallace, J. W.; Bowers, F. M. Moprphology And Functional In Tablet Excipients For Direct Compression, Pharm. Techno, 11, 136, 143, **1987**.

56. Parthasarasy, V. R. Bleaching of Npn-Wood Pulps. Research Triagle Institue , Research Triangle Park, RTP, NC 277709-2790.

57. TAPPI, 79, (3), 111-113, **1996**.

58. Ni, Y.; Li, Z.; Court, G.; Billiveauu, R.; Crowell, M. Improving Peroxide Bleaching of Mechanical Pulps By The PM Process. Pulp & Paper Canada. 104(12), 313-315, **2003**.

59. Granström, M. Cellulose Derivatives: Synthesis, Properties and Applications, Laboratory of Organic Chemistry, Department of Chemistry, Faculty of Science, University of Helsinki, Finland. **2009.**

جامعة النجاح الوطنية

كلية الدراسات العليا

تحضير مبلمرات ذات قيمة اقتصادية من السيليلوز المستخلص من جفت الزيتون

إعداد

نسرين رياض اسعد يوسف الحج

إشراف

د. عثمان حامد

د. شحدة جودة

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

2013

تحضير مبلمرات ذات قيمة اقتصادية من السيليلوز المستخلص من جفت الزيتون

إعداد

نسرين رياض اسعد يوسف الحج

إشراف

د. عثمان حامد

د. شحدة جودة

الملخص

تنتج عملية استخلاص الزيت من الزيتون نواتج فرعية تتكون من نوعين :الناتج السائل ويسمى الزبار، والناتج الصلب ويسمى الجفت حيث ينتج بكميات كبيرة وهو عبارة عن بذور ثمار الزيتون والنسيج المكون لها، اما كيميائيا فان تركيبه مشابه لتركيب الخشب حيث يتكون من الليجنين والسيليلوز وشبه السيليلوز ومواد اخرى بنسب قليله.

لقد تم في هذا العمل تطوير عملية استخلاص السيليلوز من الجفت لتصل الى 35% من السيليلوز . تمت عملية الاستخلاص بعمليات متتابعة تبدأ بالمعالجة بمذيب عضوي ثم عملية تسمى (pulping) ثم يتبعها عملية التبييض التي تتكون من عدة مراحل ايضا وصولا الى الناتج النهائي للسيليلوز الذي تم تحليله بطرق مختلفة باستخدام (FTIR, SEM, HPLC, DSC and viscometry).

اثبت تحليل السيليلوز المستخلص من الجفت انه مطابق للسيليوز التجاري بخصائصه الفيزيائية والكيميائية مما يجعل من الجفت الذي يعتبر مخلفات زراعية مادة خام ذات قيمة اقتصادية يمكن استثمارها لانتاج السيليلوز .

يعتبر السيليلوز مادة صناعية مهمه لتحضير مواد اخرى مشتقة منها ذات تطبيقات واسعة . وفي هذا العمل تم تحويل السيليلوز الى سيليلوز اسيتات بطريقتين :التفاعل المتجانس وغير المتجانس، ثم تم تحليل النواتج بطرق مختلفة (FTIR, SEM, HPLC, DSC, and SEC).

يتم تحضير السيليلوز اسيتات بالطريقة المتجانسة باذابته بمذيب DMAC/LiCl تحت تأثير حرارة مناسبة ثم اضافة مادة ال Acetic anhydride و triethylamine كعامل مساعد لفترة معينة من الزمن لإنتاج السيليلوز اسيتات بدرجة استبدال 3 ومبلمر monodisperse.

اما الطريقة غير المتجانسة تمت فيها مفاعلة السيليلوز مع ال acetic anhydride بوجود ال acetic acid وحمض الكبريتيك كعامل مساعد لفترة من الزمن تحت تأثر حرارة معينة . وتم انتاج سيليلوز اسيتات بدرجة استبدال 1,77 ومبلمر polydisperse وقد تمت دراسة هذه الطريقة تحت ظروف مختلفة من الزمن والحرارة .

هذه النتائج تظهر أن هذا جفت الناتج كنفايات صلبة مصدرا قيما للسيليلوز التي يمكن أن تستخدم كمادة أولية للمنتجات ذات قيمة تجارية مع عدد غير محدود من التطبيقات الصناعية مثل السيليلوز وثلاثي الأسيتات ثنائي الأسيتات السيليلوز .