

BIOCA – Biomass Streams to Produce Cellulose Acetate

I. Harrison, P.J.G. Huttenhuis, A.B.M. Heesink
*Department of Chemical Engineering, Twente University, Enschede,
Procede Twente B.V., Enschede, The Netherlands*

ABSTRACT: Cellulose diacetate was produced from hemp fibers. Two main stages were required to produce the product; pulp production (delignification) by soda pulping and acetylation of the pulp to cellulose diacetate. Soda pulping of hemp fibers was carried out under various conditions of temperature and liquor concentration. From a consideration of the Kappa number of pulps obtained, it could be inferred that the optimum condition for pulp production is a liquor concentration of 5-10 wt% NaOH at about 160°C. These conditions produced pulp with a maximum Kappa number of about 5. The degree of polymerization of the cellulose obtained from pulping at 160°C using 15 wt.% sodium hydroxide solution was found to be approximately 450 indicating that considerable degradation of the cellulose structure had occurred. This lends weight to the desirability of reducing the liquor concentration to the suggested range. The α -cellulose content obtained was over 98 wt.%. Cellulose acetate flake/film was produced from the pulp in three main stages; activation, acetylation and hydrolysis. Activation was carried out by mixing hemp pulp with an equal amount of glacial acetic acid followed by acetylation at 30 °C and finally hydrolysis to diacetate.

INTRODUCTION

In recent times there has been a shift in technology towards the use of processes that are sustainable and environmentally friendly. In view of environmental concerns such as global warming and limited oil reserves, it is logical that process technology moves towards minimizing the use of fossil fuels.

Cellulose acetate is a biopolymer produced by the acetylation of cellulosic biomass. In many respects it is similar to the more common fossil fuel based polymers and therefore possesses the potential to replace such polymers in certain applications. The table below shows a comparison of some physical properties of cellulose acetate and some bulk polymers.

Table 1 Some physical properties of cellulose acetate and other bulk polymers.

Property	Cellulose acetate	Polyvinyl chloride	Polystyrene	LDPE
Tensile strength (MPa)	30	20	42	10
Flexural modulus (GPa)	1.7	0.03	2.5	0.25
T _{Melt} (°C)	170-240	170-190	210-260	220-260
Strain at yield (%)	3.9	-	2.4	19.0

Cellulose acetate also possesses some unique qualities that make it indispensable in certain areas. These properties include: good transparency, toughness, a natural feel and comfort, glossiness, water absorbency and biodegradability. For this reason it is especially suited to the manufacture of cigarette filters, textile fibers, photographic and packaging films, LCD displays, tool handles and medical applications.

The production of cellulose acetate is more environmentally friendly than the production of polymers from fossil fuels. For example the CO₂ exhaust during the production of 1 kg PE/PP is approximately 1.8 kg. For the production of Cellulose Acetate, the net CO₂ emission is approximately zero kg, because the product is produced from biomass, which consumes CO₂ during the growth. Cellulose acetate has not been able to break into the market for bulk polymers because it has a relatively high cost. It is at least four times as expensive as conventional polymers like polyethylene and polystyrene. This is mainly due to the high cost of the raw materials current used in industry, namely cotton and wood pulp. For example as at 1998, the price of dry hemp fiber was between \$95 and \$200/ton in Western Europe as compared to \$1500/ton and \$630/ton for cotton and wood pulp respectively (Stutterheim et al, 1998, Lange, 1998, Rymysza, 2000).

The purpose of the present study is to explore the possibility of effecting a substantial reduction in the cost price of cellulose acetate by the substitution of cotton/wood pulp by biomass streams like hemp or flax as raw materials in the production process. However before they can be acetylated the α -cellulose has to be separated from the other components present in biomass. Lignin is removed in order to obtain a colorless product, minimize acetic anhydride consumption and hasten the rate of acetylation while hemi-cellulose is removed because a wide molecular weight distribution of cellulose in the pulp compromises the tensile strength of the product. The objective of this project is to produce acetate grade cellulose pulp from hemp/flax. This means a minimum α -cellulose content of 96 wt.% and degree of polymerization (DP) above 1000. These criteria are based on the quality of wood and cotton derived dissolving pulps for cellulose acetate production (Hurter, 2003).

BACKGROUND

The figure below shows a simplified scheme of the cellulose acetate production process from biomass. The major process steps are outlined briefly in the subsequent paragraphs.

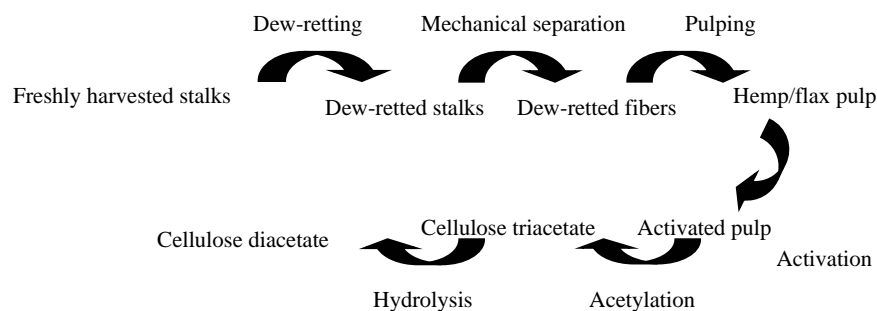


Figure 1 Outline of the process steps.

RAW MATERIAL SELECTION

As previously mentioned cellulose acetate is currently made from cotton and wood derived cellulose. In searching for suitable replacements of these expensive raw materials, a number of criteria were applied to the possible biomass sources: cotton, bagasse, straw, jute, kenaf, sisal, hemp, flax, and even garden waste. The applied criteria were:

- (1) Quality of the biomass source: Weight fraction of α -cellulose and degree of polymerization. Cotton is used as a benchmark.
- (2) Price.
- (3) Availability in the Netherlands.
- (4) Ease of separation: Extraction of α -cellulose.
- (5) Waste disposal.

By this means hemp and flax were chosen as the best alternatives to cotton. The table below shows a summary of the composition of hemp and flax in comparison to cotton and wood.

Table 2 Approximate composition and degree of polymerization of different cellulosic materials. (Han, 1998, RISO, 2002 & Saijonkari, 2001)

	Cotton linters	Wood	Flax	Hemp bast fibers
α -cellulose content (wt%)	93	40-50	62	67
Lignin content (wt%)	0	20-30	3.3	2.0
Degree of polymerization of cellulose	6500-7000	8000	2990	3270

RETTING

Retting (rotting) softens and separates the fibrous core of the plant from the woody outer layer. Also water soluble compounds are removed during this process. There are two common methods of retting: dew-retting and water-retting. Dew-retted biomass is spread on the ground and exposed to dew and rain. This process is dependent on the weather conditions and can take up to six weeks. Water retted biomass is produced by submerging the stems in either stagnant or moving water. Water retting takes about three days. Retting does not occur at all below 5 °C (bacteria are inactivated) or above 40 °C (destruction). Dew retted hemp and flax fibers were used in this work.

PULP PRODUCTION

The process of pulp production from annual plants such as flax and hemp is not well established industrially unlike for wood. Studies on the pulping of different kinds of wood are well documented.

Annual crops are not widely used at present, either for paper production or for acetate grade dissolving pulp. There has been some research on the pulping of kenaf (Aziz and Scott, 1998, Han 1999), straw (Leathwood, 1992), corn stover (Tucker and Kyoung, 2003), jute (Jahan, 2001), sugarcane bagasse (D'Agostino and Richard, 1997) and bamboo (Dhamodaran and Co, 2003). Thus the initial design of a pulping process for hemp and flax was based on current methods and conditions for these materials and systematically optimized for hemp and flax.

The aim of pulping is to obtain a cellulosic material containing at least 96 % α - cellulose by weight, remove most of the lignin and hemi-cellulose while minimizing degradation and removal of the α -cellulose. Lignin and hemi-cellulose are degraded by the alkaline pulping environment into phenolic compounds and simple sugars respectively. The degree of polymerization of cellulose is decreased during the pulping reaction due to alkaline peeling and hydrolysis reactions. Peeling is the gradual shortening of the cellulose chain beginning at the reducing end of the molecule, while hydrolysis involves cleavage of beta-1, 4-glycosidic bonds. Studies have also shown that the molecular weight stabilizes after some time due to occlusion reactions; a type of peeling reaction which produces a product that stabilizes the cellulose chain (Tapia, 2001).

A number of possible pulping processes are available, some of which include soda pulping, Kraft pulping, Steam explosion and the Duralin process. In this work Soda pulping is used because this it is suitable for annual plants with al low lignin content.

CELLULOSE ACETATE PRODUCTION FROM PULP

This process consists of three main steps: activation, acetylation and hydrolysis.

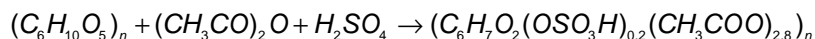
Activation

Cellulose pulp containing 4-7 wt.% moisture was mixed with equal parts of water or preferably glacial acetic acid to swell the pores of the fibers and thereby enhance mass transfer for the subsequent reaction steps. Investigation by previous researchers

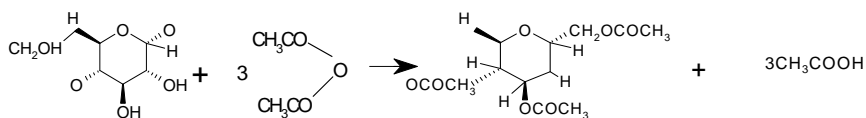
(Procede 2000) on cotton pulp showed that activated pulp is acetylated far more quickly compared with non-activated pulp.

Acetylation

Activated pulp reacts with acetic anhydride with glacial acetic acid as solvent and a small amount of concentrated sulfuric acid acting as a catalyst.



Acetate groups easily substitute the sulfoester groups. The reaction is carried out at less than 50 °C and the product is cellulose tri-acetate. Due to the susceptibility of cellulose to acidic media, some reduction in the degree of polymerization of the cellulose will occur. The rate of the reaction as well as the extent of cellulose degradation is dependent on the amount of acid and the reaction temperature.



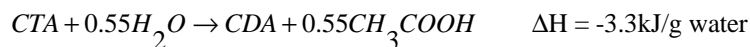
Cellulose + Acetic Anhydride = Cellulose triacetate + Acetic acid

$$\Delta H = -1.03 \text{ kJ/g cellulose}$$

Hydrolysis

Cellulose tri-acetate, the product from the previous reaction, was partially hydrolyzed, which consumes the excess anhydride to obtain cellulose diacetate. The reaction between water and acetic anhydride is highly exothermic and the quantity of water added should be such that after hydrolysis the reactor contents consist of about 7wt% water.

It is at present not possible to obtain the doubly substituted form of cellulose directly via the acetylation phase due to the nature of the solid-liquid reaction. A higher water content helps to minimize the degradation of cellulose.



The reaction is terminated by the addition of magnesium, calcium or sodium acetate.

EXPERIMENTAL 1: PULPING

The experimental work was divided into two main parts, the production of hemp/flax pulp and the subsequent production of cellulose diacetate. In this part the pulp experiments is described.

MATERIALS AND METHOD

Materials

Dry dew-retted flax fibers, sodium hydroxide, de-mineralized water.

Apparatus

0.5 L High pressure steel reactor, oven, 500 mL beaker, tong, plastic pail, and scissors.

Procedure

Extraneous materials were removed from the fiber by hand picking, followed by size reduction; cutting the fiber into approximately 20 mm pieces using a pair of scissors. A 15 wt% aqueous sodium hydroxide solution (cooking liquor) was then prepared by dissolving 150g of sodium hydroxide pellets in 850g of de-mineralized water.

The reactor, a non-stirred pressure vessel, was filled with 300 mL of cooking liquor and then 50g of chopped fibers added to give a liquor to fiber ratio of 6:1 (The liquor concentration was varied with subsequent trials). The reactor was then sealed and the oven switched on to a temperature of 160 °C. The reaction was carried out for a maximum of 2 hours, the reactor cooled to about 60 °C, when the pressure in the reactor was almost atmospheric. Liquor was then drained from the reactor. The remaining solids were removed using metal tongs and washed with copious amounts of water in a plastic pail. Washed pulp was dried to a constant weight in the oven at 70 °C.

RESULTS

Color

The pulp was dark brown in color before washing and light grey after drying. Liquor drained from the reactor was black. This is what is referred to in the paper industry as “black liquor”. The organic materials in black liquor consist mainly of degradation products of dissolved lignin and hemi-cellulose.

Texture and appearance

After the pulp was removed from the reactor it retained a fibrous but pulp like appearance and after drying became softer, resembling cotton. However the texture was coarser than cotton.

Pulp quality

Two parameters were used to determine the quality of the pulp: the weight fraction of α -cellulose in the pulp and the degree of polymerization of the α -cellulose. As previously mentioned, the target was a DP of at least 1000 and minimum cellulose weight fraction of 0.96. The weight fraction of α -cellulose was determined using

TAPPI test method T203 OM-93 while the degree of polymerization was determined by intrinsic viscosity measurements using CED (Copper-Ethylenediamine) as solvent.

The degree of polymerization of the pulp was determined by soaking about 30mg of pulp in 25 ml of water in an Erlenmeyer flask overnight followed by dissolution in 25ml of CED for 3 hours, filtration and finally, measurement of the filtrate flow time in an Ubbelohde viscometer.

The weight fraction of α -cellulose was determined by reacting the pulp with 17.5 wt% aqueous sodium hydroxide solution for about 1 hour followed by filtration. 10ml of 0.5N potassium dichromate solution was added to 25 ml of the filtrate in a 350 ml conical flask, acidified with 50 ml conc. sulfuric acid and titrated against 0.1N ferrous ammonium sulphate solution.

The Kappa number was calculated by the determination of the amount of 0.1N potassium permanganate consumed by 1g of pulp in 10 minutes at 25°C in the presence of 0.1N sulfuric acid. Kappa number is an indirect method of lignin quantification by the determination of the amount of permanganate ions consumed by lignin. The test method used was to react 1g of the pulp with 0.1N potassium permanganate solution, terminating the reaction after 10 minutes by the addition 1N potassium iodide solution. The amount of consumed permanganate was then determined by back titration of free iodine with 0.1N sodium thiosulphate solution. Typical values for the Kappa number of bleached wood pulp is between 1.4 and 5.5 for bleached spruce pulp depending on the method of pulping (Knoblauch J. et al, 2000) and about 5 for commercial spruce dissolving pulp.

The results and conditions are shown in the figures below

In the figure below a graph is presented of the pulp yield as function of the residence time in the reactor. The yield is defined as the amount of pulp after the pulping process divided by the amount of added biomass to the reactor. Subsequent figures show the effect of temperature and liquor concentration on the kappa number of the pulp produced.

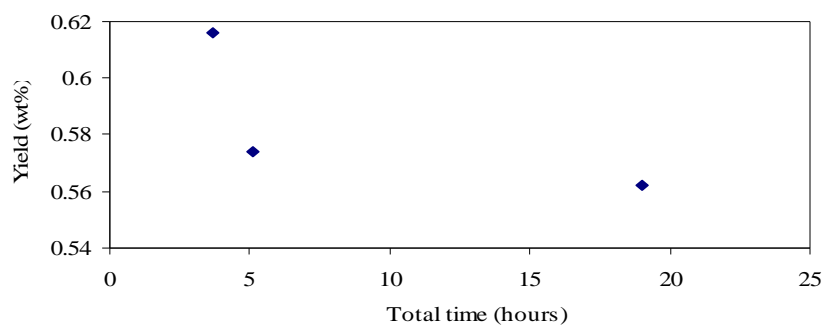


Figure 2 Variation of mass yield of hemp with time during soda pulping (15 wt.% NaOH solution and 160 °C).

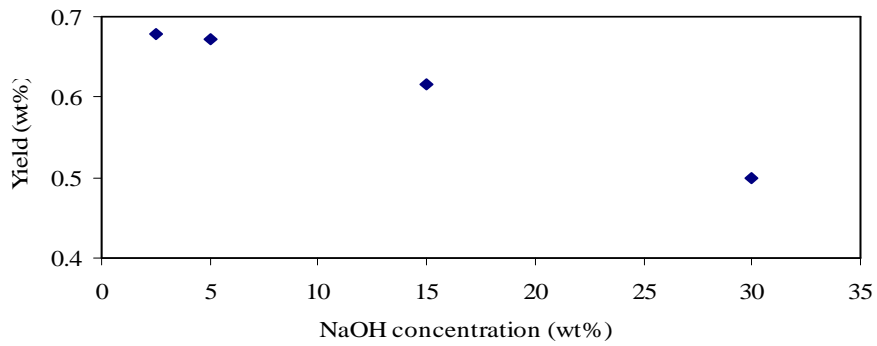


Figure 3 Influence of NaOH concentration on mass yield of hemp at 160°C.

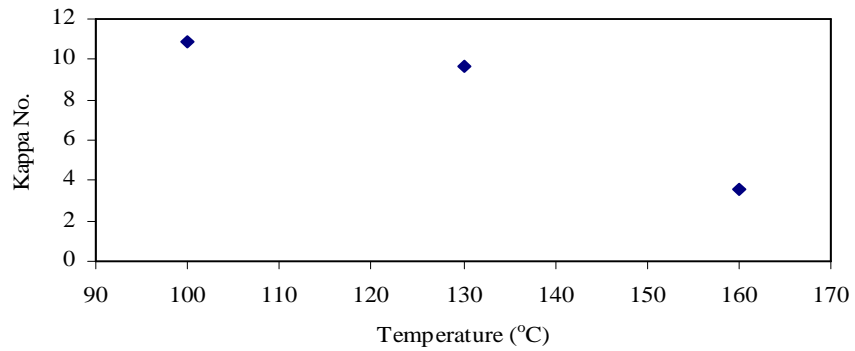


Figure 4 Influence of pulping temperature on Kappa number for 10 wt% NaOH solution.

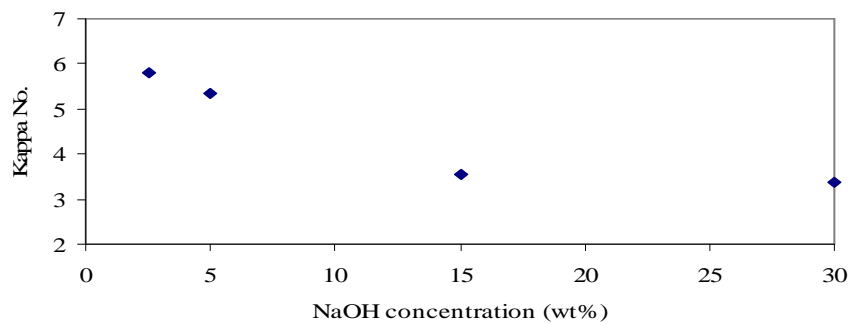


Figure 5 Influence of NaOH concentration on Kappa number at 160°C.

DISCUSSION OF RESULTS

As expected the yield of the pulping process (excluding losses during washing) increased with a reduction in the total reactor residence time and liquor concentration while the α -cellulose content of the obtained pulp is sufficiently high. The DP of the pulp obtained from the 15wt% NaOH solution at 160°C was 469, about half the desired value and less than 20% of the estimated value of the untreated hemp fibers, indicating that treatment conditions were too severe. Later tests will investigate the influence of liquor concentration on the DP. However the DP remained the same between a residence time of 5 hours and 19 hours. This suggests that cellulose degradation does not continue indefinitely, but stabilizes to a constant value with time for a given set of conditions. Thus the bulk of degradation most likely occurred during the earlier part of the reaction, a phenomenon also observed in the pulping of eucalyptus globulus and pinus radiata (Tapia et al, 2001). The desired degree of cellulose polymerization is therefore to be obtained either by a reduction in operating temperature or caustic soda concentration (because of the long cooling time of the reactor). This will be investigated in future work.

The Kappa number of the pulp dropped with temperature within the range of temperatures investigated. For 10 wt.% NaOH concentration, there was a steeper drop in Kappa number with temperature at higher temperature ranges; between 100°C and 130°C there is only about 11% drop in kappa number as compared to about 60% drop between 130°C and 160°C. The results of tests on the influence of liquor concentration on pulp Kappa number showed that the kappa number is somewhat less dependent on liquor concentration than temperature. The maximum reduction in Kappa number between 2.5 and 30 wt.% NaOH concentrations was about 40%. The greatest reduction in kappa number occurred between 5 and 15 wt.% NaOH concentration. From a consideration of the results obtained therefore, the optimum liquor concentration to be used for pulp production is between 5 and 10 wt.% at a temperature not less than 155°C.

EXPERIMENTAL 2: CELLULOSE ACETATE PRODUCTION FROM HEMP

MATERIALS AND METHOD

Materials

Pulp, glacial acetic acid, acetic anhydride, conc. sulfuric acid, sodium acetate, demineralized water and acetone.

Apparatus

1L jacketed glass reactor, thermostat bath, condenser, 5ml syringe, four 20 ml syringes, 10ml syringe, one 20ml syringe with large diameter steel needle, 2L flask, measuring cylinders, filtration flask, funnel, wash bottle, vacuum pump, nitrogen cylinder, nitrogen flow-meter.

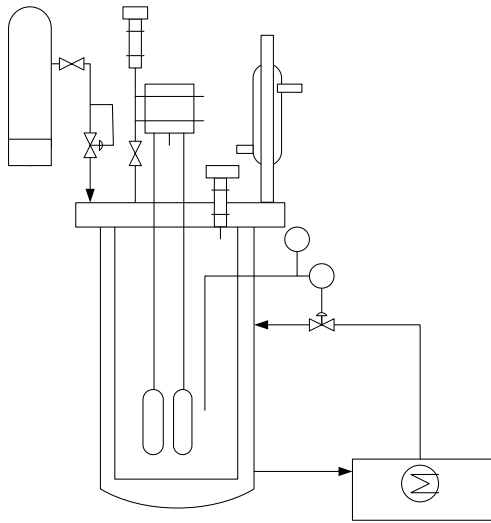


Figure 6 Sketch of acetylation reactor.

- (1) Reactor.
- (2) Water bath.
- (3) Liquid feed for acetic acid.
- (4) Liquid feed port for syringes.
- (5) Water condenser.
- (6) Stirrer.
- (7) Cooling jacket.
- (8) Nitrogen feed bottle.
- (9) Reducer.
- (10) Flow controller.

8

3

9

Procedure

6

The pulp was shredded by hand to reduce the size and minimize potential mixing difficulties. Water was sprinkled onto the dry pulp to bring it to about 5wt.% moisture content. Pulp was then put in the reactor, the vessel flushed with nitrogen and then activated by putting in an equal amount of glacial acetic acid while stirring vigorously for 2 hours at room temperature. After activation the pulp had a fluffy appearance.

Acetylation was then initiated by introducing glacial acetic acid from the feed bottle into the reactor followed by acetic anhydride and finally concentrated sulfuric acid as a catalyst. The reaction was allowed to proceed at a set temperature for about 1.5 hours. During this procedure the fibers became completely dissolved and the reactor contents appeared like a viscous quality similar to glue.

After acetylation, hydrolysis was initiated by gradually introducing water into the reactor and hydrolysis continued until such a time as a sample became soluble in acetone. This was used as a quick test of the conversion of the triacetate to diacetate. At this point the cellulose diacetate was stabilized by the addition of sodium acetate for about 30 minutes.

Following stabilization, the cellulose acetate product was precipitated out by slowly pouring the reactor contents into a stirred vessel containing a volume of water about thrice the reactor contents. The light flakes precipitated were filtered and washed in demineralized water using vacuum filtration to speed up the filtration process.

The wet flakes were then dried to a constant weight.

RESULTS

Color:

The color of the reactor content was dark brown before precipitation. The wet precipitated flakes were light brown and semi-transparent in color with some quantity being precipitated as films. Upon drying the flakes darkened considerably, becoming dark brown. For a picture of the cellulose acetate reference is made to figure 7.

Texture and appearance:

The product after precipitation was in the form of flakes and films, after drying the flakes assumed a more crispy looking appearance.

Pulp quality

The quality of the cellulose acetate product was assessed by consideration of the degree of substitution and the degree of polymerization.

Table 3 Production of Cellulose Acetate.

SAMPLE NO	1	2	3
ACTIVATION			
Temp ©	Ambient	Ambient	Ambient
Time (hr)	3	2.5	2
Appearance	Fluffy	Fluffy	Fluffy
ACETYLATION			
Temp ©	40	30	30
Time (hr)	3	2	2
Acetic acid (ml)	150	145	145
Acetic anhydride (ml)	60	75	75
Sulfuric acid (ml)	2	2	1.2
HYDROLYSIS			
Temp ©	50	30	30
Time (hr)	2	0.5	0.5
Water (ml)	6	15	10
DRYING			
Temp©	70	Ambient	Ambient
Time (hr)	15		48
Appearance	Grey	Dark brown	Large particles: black

	grains	flakes	shriveled Thin films: light brown
SOLUBILITY			
Acetone	Yes	Yes	Yes
Water	No	No	No

DISCUSSION OF RESULTS

Cellulose diacetate was produced from pulped hemp within 5-7 hours. This was considerably faster than the reaction time recorded in literature for its production from cotton. This may be due to the lower molecular weight of the pulp used here as compared to cotton. A higher product quality was obtained when the reaction temperature during the acetylation was reduced from 40 to about 30 °C. There was no difference in the required reaction time even when the amount of sulfuric acid was reduced from 1% to 0.5% (wt% based on pulp). Subsequent analysis will investigate the DP of the cellulose acetate product and the relationship with some of the reaction conditions, particularly the amount of sulfuric acid used, as cellulose is known to be very susceptible to acidic conditions.

The precipitation and washing step was found to be very critical. Cellulose acetate obtained as 3-4 mm diameter particles darkened quite considerably, becoming black when dried even under ambient temperature conditions. In contrast particles, which were precipitated as thin films/sheets and thin flakes darkened only slightly, thinner films being almost transparent. The pH of the larger particles was checked with indicator paper and while the pH of the outside surface was almost neutral, the core was found to be quite acidic (pH 3-4). It has been suggested that residual sulfuric acid in the Cellulose Acetate product is responsible for the observed discoloration. Thus it appeared to be very crucial that the cellulose acetate be precipitated as thinly as possible to allow for effective washing.



Dry hemp fibers → *Hemp pulp* → *Cellulose diacetate*

Figure 7 Raw materials and products of cellulose acetate production from hemp fibers.

CONCLUSIONS/RECOMMENDATIONS

It appears that cellulose acetate can be produced from hemp. The first step is the production of pulp by the soda process using 15 wt.% aqueous sodium hydroxide solution at 160 °C for about 2 hours. The degree of polymerization of the obtained cellulose under these conditions was about 460. This value is low compared to the DP

of cotton used in the cellulose acetate process. Less severe conditions would therefore be more suitable to prevent cellulose degradation.

The pulp was activated using an equal amount of glacial acetic acid while stirring vigorously for about 2 hours at room temperature after which it became fluffy. Acetylation followed using reagents in the following proportions relative to the pulp mass; acetic anhydride (3:1), acetic acid as solvent (6/7:1), sulfuric acid (0.05-0.1:1) as catalyst. The acetylation reaction did not start until the catalyst was added and a temperature rise of a few degrees was noted, indicating that the exothermic acetylation reaction started. From that time the fibers began to dissolve. The acetylation reaction was carried out at 30 °C for 2 hours during which cellulose triacetate was formed. The triacetate was then hydrolyzed to diacetate by the addition of water for 30 minutes at 30°C. The hydrolysis reaction was stopped by the addition of sodium acetate when the reactor contents became soluble in acetone.

Precipitation of acetate flakes followed by pouring the reactor contents into a well-stirred vessel of water, the particles were then filtered washed and dried. It is important that particles are precipitated as thinly as possible as they are then more thoroughly washed of sulfuric acid traces. Thus the strong discoloration of the product during the drying process can probably be prevented.

The research will be continued by optimizing the reaction conditions of the pulping and acetate production steps. First the optimum pulping conditions will be investigated by a consideration of the degree of polymerization, in addition to the concentration α -cellulose and the Kappa number of the pulp. This will be followed by optimization the conditions for the cellulose acetate production from pulp, applying the degree of polymerization and degree of substitution of the product as quality criteria as well as finding the best way to prevent product discoloration.

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