DETERMINATION ON THE OPTIMUM CONDITION FOR THE PREPARATION OF CELLULOSE ACETATES FROM MAIZE STRAW POWDER, WHEAT STRAW POWDER AND SAWDUST POWDER

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Abstract

In this research, the optimum condition for the preparation of cellulose acetate from maize straw powder, wheat straw powder and sawdust powder could be determined by four different acetylation methods. Firstly, the three sample powders were dewaxed. In the preparation of cellulose, the dewaxed sample powders were refluxed only with 15% NaOH for 9 h. Then the delignified sample masses were bleached with 5% sodium hypochloride solution for 24 h and neutralized with 5% acetic acid and water. The resultant neutral cellulosic pulps were acetylated with acetic anhydride and acetic acid in the presence of concentrated sulphuric acid as a catalyst using magnetic stirrer in method 1. In method 2, the apparatus used is ultrasonic cleaner instead of magnetic stirrer. In the third method, acetylation was carried out by using one more solvent (toluene) with ultrasonic cleaner. In the fourth method, solvents used were similar as in method 3 but with different catalyst (perchloric acid) instead of using sulphuric acid. The yield percentages of three cellulose acetates were determined and compared and then identified by FT IR spectroscopic analysis. At the same time, more reliable method that gave a good yield % and more purified product was observed.

Keywords: cellulose, cellulose acetate**,** acetylation, FT IR analysis

Introduction

Cellulose acetate is the acetate ester of cellulose. It was first prepared in 1865. Cellulose acetate was derived from cellulose by initially deconstructing wood pulp into the purified fluffy white cellulose. The cellulose is reacted with acetic acid and acetic anhydride in the presence of sulphuric acid to form cellulose acetate. The anhydroglucose unit is the fundamental repeating structure of cellulose and has three hydroxyl groups which can react to form acetate esters. The most common form is cellulose di-acetate. Cellulose triacetate is a chemical compound produced from cellulose and a source of acetate esters, typically acetic anhydride. It is commonly used for the creation of fibers and film base. It is chemically similar to cellulose acetate (diacetate). Its distinguishing characteristic is that in triacetate, at least "92 % of the hydroxyl groups are acetylated. In manufacturing process, the cellulose is completely acetylated; whereas in normal cellulose acetate or cellulose diacetate, it is only partially acetylated. Cellulose triacetate is significantly more heat resistant than cellulose diacetate. Cellulose diacetate is a synthetic polymer made by treating cellulose with acetic anhydride and acetic acid. It consists of two acetyl functional groups on each unit of D-anhydroglucopyranose of the cellulose molecule. Cellulose acetate is used as a film base in photography, as a component in some coatings, as a frame material for eyeglasses, as a synthetic fiber in the manufacture of cigarette filters and playing cards and in textiles, as a substrate for motion picture camera film, and as ingredient in sheet and molded objects etc. (Morgan E., 2013)

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to many thousands of β (1-4) linked D-glucose units. It is a natural polymer comprising at least one third of the vegetable materials in the world and it is present in materials such as wood, seeds and agricultural wastes. Cellulose can be produced from sources of lignocellulosic materials such as corn stalks and wheat straw and rice

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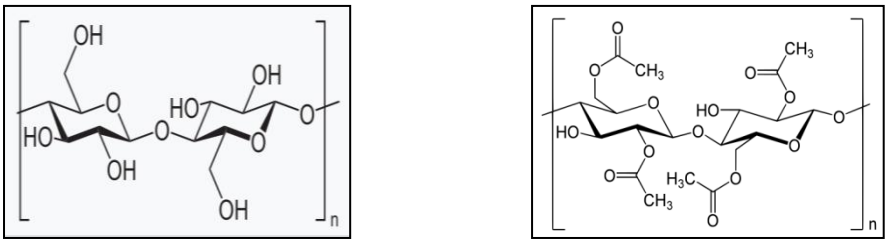
straw, agricultural byproducts such as corn fiber, rice hulls etc., and energy crops such as high fiber sugarcane. (Updegraff, D. M., 1969) Lignocellulosic materials are heterogeneous complexes composed of polymers (cellulose and hemi-cellulose) and lignin. They can be used to produce cellulose, such as wood (sawdust), cotton, sugarcane, sisal and others (Piotrowski S., Carus M., 2011) The pulping method used to isolate cellulose which consists of delignification and bleaching. Cellulose is insoluble in water and easily separated by pulping process from the other constituents of a plant (Crowford R. L., 1981**).**

In this research, the preparation of cellulosic pulp from maize straw powder, wheat straw powder and sawdust powder had been performed by pulping process and determination of the optimum condition for the preparation of cellulose acetates by acetylation with four different conditions had been carried out. Among these conditions, the optimum preparative condition could be specified. The resultant CAs from the respective samples had been identified by FT IR spectroscopy.



(a) (b)

Figure 1 Structural formulae of (a) Cellulose and (b) Cellulose acetate

Material and Methods

Sample Collection and Sample Preparation (Sampling)

Three types of agricultural residues such as maize straw, wheat straw and sawdust were collected from Myingyan Township, Myingyan District, Mandalay Region.

Figure 2 Raw materials of maize straw, wheat straw and sawdust

The raw materials were cut into small pieces and rinsed with water and dried. The dried pieces were blended and sieved with a 120-mesh sieve. The powder dusts under 120-mesh sieve were sieved again with 150 mesh sieve. The sample powders on the 150-mesh sieve were shown in Figure 3 and stored for cellulose isolation and acetylation.

(a) (b) (c)

Figure 3 (a) Maize straw powder (b) Sawdust powder and (c) Wheat straw powder

Methods
Preparation of Cellulose

Dewaxing process

100 g of each powdered sample was immersed in the mixture of 300 mL of toluene and 150 mL of ethanol (2:1, v/v) for 24 h to remove fats.

Pulping process

Pulping process consists of two steps: removing lignin (delignification) and removing non-cellulosic coloured materials (bleaching).

10 g of each sample powder and 100 mL of 15% NaOH were mixed in each volumetric flask and the flasks were heated to start refluxing for 3 h. Then the flasks were removed from the reflux condensers and cooled. The liquid in the flasks were decanted and 15 % NaOH was added to each flask and refluxed for another 3 h by similar performance as the previous procedure. Next, 15 % NaOH was added to each flask and refluxed similarly as the above procedures.

Bleaching

In the bleaching step, the delignified masses were suspended in 5% sodium hypochlorite solution for 24 h. Then three suspensions were filtered and the residual masses on the filter paper were washed with 5% acetic acid and then washed with water to neutral. The residues on the filter papers were dried and were allowed to stand for 24 h to obtain the constant weight. Then the yield (%) of each sample powder was calculated.

Preparation of Cellulose Acetate

Cellulose acetates from each sample were prepared by acetylation with the following four different conditions.

Acetylation with condition (1)

5 mL glacial acetic acid and 0.5 mL concentrated sulphuric acid were mixed and allowed to stand for 30 min. Then 1g of cellulose pulp was added to the flask and shaken thoroughly for 10 min. After shaking the mixture, 5 mL of acetic anhydride was added and the flask was shaken again for 30 min. After dissolving the cellulose pulp, 15 % acetic acid was added and the suspended solution was heated at 80 °C and stirred at 300 rpm with electromagnetic stirrer for 3 h. Then acetylated cellulose solution was poured into the beaker containing 150 mL distilled water. Cellulose acetate was precipitated as a suspension. The suspension was centrifuged and dried and weighed. The yield (%) of cellulose acetate in each sample powder was calculated.

Acetylation with condition (2)

In condition (2), the proportions of chemicals used were the same as in method (1), but the apparatus used is an ultrasonic cleaner under operating temperature of 80 °C for 1 h. The yield (%) of cellulose acetate in each sample powder was calculated.

Acetylation with condition (3)

In condition (3), one more solvent (toluene) was used than in method (2) and the reaction was carried out with an ultrasonic cleaner under operating temperature of 80 °C for 1 h. The yield (%) of cellulose acetate in each sample powder was calculated.

Acetylation with condition (4)

In condition (4) the solvents used were the same as in method (3), but the catalyst used was perchloric acid instead of using sulphuric acid. The yield (%) of cellulose acetate was calculated.

(a) (b) (c)

Figure 4 (a) Delignification of dewaxed samples by refluxing and acetylation of cellulose by (b) magnetic stirrer and (c) centrifuge machine

Results and Discussion

Preparation of Cellulose

Dewaxing process

The yield percentages of dewaxed sample powders were shown in Table 1.

Table 1 The Yield (%) of the Dewaxed Sample Powders

Sample powders	Yield (%)
Maize straw	96.35
Wheat straw	95.22
Wood sawdust (In)	93.46

From the above table, maize straw powder has the highest yield %. So it contains the lowest composition of pectin which is one of the main constituent of plant.

Pulping process (Preparation of Cellulose)

After pulping the three powdered samples, the yield percentages of prepared celluloses and cellulose acetates are shown by the following Tables 2 and 3.

Table 2 The Yield percentages of Celluloses

Sample powders	Yield (%) of celluloses
Maize straw	31
Wheat straw	33
Sawdust	54

According to the above table, sawdust cellulose provides the highest yield %.

Table 3 The Yield (%) of Cellulose Acetates by Acetylation with Four Different Conditions

Different Acetylation Methods	Yield (%) of Cellulose Acetates		
	Maize Straw CA	Wheat Straw CA	Sawdust CA
Condition (1)	41.89	48.61	54.21
Condition (2)	50.15	52.87	46.95
Condition (3)	58.76	60.43	57.86
Condition (4)	62.84	63.24	72.38

According to the above table, the yield (%) of cellulose acetates by condition (4) from the respective sources such as maize straw powder, wheat straw powder and sawdust powder had been found to be the highest values. So, condition (4) which was the optimum condition for the preparation of cellulose acetate had been specified.

Identification of celluloses and cellulose acetates by FT IR spectroscopic analysis

The FT IR spectra for identification of cellulose and cellulose acetates prepared from maize straw powder are shown in figure 5 (a), (b), (c) and (d) and the respective spectral assignments were shown in Table 4.

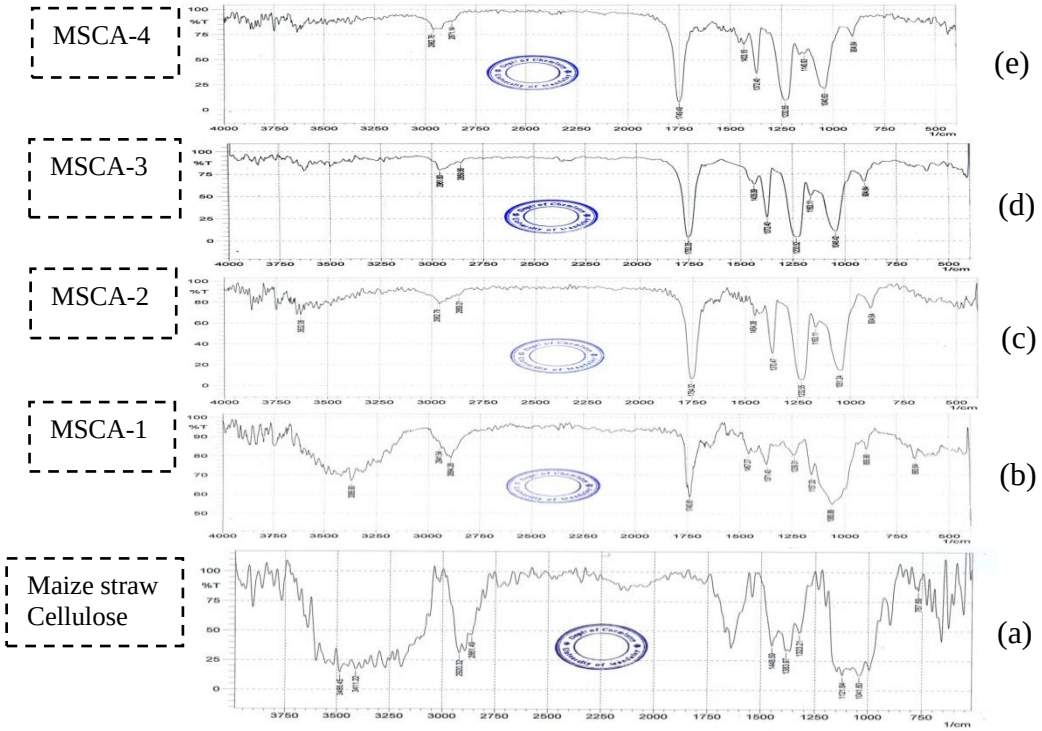


Figure 5 FT IR spectra of (a) maize straw cellulose and maize straw cellulose acetates prepared by (b) condition (1), (c) condition (2), (d) condition (3) & (e) condition (4)

Table 4 Comparison between FT IR Spectral Data of Cellulose and Cellulose Acetates Prepared from Maize Straw Powder

No.	Types of methods and compounds	υ_{O-H} (cm^{-1}) of alcohol	$\upsilon_{C=O}$ (cm^{-1}) of ester	υ_{C-O} (cm^{-1}) of ester
1.	Pulping method (Cellulose)	3486, 3411	-	-
2.	Condition-1 (Cellulose acetate)	3632	1754	1232
3.	Condition-2 (Cellulose acetate)	3365	1740	1239
4.	Condition-3 (Cellulose acetate)	-	1749	1232
5.	Condition-4 (Cellulose acetate)	-	1753	1233

From the above spectral data, the -OH stretching vibrations of alcohol groups appear at 3486 cm^{-1} and the intensity of –OH peak is distinct and there are no appearance of stretching vibrations of carbonyl (>C=O) peak and (C-O) peak of ester group. So, these spectral data assign that the compound is cellulose. In the spectra (b) and (c), there is -OH stretching vibrations appear at 3632, and 3365 cm^{-1} and the intensities of these -OH peaks gradually low. So, acetylation reactions occur but are not completely. In spectra (d) and (e), there are no -OH vibration peaks and in spectra (a), (b), (c) and (d), C=O stretching vibrations of ester groups appear at 1754, 1740, 1749, and 1753 cm^{-1} and then C-O stretching vibrations of ester group appear at 1232, 1239, 1232, and 1233 cm^{-1}, respectively. So, complete acetylations occur in condition (3) and (4). However, the yield % of condition (4) is the highest and hence the most suitable condition for preparation of maize straw cellulose acetate is condition (4).

Furthermore, FT IR spectra of wheat straw cellulose and cellulose acetates prepared from different methods are shown in Figures 6 (a), (b) (c), (c), (d) and (e). The spectral data were presented in Table 5.

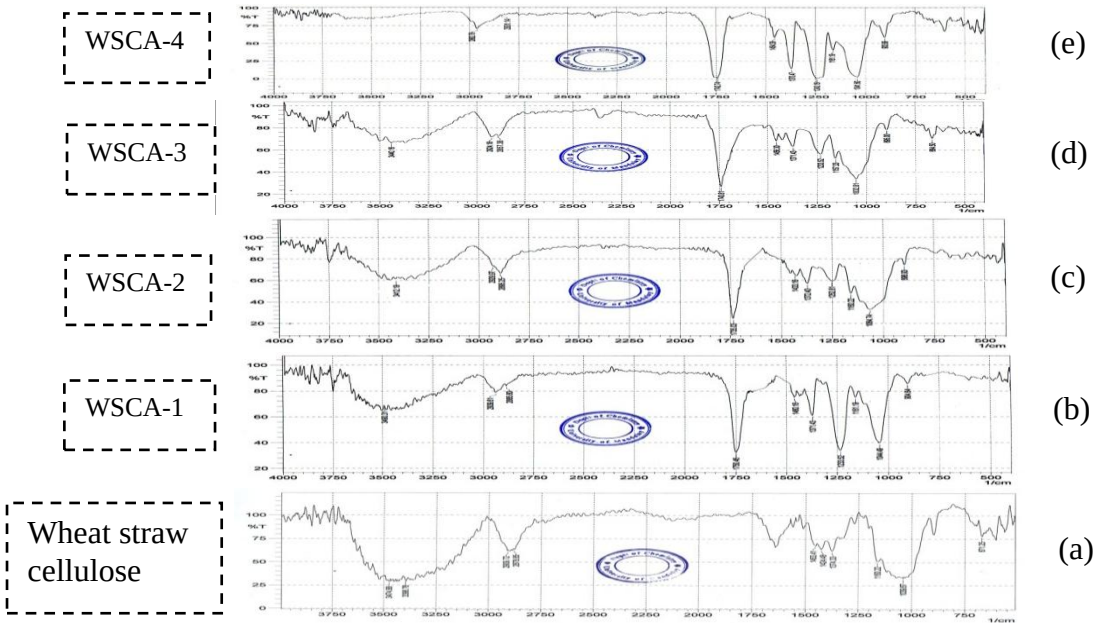


Figure 6 Comparison between FT IR spectra of (a) wheat straw cellulose and cellulose acetates by (b) condition (1),(c) condition (2), (d) condition (3) & (e) condition (4)

Table 5 Comparison between FT IR Spectral Data of Cellulose and Cellulose Acetates Prepared from Wheat Straw Powder

No.	Types of methods and compounds	υ_{O-H} (cm^{-1}) of alcohol	$\upsilon_{C=O}$ (cm^{-1}) of ester	υ_{C-O} (cm^{-1}) of ester
1.	Pulping method (Cellulose)	3474, 3396	-	-
2.	Condition-1 (Cellulose acetate)	3490	1750	1233
3.	Condition-2 (Cellulose acetate)	3412	1740	1252
4.	Condition-3 (Cellulose acetate)	3440	1749	1232
5.	Condition-4 (Cellulose acetate)	-	1742	1243

In the FT IR spectrum (a), there are two –OH stretching vibration peaks of alcohol groups of cellulose at 3474, 3396 cm^{-1}. In spectra (b), (c), (d), the intensities of OH peaks gradually low. However, C=O stretching vibrations of ester groups occur at 1750, 1740, 1749, and 1742 cm^{-1}respectively. C-O stretching vibrations of ester groups were observed at 1233, 1252, 1232, and 1243 cm^{-1} in spectra (a, b, c and d). So, complete acetylation were found to occur in condition (4).

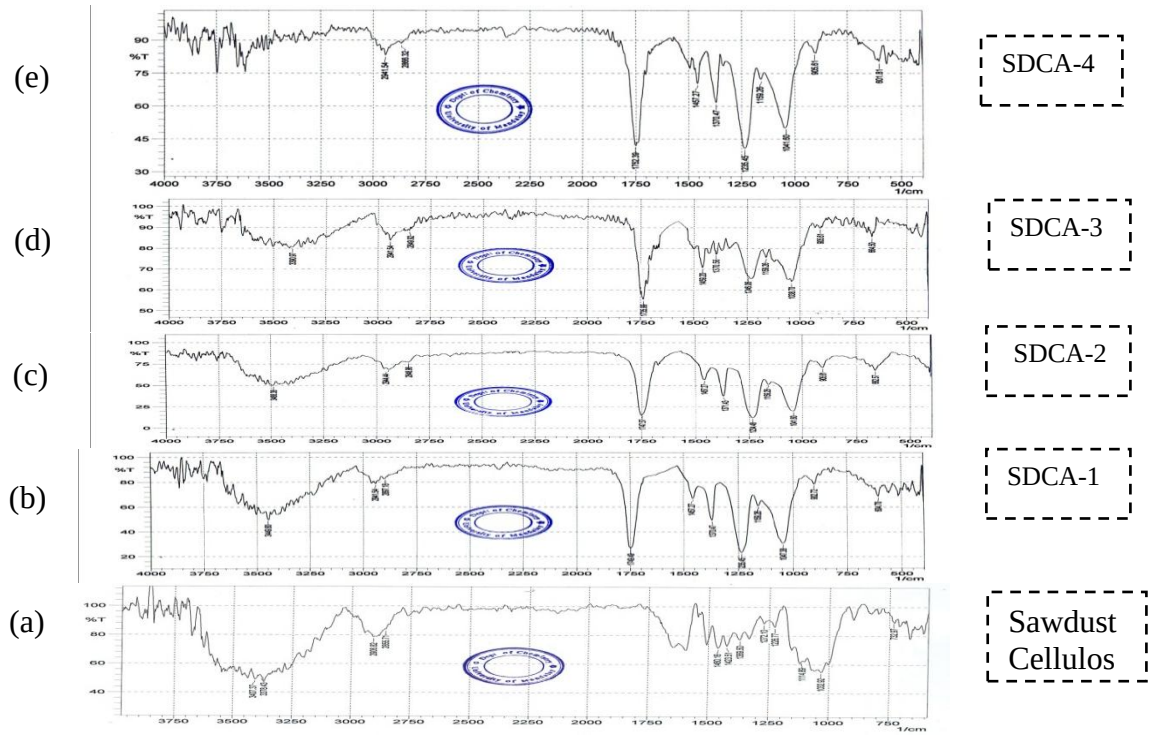


Figure 7 Comparison between FT IR spectra of (a) sawdust cellulose and prepared cellulose acetates by (b) condition (1), (c) condition (2), (b) condition (3), (e) condition (4)

Table 6 Comparison between FT IR Spectral Data of Sawdust Cellulose and Cellulose Acetates

No.	Types of method, conditions and compounds	υ_{O-H} (cm^{-1}) of alcohol	$\upsilon_{C=O}$(cm^{-1}) of ester	υ_{C-O} (cm^{-1}) of ester
1.	Pulping method (Cellulose)	3407, 3378	-	-
2.	Condition-1 (Cellulose acetate)	3449	1749	1235
3.	Condition-2 (Cellulose acetate)	3488	1747	1252
4.	Condition-3 (Cellulose acetate)	3440	1740	1233
5.	Condition-4 (Cellulose acetate)	-	1742	1243

In spectrum (a), there are two stretching vibration OH peaks of alcohol groups of cellulose at 3407, 3378 cm^{-1}. In spectra [(b), (c), (d),] the intensities of OH peaks gradually low. However, C=O stretching vibrations of ester groups occur at 1749, 1747, 1740, and 1742 cm^{-1}respectively. Furthermore, C-O stretching vibrations of ester groups were observed at 1235, 1252, 1233, and 1243 cm^{-1} in spectra [(b), (c), (d) and (e)]. So, complete acetylation also occurs in condition (4).

Conclusion

In this research, the optimum condition for the preparation of cellulose acetates from maize straw cellulose, wheat straw cellulose and sawdust cellulose had been specified. Firstly, the removal of pectin present in each sample powder was carried out by immersing into (2:1 v/v) toluene-ethanol mixture solution for 24 h. Then, in the preparation of celluloses, the pulping process had been performed by delignification and bleaching. Then, cellulose acetates were prepared by acetylation with four different conditions. From dewaxing process, the yield percentages were found to be 96.35 % for maize straw powder, 95.22 % for wheat straw powder and 93.46 % for sawdust powder. From the preparations of celluloses, the yield percentages were 31 % from maize straw powder, 33 % from wheat straw powder and 54 % from sawdust powder. After acetylation with conditions (1), (2), (3), and (4), the yield (%) of maize straw cellulose acetates were 41.89 % , 50.15 % , 58.76 % and 62.84 % .The yield (%) of the wheat straw cellulose acetates by acetylation with conditions (1), (2), (3), and (4) were 48.61 % , 52.87 % , 60.43% and 63.24 %. The yield (%) of sawdust cellulose acetates by acetylation with conditions (1), (2), (3), and (4) were 54.21 %, 46.95 %, 57.86 % and 72.38 %. The prepared cellulose acetate for each sample from different conditions had been identified by FT IR spectroscopy. From the FT IR spectral data, the optimum condition for the preparation of cellulose acetate was specified. Thus, condition (4) provides the complete acetylation and the highest yield percent.

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