A STUDY ON ACETYLATION OF SUGARCANE BAGASSE (SCB)

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ABSTRACT: The esterification of cellulose has acquired great importance due to the wide applicability of the products for various useful purposes. Esterification is a well known reactions by which polysaccharide can easily be transformed into the modified form. SCB powder was activated by alkali treatment prior to modification. The acetate derivative of SCB was synthesized by employing acetic anhydride as the esterifying agent. Pyridine was used as the catalyst for preparation of the ester derivatives. The effect of reaction influencing factors like concentration of acetic anhydride and pyridine, reaction period were studied. The products were characterized by determination of esterifying group of esters, IR-Spectroscopy and by Thermogravimetry.

Keywords: Esterification, Sugarcane Bagasse (SCB), Acetylation, Cellulose.

INTRODUCTION

In recent years, there has been an increasing trend toward more efficient utilization of agro industrial residues such as sugarcane bagasse (generally known as "bagasse"), sugar beet pulp, and coffee pulp. These lignocellulosic materials are abundant and renewable, and they are expected to be used as alternatives to fossil resources [1]. Nowadays chemically modified SCB use to remove water pollution as its adsorption capacity of metal ions from aqueous solution was achieved [2,3].

Because of the increasing need for high performance, biocompatible polymers, new synthesis paths for the defined chemical modification of the polyglucan cellulose were investigated [4]. Cerqueira A. D. et al. [5] reported membrane from cellulose acetate using poly (ethylene glycol) as additive. They used SCB as a cellulosic source for the study. Xie W. et al. [6] reported the chemical modification of corn starches by using ionic liquid as a catalyst. Succinic anhydride or acetic anhydride was employed as an esterifying agent and reaction was carried out using 1-butyl-3-methylimidazolium chloride ([bmim]Cl) as a reaction medium.

Acetylation of SCB was reported using NBS as a catalyst and use the resultant product for the production of oil sorptionactive materials [7,8]. Acetylation of sugarcane bagasse hemicelluloses also reported under mild reaction conditions by using NBS as a catalyst [9]. Cellulose and cellulignin extracted from SCB was used for the fabrication of composites reinforced with polypropylene and effect of Acetylation was also studied on mechanical and thermal properties of the fabricated composites [10]. H. M. Shaikh et al. have fractionated SCB to cellulose, hemicellulose and lignin by a proprietary steam explosion process, followed by downstream purifications. They demonstrated that the residual hemicellulose need not be considered as an impurity; rather it can be used in acetylated form as a plasticizer as well as a biodegradable additive for cellulose acetates made from slightly impure cellulose produced from non-wood origin [11]. SCB cellulosic phthalate was prepared using 1-butyl-3methylinidazolium chloride ionic liquid as an ionic liquid as reaction medium [12].

From the literature survey, it reveals that very little work reported on esterification of SCB powder in its native form. We have prepared SCB acetate by using SCB powder in its native form in order to get valuable product by deducing cost due to fractionation of SCB into cellulose, hemicelluloses and lignin.

EXPERIMENTAL

Materials:

SCB was procured from local market. Procured bagasses were washed thoroughly to remove traces of sugar and then dried in sunlight. Then it was cut into small pieces and it again dried in oven at 60°C for 24 hours. It was then powdered and used for the modification purpose.

Activation of SCB powder:

SCB powder was precautionally mixed with aq. Sodium hydroxide solution in order to control temperature of the reaction flask at 15°C. The reaction mixture was stirred for 1.5 hours at 15°C then neutralized with 10% acetic acid solution. The product was then filtered and washed with water until the filtrate became neutral. Finally it was washed with methanol and dried in oven at 60°C for two to three hours. This dried material was used for further modification.

Preparation of SCB Acetate:

2.5 g activated SCB powder in 2.5-12.5 mL pyridine (30.91 to 154.55 mmol) was mixed with 18-26 mL acetic anhydride (190.78 to 275.57 mmol). The reaction mass was thoroughly mixed and the homogeneous paste thus obtained was kept for refluxed at 145°C for different time intervals (2 to 10 hours) in an oil bath. After the completion of reaction, the reaction mixture was cooled to room temperature and discharged in 200 mL of distilled water, acidified with dilute hydrochloric acid to remove pyridine. This solution was subjected to high speed agitation for the precipitation of product. The solvent mixture was decanted

after the product settled down. The whole procedure of precipitation was repeated until the washings became acid free. The solid product was then filtered and dried in oven at 60°C and powdered to approximately uniform particle size.

Determination of Extent of esterifying group (acetyl group) of esters:

In the current study the extent of esterification by evaluation of percentage of esterifying group was determined rather than evaluating DS. The SCB powder was directly employed without any extraction of cellulose in order to search for the user friendly process. Evaluation is based upon saponification of ester with a measured excess of alcoholic sodium hydroxide solution of known concentration and then back titration of excess sodium hydroxide with standard hydrochloric acid using phenolphthalein indicator [13]. The calculation formula employed for the calculation of percentage of acetyl group is:

% Esterifying group =
$$\frac{(BR - SR) \times N_{HCl} \times MW}{W}$$

Where,

BR : The volume of hydrochloric acid required for blank determination,

SR : The volume of hydrochloric acid required for Sample determination,

- NHCl: The normality of hydrochloric acid solution,
- MW : The molecular weight of acetyl group (4.3 mol)
- W : Weight of Sample (in gram)

RESULTS AND DISCUSSION

Various set of products obtained upon acetylation were characterized by determination of Extent of acetyl group, Thermogravimetry and Infra-Red (IR) Spectroscopy. The experimental data comprising of the effects of reaction influencing factors are given in Table 1 to 6. The extent of acetyl group was also measured for unmodified SCB powder which is 2.31%. This value is small enough to neglect in the prescribed study.

Effect of amount esterifying agent:

Table 1show the dependency of extent of acetylation on the amount of acetic anhydride in the acetylation of SCB. The above specified Table and corresponding Figure 1 represent the effect for acetyl derivative.

Sr. No.	Sampla Coda	Amount of	acetic anhydride	0/ A actul group	
SI. NO.	Sample Code	mL	mmol	% Acetyl gloup	
1	SCBACAC-18	18	190.78	25.74%	
2	SCBACAC-20	20	211.98	28.53%	
3	SCBACAC-22	22	233.17	30.57%	
4	SCBACAC-24	24	254.37	33.56%	
5	SCBACAC-26	26	275.57	27.16%	

 Table 1: Effect of amount of acetic anhydride on acetylation of SCB

SCB: 2.5 g; Pyridine: 2.5 mL; Reaction Time: 6 hrs; Reaction Temperature: 145°C



Figure 1: Effect of Acetic anhydride concentration on formation of SCB Acetate

The extent of esterification was found to increase with increase in esterifying agents. Maximum esterification of 33.56% was obtained when the amount of acetic anhydride was increased from 190.78 mmol to 254.37 mmol. Further increasing the concentration of acetic anhydride from 254.37 mmol to 275.57 mmol, there observed a decrease of 6.4% in acetylation. The graphical representations as a function of reagent concentration for acetates are shown in Figures 1. Any increase in the percentage esterification with increasing the anhydride group is obvious in the sense that esterification, an equilibrium process, can be shifted more towards the ester formation by using an excess of reagent. The enhanced availability of the anhydride molecules in the immediate environment of the SCB fiber molecules, which are kept in the fixed concentration throughout the series, may be considered responsible for the increments.

The acetate attained a maximum level for extent of esterification within the concentration range of acetic anhydride under question. The leveling-off was observed at 33.56%. This is evident from Table 1. About 1.08 times increase in acetic anhydride

(i.e. from 254.37 to 275.57 mmol) affects the percent esterification value to an extent of only 6.4%. The saturation in the degree of reaction may be ascribed to the reversibility of the reaction which is not driven only in the forward direction due to the formation of water in the product mixture. The dominance of the reverse reaction, acid catalyzed hydrolysis of ester, may be considered responsible for the abnormal development observed for acetates beyond 254.37 mmol of acetic anhydrides (Table 1).

Effect of amount Pyridine concentration:

The effect of the concentration of pyridine as a catalyst on percentage esterification of various esters studied is depicted in Tables 2. It is also represented graphically in Figures 2. The retarding effect of pyridine was observed. A fivefold increase in pyridine concentration brought 1.43 times decrease in acetylation value. A decrease in the amount of acetic anhydride actually available for the reaction enhances the difference between the moles of anhydride taken and used-up for the purpose. This result into the lowering ratio of moles of anhydride bound to the substrate to the moles of anhydride initially taken into the reaction mixture.

Sr. No.	Sample Code	Amount	of Pyridine	Acetic anhydride: Pyridine	% A cotul group	
	Sample Code	mL	mmol	mole ratio	70 Acetyl gloup	
1	SCBACPy-2.5	2.5	30.91	8.23	33.56%	
2	SCBACPy-5.0	5.0	61.82	4.11	32.76%	
3	SCBACPy-7.5	7.5	92.73	2.74	31.41%	
4	SCBACPy-10.0	10.0	123.64	2.06	27.31%	
5	SCBACPy-12.5	12.5	154.55	1.65	23.51%	

SCB: 2.5 g; Amount of acetic anhydride: 24 mL (254.37 mmol); Reaction Time: 6 hrs; Reaction Temperature: 145°C



Effect of Reaction Time:

Tables 3 show the effect of reaction time on extent of acetylation. The results are also represented graphically as depicted in Figures 3. The extent of values of percent acetylation were found to increase with prolonging the reaction period from 2 to 6 hours for all the experiments performed under the study. Further increase in the reaction time from 6 to 10 hours, the percent acetylation was found to decrease from 33.56% to 28.58% i.e. about ~1.2 times lower value was observed (Table 3). The maximum value of acetate formation was observed to be 33.56% at reaction time of 6 hours. Figure 3 shows the graphical representation of the effect of reaction time on acetate formation.

Table S	Table 5. Effect of Reaction Time on Seb acctate preparation									
Sr. No.	Sample Code	Reaction Time (hrs)	% Acetyl group							
1	SCBACRT-2	2	24.91%							
2	SCBACRT-4	4	25.78%							
3	SCBACRT-6	6	33.56%							
4	SCBACRT-8	8	28.41%							
5	SCBACRT-10	10	28.58%							

Table	3: Effect	of Reaction	Time on SCB	acetate preparation
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SCB: 2.5 g; Amount of acetic anhydride: 24 mL (254.37 mmol); Pyridine: 2.5 mL (30.91 mmol); Reaction Temperature: 145°C



Figure 3: Effect of Reaction Time on formation of SCB Acetate

It can be concluded, from the time variation study, that a maximum level of acetylation of SCB was reached by continuing the reaction for the optimum time period under the set of reaction condition studied. After acquiring the optimum extent of esterification, the cellulose molecule did not undergo further electrophilic displacement with the acylpyridinium complex. Thus the leveling-off in the esterification value may be viewed as the establishment of equilibrium between the products and the reactants under the chosen set of reaction conditions. The maximum values achieved for the percent esterification after the optimum time duration of the reaction was found to be 6 hours. CHARACTERIZATION

By Infra-Red (IR) Spectroscopy:

The spectral data of unmodified SCB and its derivatives are shown in the Table 4. The spectra were recorded on "PerkinElmer USA Spectrum GX" spectrophotometer using KBr pellets. The most striking evidence for the presence of >C=O group [14] shows the band at 1750 – 1735 cm⁻¹. A new band was observed in derivative at this region of IR spectrum. It was observed at 1753 cm⁻¹. Table 4 and Figures 4 & 5 represent unmodified SCB and SCB acetate. In the IR spectra of SCB acetate, the presence of $-COCH_3$ group was confirmed by strong absorption band at 1377 cm⁻¹. The band observed in the range of 1610–1632 cm⁻¹ corresponds to the bending mode of the absorbed water [15,16,17,18] and is found in both the cases. The O–H bending vibration of the hydroxyl in plane deformation is characterized by the band at about 1380 cm⁻¹. A series of peaks in both the spectra over the range 3750–3000 cm⁻¹ may be considered as a broad band due to –OH absorption. In the spectra, the band observed at about 1160 cm⁻¹ may be due to C–O stretching in C–O–C linkages. The sharp band at 897 cm⁻¹ is originated from the β -glucosidic linkages between the sugar units [15].

Unmodified SCB cm ⁻¹	3425	2 <mark>92</mark> 0		1638	1377	1163	1060	897
SCB Acetate cm ⁻¹	3439	2936	1753	1636	1377	1163	1044	897

Table 4	: Main	features	observed	from	IR stu	dies for	the pre	epared	esters	of S(CB
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The strong and broad band extending from $1200-950 \text{ cm}^{-1}$ consisting of several close bands which are typical of all cellulosic fibers has been found to change to a relatively transparent region and having only a few individual weaker bands [19].



Figure 4: FTIR Spectrum of Unmodified SCB



Figure 5: FTIR Spectrum of SCB acetate

By Thermogravimetric Analysis (TGA):

Thermal behavior of prepared ester derivatives of SCB with different substitutions were studied. "PerkinElmer model Pyris 1 Thermo-gravimetric analyzer" was employed to study the thermal behavior of prepared derivatives of SCB. The thermobalance consists of furnace, sample holder, glass enclosure and recording balance mechanism. The samples were powdered to the same average mesh size and dried carefully in vacuum desiccator. 10 mg of exact weight of sample was taken for each Thermo Gravimetric Analysis (TGA). Tables 5 and 6 show thermal behavior of prepared acetyl derivatives and also represented by Figures 6 to 9. Ti, initial decomposition temperature, was found to increase from 162°C (for native SCB) to 179°C i.e. the values of Ti was found to increase with the maximum possible substitution of esterifying group. The observed increase in the thermal stability may be due to the reduced reactivity of the hydroxyl group by its esterification [20].

Temperature	% wt. loss at various decomposition temperature					
(°C)	Unmodified	SCBACAC-20	SCBACAC-22	SCBACAC-24		
100	95.60	99.60	99.85	99.97		
150	95.31	99.40	99.63	99.83		
200	93.63	98.72	99.10	99.35		
250	80.27	96.58	97.21	97.73		
300	47.94	87.93	89.55	89.97		
350	28.29	30.09	32.16	33.37		
400	25.27	19.53	18.23	19.19		
450	23.19	17.73	16.55	17.48		
500	21.89	16.71	15.43	16.48		
550	20.80	15.85	14.58	15.77		
600	19.79	15.16	13.84	15.12		

Table 5: % weight loss at various decomposition temperatures for SCB acetate.

Table 6: Thermal parameters of SCB acetate.

Sample code	% Substi- tution	Ti °C	T ₁₀ °C	T ₅₀ °C	T _{max} °C	IPDT °C	E kJmol ⁻¹	% Char
Unmodified	-	162	223	298	303	442	65.67	19.79
SCBACAC-20	28.53	174	293	336	337	598	50.01	15.16
SCBACAC-22	30.57	175	298	339	339	601	54.08	13.84
SCBACAC-24	33.56	179	300	340	340	603	60.48	15.12

 T_{10} values observed for the derivatives were found to increase as compared to native SCB. This indicates that modification retards the rate of thermal degradation up to first 10% weight loss. T_{50} values for the prepared derivatives were found to be improved. T_{max} values observed for the different derivatives were found to increase as compared to the native SCB. IPDT values have been greatly influenced by modification of bagasses. For the prepared derivatives, it was observed almost 150°C higher as compared to native SCB (i.e. 442°C). Activation energy values were found to decrease for all the derivatives covered under the thermal study as compared to native SCB.



Figure 6: Thermogram of unmodified SCB



Figure 7: Thermogram of SCB acetate (28.53%)



Figure 8: Thermogram of SCB acetate (30.57%)



Figure 9: Thermogram of SCB acetate (33.56%)

Conclusion:

Treatment of Sugarcane Bagasse with alkali leads to remove lignin. This modification provided very good esterification. Further, the acetylation process were studied by varying amount of acetic anhydride concentration, pyridine concentration, liquid to solid ratio in reaction mixture and reaction time. By this, optimum reaction condition was achieved which may help for further study in all aspect of science. Further, the cost and time is also reduced by direct use of Sugarcane Bagasse for the modification. So far as the industrial process concern, we have just initiated a small step for modification of Sugarcane Bagasse without any need of extraction process separately.

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