A convenient acetylation of sugarcane bagasse using NBS as a catalyst for the preparation of oil sorption-active materials

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The esterification of sugarcane bagasse with acetic anhydride using *N*-bromosuccinimide (NBS) as a catalyst under mild conditions in a solvent free system has been investigated. The extent of acetylation was measured by weight percent gain, which increased with an increment of reaction temperature (30–120°C) and time (0.5–72.0 h) and NBS concentration from 0.5 to 1.5%. In comparison with four tertiary amine catalysts (4-dimethylamino pyridine, pyridine, *N*-methyl pyrrolidine, and *N*-methyl pyrrolidinone) and one acidic catalyst (0.5% H_2SO_4), *N*-Bromosuccinimide was found to be the most effective and inexpensive catalyst for acetylation of hydroxyl groups in the cell walls of bagasse under mild reaction conditions. At a concentration of 1.5% of the NBS catalyst in acetic anhydride, a weight percent gain of 22.3% was achieved at 80°C for 2 h. FT-IR and CP-MAS ^{13}C-NMR studies produced evidence for acetylation. More importantly, the acetylation substantially increased hydrophobic properties of the bagasse. The oil sorption capacity of the acetylated bagasse (18.8 g machine oil/g of bagasse fibre at room temperature), obtained at 80°C for 2 h, was approximately 1.9 times higher than those of the commercial synthetic oil sorbents such as polypropylene fibres. Cyclic sorption/desorption studies showed that a simple squeezing operation was sufficient to remove most of the oil absorbed on the fibre and the sorbents can be used several times. These novel oil sorption-active materials could be used to substitute those of non-biodegradable materials in oil spill cleanup.
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1. Introduction

About 54 million dry tons of sugarcane bagasse (SCB), a by-product of cane sugar processing, is produced annually throughout the world. The bagasse is used either as a fuel for the boilers by the sugar factory or as a raw material for the manufacture of pulp and paper products, various types of building boards, and certain chemicals. For example, pulp produced from SCB is used in such products as facial and toilet tissue, various type of writing and printing papers, bag and wrapping papers. However, these represent only a small fraction of the total bagasse produced [1]. Huge quantities of the remaining SCB are not used as industrial raw materials and is burnt in the fields or on the road, particularly in China today. The pollution, therefore, is a serious problem by burning agricultural residues in this area. However, these agricultural residues represent an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass, particularly for the production of oil sorption-active materials.

The chemical composition of bagasse is similar to that of hardwoods. It consists of approximately 40% cellulose, 30% hemicelluloses, and 20% lignin [2]. It is subject to be serious disadvantage of exposure to moisture, the principal disadvantage being the ready exchange of water by the porous, cellular

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lignocellulosic material when exposed to fluctuating humidity. The varying moisture content of wood results in dimensional and conformational instability. One option to stabilise wood and fibreboards made from bagasse fibre which has been explored over many years involves the esterification of SCB fibre using a carboxylic acid anhydride, the most studied chemical being acetic anhydride [3–5]. Acetylation also greatly improves biological resistance because of the reduced moisture sorption and substrate blocking of the reacted cell-wall polymers [6].

Hydroxyl groups are the most abundant and reactive sites on the cell wall polymers of a lignocellulosic material such as SCB [7]. So far, chemical modification of lignocellulosics using acetic anhydride is perhaps the simplest, safest, and cheapest method for improving the strength, dimensional stability, and decay resistance of biocomposites. Acetylation is a single-site reaction, that is, one acetyl per reacted hydroxyl group with no polymerization. In addition, acetyl groups are more hydrophobic than hydroxyl groups, therefore, replacing some of the hydroxyl groups with acetyl groups reduces the hydrophilic property of the cell wall polymers [8]. In the reaction with acetic anhydride, acetylation occurs and acetic acid is produced as a by-product, which must be removed to prevent degradation. The acetic acid co-product can affect the reaction rate, but a significant retardation of the rate does not occur until the acid concentration exceeds 30% [9]. This is important when considering a commercial process, where acetic anhydride is recycled, since the recycled acetic anhydride contains some amounts of acetic acid, especially as it is mixed with fresh acetic anhydride.

In spite of a number of reports investigating various catalysts for acetylation in a solvent free system [10, 11], the search for new catalysts is still actively pursued to address such problems as harsh reaction conditions. In addition, environmental and economic considerations have required the redesign of these commercially important processes. As a result, there is further scope to explore mild and efficient methods for acetylation. Based on the study of acetylation of alcohols under mild reaction conditions, Karimi and Seradj [12] reported that *N*-bromosuccinimide (NBS) is an inexpensive and commercially available reagent, and is a novel and highly effective catalyst for acetylation of alcohols under nearly neutral reaction conditions. As far as the authors are aware, there have been no reports of its use as a catalyst for the acetylation of bagasse using acetic anhydride. We therefore decided to investigate the possibility of the acetylation of SCB using NBS as a new catalyst in the presence of acetic anhydride under a solvent free system. The products were characterised by weight percent gain (WPG). FT-IR and solid-state ¹³C-NMR spectroscopy was performed to investigate the reaction. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out to study the thermal behavior of acetylated SCB and to compare it with the unreacted material.

In recent years, tremendous increases of accidental and intentional oil discharges have occurred during production, transportation, and refining. Spilled oil causes immense environmental damage unless it is removed as quickly as possible. One of the most economical and efficient means for the removal of spilled oil from either land or sea is the use of sorbents [13]. Since the sorbent oil mixture has decidedly different physical properties in comparison with those of a fluid, this will aid in retrieval operations. Another benefit of using a sorbent is its ability to capture and retain oil for retrieval at a later time. This may be a major advantage due to the rapid initial rate of spreading of oil slicks on water. Additional advantages of a properly chosen sorbent are selectivity, effectiveness and general application. Ideally, a sorbent should pick up at least 90% of the oil from the water surface. Finally, sorbents can function with oil slicks of varying thicknesses and viscosities. Such a property is essential to allow the design of general systems that can handle a majority of spill situations [14].

Oil-sorbent materials can be categorised into three major classes: inorganic mineral products, organic synthetic products, and organic vegetable products. Mineral products include perlite, vermiculites, sorbent clay, and diatomite. These materials do not show adequate buoyancy retention and their oil sorption capacity is generally low [15]. Synthetic sorbents such as polypropylene and polyurethane are the most commonly used commercial sorbents in oil-spill cleanup, due to their oleophilic and hydrophobic characteristics [16]. A disadvantage of these materials is that they degrade very slowly as compared with mineral or vegetable products. Organic vegetable products such as straw, corn cob, and wood fibre showed poor buoyancy characteristics, relatively low oil sorption capacity, and low hydrophobicity [15]. Interestingly, the results from our laboratory recently found that natural sorbents such as acetylated cereal straws can offer distinct advantages in such regard. The modification with acetic anhydride substitutes the hydroxyl groups of cell wall polymers from vegetable products such as cereal straws with acetyl groups, modifying the properties of these polymers so that they become hydrophobic. These absorbents have the characteristics of low cost, high capacity, and quick uptake and are easy to desorb by a simple squeezing method [17]. They could be used effectively to recover oil spilled in bodies of refining or heavy industrial waste water and in the water of lakes, revivers, and oceans. Therefore, the purpose of this study is also to investigate the oil absorbency of the acetylated bagasse using machine oil so as to replace the synthetic sorbents.

2. Methods and methods
2.1. Materials and regents
Sugarcane bagasse was obtained from a local sugar factory (Guangzhou, China). It was first dried in sunlight and then cut into small pieces (1–3 cm). The cut SCB was further dried in a cabinet oven with air circulation for 16 h at 60°C. Acetic anhydride, NBS, 4-dimethylamino pyridine (DMAP), pyridine, *N*-methyl pyrrolidine (MPI), and *N*-methyl pyrrolidinone (MPO) were purchased from Sigma Chemical Company (Guangzhou, China).

2.2. Acetylation of SCB

This was carried out as recommend elsewhere [17], with the modification that acetylation was performed under mild conditions using NBS as a catalyst. A quantity of dry straw (approx. 15 g) was placed in a 500 ml round bottom flask containing 300 ml acetic anhydride and 0.5–3.0% NBS (1.5–9.0 g NBS dissolved in 300 ml acetic anhydride). The flask was then placed in an oil bath set at the required temperature (30, 50, 80, 100, or 120°C) using atmospheric pressure with a reflux condenser fitted. After the reaction for the required time (1.5, 2.0, 5.0, 16.0, 28.0, or 72.0 h), the flask was removed from the oil bath, and the hot reagent was decanted off. The bagasse was then thoroughly washed with ethanol and acetone to remove the un-reacted acetic anhydride and acetic acid by-product. The products were then dried in an oven at 60°C for 16 h. The oven-dry materials were weighted to determine the weight percent gains (WPG) on the basis of initial oven-dry measurements (WPG (%) = [(weight gain/original weight)] × 100). To reduce errors and confirm the results, each experiment was repeated three times under the same conditions, and the weight percent gain represents the average values. In comparison, DMAP, pyridine, MPI, MPO, and 0.5% H_2SO_4 were also used as catalysts and the results are discussed.

2.3. Characterization of the acetylated SCB

The acetylation of SCB was evaluated by FT-IR and solid-state ^{13}C NMR spectroscopies. The FT-IR spectra were recorded on a Nicolet 510 spectrophotometer using a KBr disc containing 1% finely ground samples. The solid-state ^{13}C-NMR spectra were obtained on a Bruker MSL-300 spectrometer at 74.5 MHz with magic-angle spinning and cross-polarisation (CP-MAS). About 300 mg of sample was packed into zirconia rotors for MAS at approximately 4 KHz. The CP contact time was 5 s, acquisition time 0.1, and total acquisition time 1 h.

Thermal stability of the unmodified and acetylated SCB was performed using thermogravimetric analysis (TGA), and measurement of calorimetric properties of the materials was determined by differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (NETZSCH STA-409). The sample weighed between 10 and 13 mg. The scans were run from 20 to 600°C at a rate of 10°C per minute under a dry air atmosphere.

2.4. Oil absorptivity

Machine oil (20 g) was suspended in water in a beaker. The acetylated SCB (0.5 g) was added and mixed for 1 min at room temperature. The oil was found to be absorbed immediately by the acetylated SCB. The SCB was then picked out and weighed to determine the oil absorptivity.

3. Results and discussion
3.1. Effect of reaction conditions on WPG

In this study the acetylation was performed without solvent because the solvent reduces the reaction rate by dilution of modifiers. In addition, use of a solvent would require complicated separation procedures to recover the chemicals after the reaction. Furthermore, organic solvents are often harmful to humans and the environment. Acetylation of SCB is a single-site reaction that replaces a hydroxyl group with an acetyl group. Chemically, the hydroxyl groups can be distinguished as being phenolic, benzylic, or alcoholic on the lignin regions, and alcoholic in the carbohydrate. The alcoholic hydroxyl groups are either primary or secondary, and the phenolic hydroxyl groups are attached to an aromatic ring which has various substituents attached. Thus, the rate of acetylation is dependent on the relative reactivities of the hydroxyl groups in the substrate, and the rate of diffusion of the reagent into the fiber matrix [18, 19]. Based on the modification of wood using acetic anhydride, Rowell *et al.* [7] reported that the wood cell wall polymers react in the order lignin > hemicelluloses > cellulose. Similar results, obtained from the chemical modification of coir, oil palm fiber, flax, and jute fibers using acetic anhydride, revealed that the acetylation is proportional to the lignin content of the fibers [10]. Since bagasse is similar in chemical composition to hardwood, it should be expected that SCB would react with acetic anhydride and the properties of acetylated bagasse would be much the same as the properties of acetylated wood.

Table I gives the effect of the reaction conditions such as reaction temperature and time, concentration of NBS, and various catalysts on the WPG of the treated SCB. In comparison with a control sample 1, it is apparent that the NBS catalyst accelerated the rate of reaction. As can be seen from Table I, addition of 1.0% NBS in the reaction system at 120°C for 1.5 h (sample 8) resulted in a significant increase of WPG by 19.6%, which was approximately four times higher than the WPG obtained under the same conditions without catalyst. Similarly, an increment of NBS concentration from 0.5 to 1.0, and to 1.5% at 80°C for 2 h led to an increment of WPG from 14.3 to 18.7, and to 22.3%, respectively. In contrast to this increasing trend, the WPG decreased from 22.3 to 16.0% by increase of the NBS concentration from 1.5 to 3.0%. This is a satisfactory result since NBS recovery is a crucial economic factor. Thus, its use must be limited.

The acetylation is generally carried out in the presence of bases such as triethylamine or pyridine along with DMAP as co-catalyst [11]. On the other hand, there is still a great demand for acid catalysts to generate esters under mild conditions [20]. To compare the effect of NBS catalyst on the acetylation of SCB, several other tertiary amine catalysts such as DMAP, MPI, MPO and pyridine, and one acid catalyst of 0.5% H_2SO_4, have been examined. Among these, pyridine-catalyst esterification is a standard method for the modification of hydroxyl compounds and other acylable substances since it not only swells the fibres, thereby permitting effective ingress of reagent, but also catalyses the reaction via nucleophilic mediated catalysis [21]. However, this chemical is toxic, has an unpleasant odour and is not suitable for use in large scale reactions. DMAP has been found to be an effective catalyst for some

TABLE I Yield of acetylated sugarcane bagasse obtained under various conditions

Acetylation conditions				Acetylated bagasse		
Solid to liquid ratio[a] (g/ml)	Temperature (°C)	Reaction time (h)	Catalyst (g/100 ml liquid)	Sample no.	WPG[b]	OA[c] (g oil/g bagasse)
1:20	120	1.5	0%	1	7.2	8.9
1:20	50	5.0	1.0% NBS[d]	2	9.5	11.4
1:20	50	16.0	1.0% NBS	3	15.6	16.4
1:20	30	28.0	1.0% NBS	4	13.4	15.6
1:20	30	72.0	1.0% NBS	5	16.8	16.9
1:20	80	3.5	1.0% NBS	6	21.4	18.2
1:20	100	1.5	1.0% NBS	7	22.6	18.8
1:20	120	1.5	1.0% NBS	8	26.8	21.5
1:20	80	2.0	0.5% NBS	9	14.3	16.0
1:20	80	2.0	1.0% NBS	10	18.7	17.6
1:20	80	2.0	1.5% NBS	11	22.3	18.8
1:20	80	2.0	2.0% NBS	12	20.7	17.9
1:20	80	2.0	2.5% NBS	13	16.0	16.6
1:20	80	2.0	3.0% NBS	14	16.0	16.5
1:20	80	2.0	1.0% DMAP[e]	15	18.7	17.7
1:20	80	2.0	1.0% MPI[f]	16	9.7	12.1
1:20	80	2.0	1.0% MPO[g]	17	3.3	7.2
1:20	80	2.0	1.0% pyridine	18	7.0	9.6
1:20	80	2.0	0.5% H_2SO_4	19	10.0	13.2

[a]Solid to liquid ratio represents ratio of dried sugarcane bagasse (g)/acetic anhydride (ml).

[b]WPG represents the weight percent gain of sugarcane bagasse due to acetylation and it was calculated according to: WPG (%) = [(weight gain/original weight)] × 100.

[c]Abbreviation for oil absorptivity (g oil/g acetylated bagasse).

[d]Abbreviation for N-bromosuccinimide.

[e]Abbreviation for 4-dimethylamino pyridine.

[f]Abbreviation for N-methyl pyrrolidine.

[g]Abbreviation for N-methyl pyrrolidinone.

synthetic acylations, having a specific catalytic activity about 10^4 times greater than that of pyridine, but it is expensive and not commercial available [22]. In this study, NBS was, therefore, used as a possible acetylation catalyst. As can be seen from Table I, addition of 1.0% NBS (sample 10) or DMAP (sample 15) in the reaction system at 80°C for 2.0 h resulted in the highest WPG (18.7%) as compared to other catalysts, such as MPI (WPG 9.7%), MPO (WPG 3.3%), pyridine (WPG 7.0%), and 0.5% H_2SO_4 (WPG 10.0%). The current results indicated that both 0.5% H_2SO_4 and MPI are the better catalysts than MPO and pyridine. Clearly, NBS or DMAP is the best one studied in the acetylation of SCB under the mild conditions. More importantly, NBS is an inexpensive and commercially available reagent, and the reactions are clean and no detectable by-products was found. Therefore, NBS can be used as a novel and highly effective catalyst for acetylation of SCB fibres with acetic anhydride under mild reaction conditions.

In addition to various catalysts used in the reaction, the effect of reaction time and temperature was also studied. As the data shown in Table I, at 50°C the WPG increased from 9.5% (sample 2) to 15.6% (sample 3) when the reaction duration was increased from 5.0 to 16 h. Similarly, under an extremely mild reaction condition (30°C, samples 4 and 5), an increment of reaction time from 28 to 72 h resulted in an increase of the WPG value by 3.4%. This increment of degree of acetylation by prolonging the reaction time was a direct consequence of the favourable effect of time on diffusion and adsorption of the reactants between the acetic anhydride and the SCB fiber. Furthermore, as the data given in Table I, an increase of reaction temperature from 100 to 120°C led to an increment of the WPG from 22.6% (sample 7) to 26.8% (sample 8).

As a primary and first study of acetylation of SCB fibres as novel oil sorption-active materials using NBS as a catalyst in a solvent free system, the actual role of NBS is not clear but a plausible explanation is that NBS might act as a source for Br^+, which in turn activates the carbonyl groups of acetic anhydride to produce the highly reactive acylating agent ($CH_3-CO-N-(OCCH_2CH_2CO-)$. This acylating agent reacts with hydroxyl groups of SCB, which upon elimination of NBS produces acetylated SCB ($SCB-O-CO-CH_3$) (Scheme 1) [12]. However, the actual role of this reagent should be further studied in detail.

3.2. FT-IR spectra
FT-IR spectra of unmodified SCB (spectrum 1) and acetylated SCB (spectrum 2, sample 6), prepared with 1.0% NBS as a catalyst at 80°C for 3.5 h, are depicted in Fig. 1. Obviously, the acetylated SCB spectrum 2 is characterized by the occurrence of three important ester bands at 1745, 1367, and 1242 cm^{-1}, which are attributed to absorption by carbonyl bonds (C=O ester), C—H stretching ($-C-CH_3$), and C—O stretching in esters ($-O-C-CH_3$), respectively. In contrast, a decrease in the intensity of the O—H absorption band at 3430 cm^{-1} in spectrum 2 indicated that the hydroxyl group contents in SCB were reduced after reaction. This increase in carbonyl absorption and a decrease in free
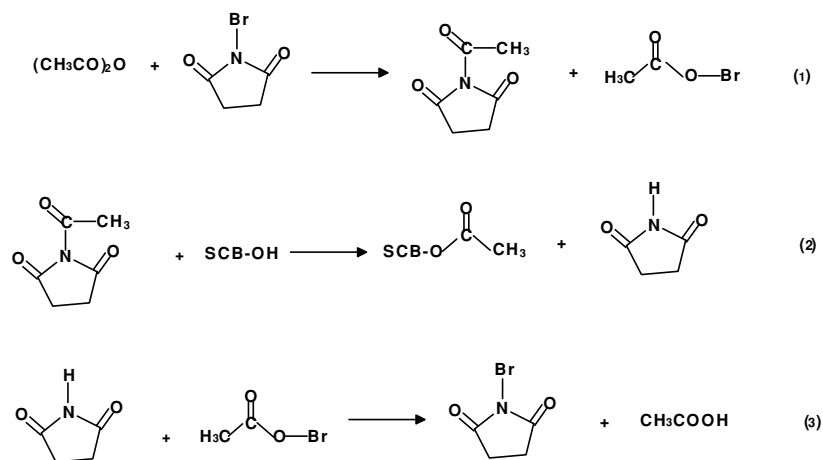
Scheme 1 Mechanism of acetylation of sugarcane bagasse using NBS as a catalyst.
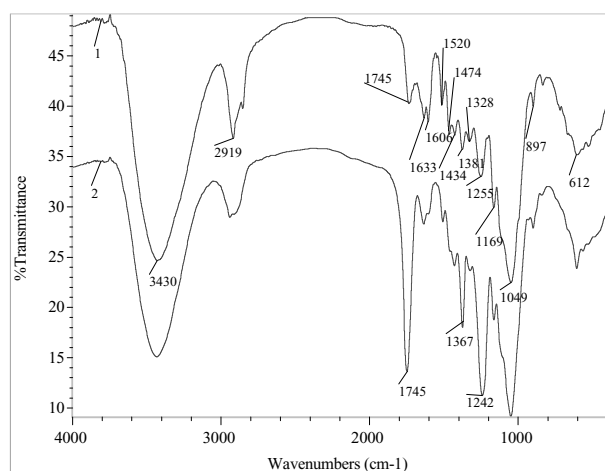

Figure 1 FT-IR spectra of unmodified sugarcane bagasse (spectrum 1) and acetylated sugarcane bagasse sample 6 (spectrum 2) prepared at 80°C for 3.5 h with 1.0% NBS as a catalyst.
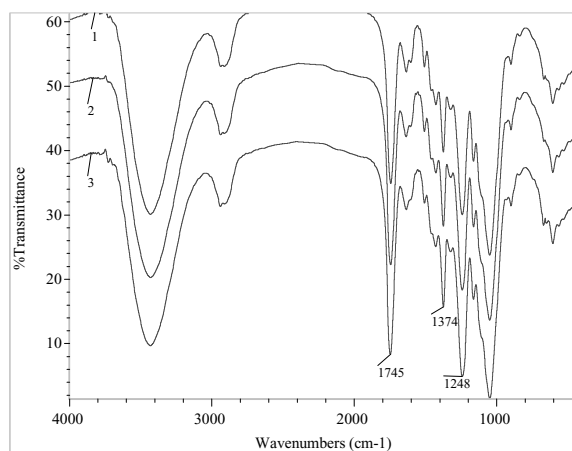

Figure 2 FT-IR spectra of acetylated sugarcane bagasse samples prepared at 80°C for 2 h with 0.5% NBS (spectrum 1, sample 9), 1.0% NBS (spectrum 2, sample 10), and 1.5% NBS (spectrum 3, sample 11) as a catalyst.

hydroxyl group peak confirmed the formation of ester bonds [23]. Another strong band at 1049 cm^{-1} in both spectra is assigned to C—O stretching in C—O—C linkages. A small bands at 1633 cm^{-1} arises from the absorbed water. The sharp band at 897 cm^{-1} is originated from the β-glucosidic linkages between the sugar units. Four intensive bands at 1606, 1520, 1474, and 1434 cm^{-1} correspond to the aromatic ring vibrations and ring breathing with C—O stretching in lignins [24]. As to be expected, the absence of absorption region 1840–1760 cm^{-1} in spectrum 2 stated that the products are free of the unreacted acetic anhydride. The lack of peaks at 1700 cm^{-1} for carboxylic group revealed that the products are also free of the by-product of acetic acid.

The effect of NBS concentration and different catalysts on the WPG was also investigated by the peak intensity of acetylated SCB samples. As illustrated in Fig. 2, an increment in NBS concentration from 0.5 (spectrum 1, sample 9) to 1.0 (spectrum 2, sample 10), and to 1.5 h (spectrum 3, sample 11) led to an increment in the intensity of the three ester bands at 1745, 1374, and 1248 cm^{-1}, but a decrease in OH stretching, indicating an increae in the level of acetylation, corresponded to the increasing WPG from 14.3 to 18.7, and

to 22.3%, respectively. Similarly, the intensity of the ester carbonyl absorbance at 1745 cm^{-1}, a frequency for C—O stretching in acetic groups at 1248 cm^{-1}, and CH$_3$ bending of the acetic groups at 1381 cm^{-1} in Fig. 3 parallel well the values of WPG between sample 15 and
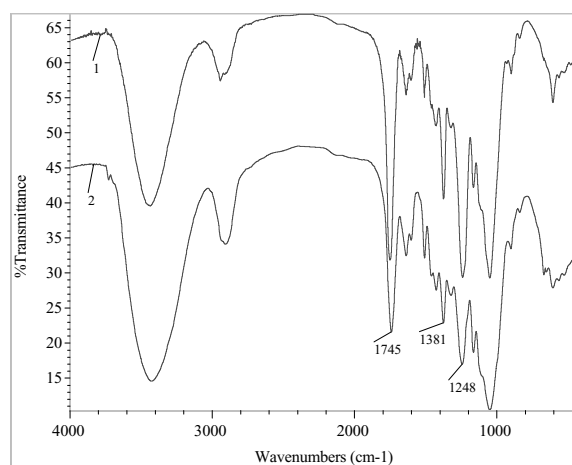

Figure 3 FT-IR spectra of acetylated sugarcane bagasse samples prepared at 80°C for 2 h with 1.0% DMAP (spectrum 1, sample 15) and 1.0% MPO (spectrum 2, sample 17) as a catalyst.
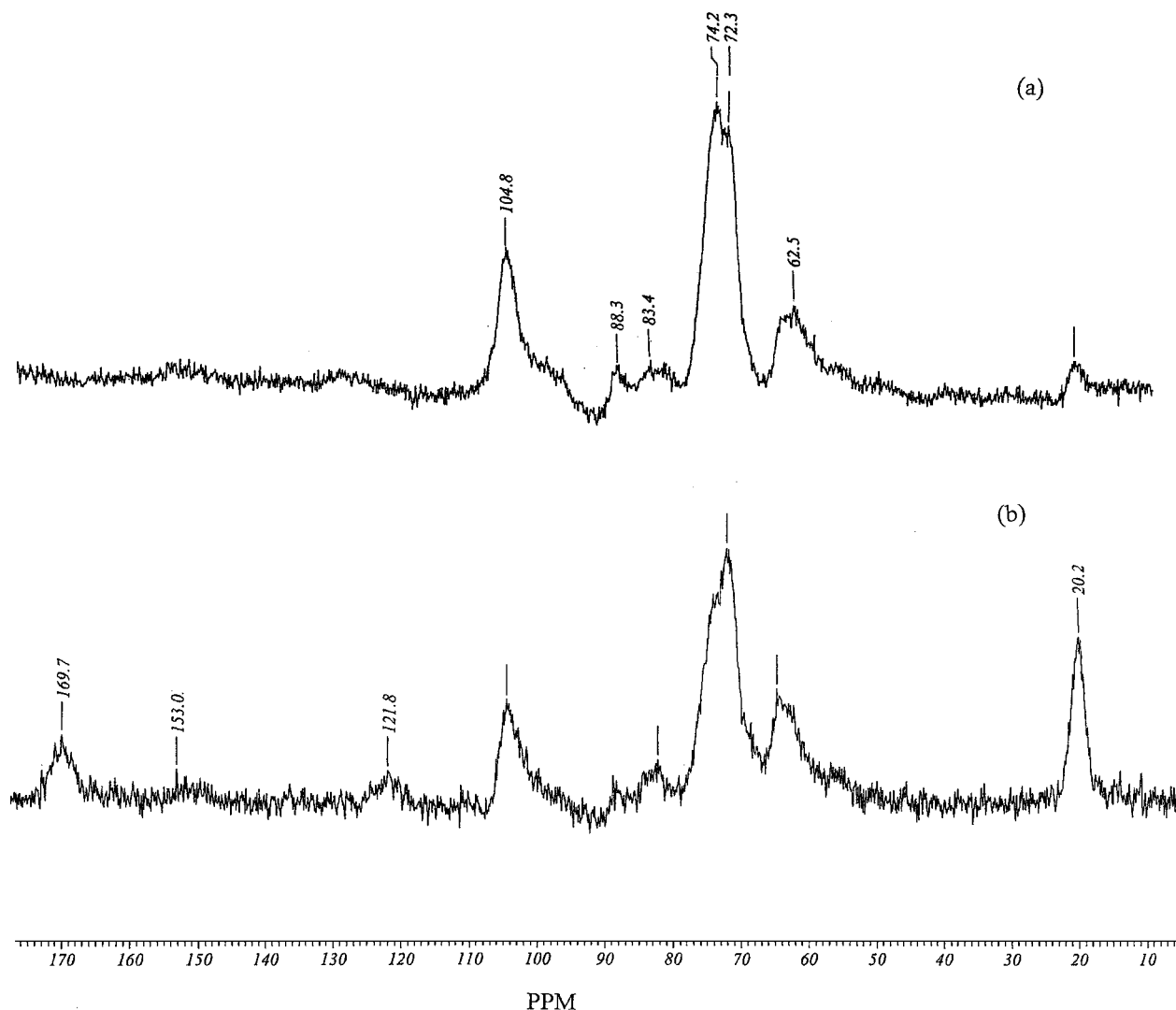
Figure 4 CP MAS ^{13}C-NMR spectra of un-modified sugarcane bagasse (spectrum a) and acetylated bagasse sample 11 (spectrum b) prepared at 80°C for 2.0 h with 1.5% NBS as a catalyst.

17 in Table I. This demonstrated again that DMAP is more efficient than MPO for the acetylation of SCB in a solvent free system, however, DMAP is too expensive and not commercial available, which limits its industrial application.

3.3. CP MAS ^{13}C-NMR spectra

CP MAS ^{13}C-NMR spectroscopy is more attractive technique for the characterization of the lignocellulosic materials and is capable of providing detailed information directly on solid samples [25]. Fig. 4 shows the CP MAS ^{13}C-NMR spectra of both un-modified SCB (spectrum a) and acetylated SCB sample 11 (spectrum b), prepared at 80°C for 2.0 h with 1.5% NBS as catalyst. Evidently, in spectrum b the methyl band of the acetyl groups at 20.2 ppm and the carbonyls of the acetyl groups at 169.7 ppm indicated the presence of acetyl groups and occurrence of acetylation in sample 11. It would be expected that the both spectra would be very similar in the carbohydrate region (60–110 ppm), namely C-1 (104.8 ppm), C-4 (88.3 ppm, crystal cellulose, and 83.4 ppm, amorphous cellulose or less ordered surface cellulose molecules), C-2, C-3 (74.2 ppm) and C-5 (72.3 ppm), and C-6 of cellulose and C-5 of xylan

(62.5 ppm) [25]. However, a close examination of the two spectra revealed a noticeable difference between the carbohydrate regions. A decrease in the intensity of the C-2 and C-3 bands in the spectrum of acetylated SCB suggested that acetylation at C-2 and C-3 might have occurred. This is important because it infers that in the SCB itself, reactions of acetic anhydride on SCB carbohydrates do occur. A similar observation has been reported by Ohkoshi *et al.* [26] in the acetylation of wood polysaccharides. The authors reported that the cellulose in the wood was less reactive than the xylan, and the increase in WPG increased the di-substitution in the xylan.

3.4. Thermal analysis

Fig. 5 shows the thermograms of un-modified SCB (a) and acetylated SCB samples prepared at 80°C for 2.0 h with 0.5% NBS (b, sample 9) and 1.5% NBS (c, sample 11) as a catalyst. As can be observed from the figure, the native SCB starts to decompose at 233°C, while the two acetylated SCB samples 9 and 11 begin to decompose at 200°C. At 50% weight loss, the decomposition temperature occurs at 316°C for native SCB, 314°C for acetylated SCB sample 9, and 310°C for acetylated
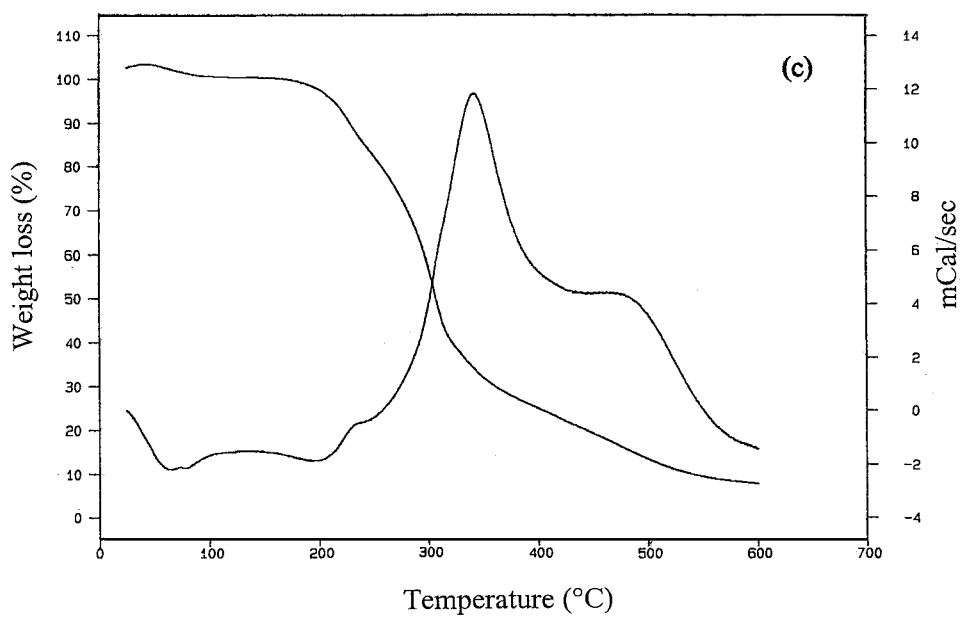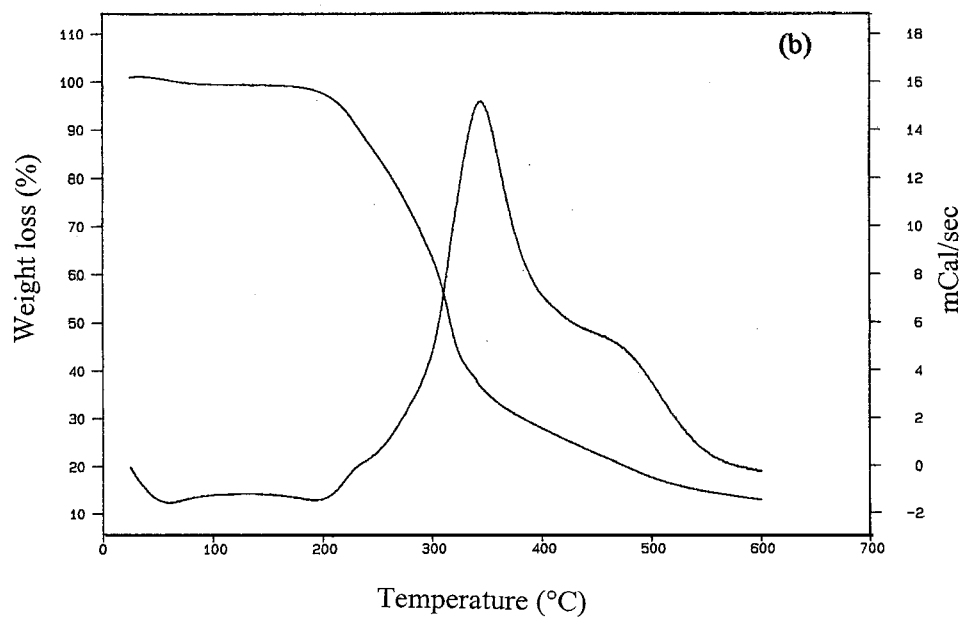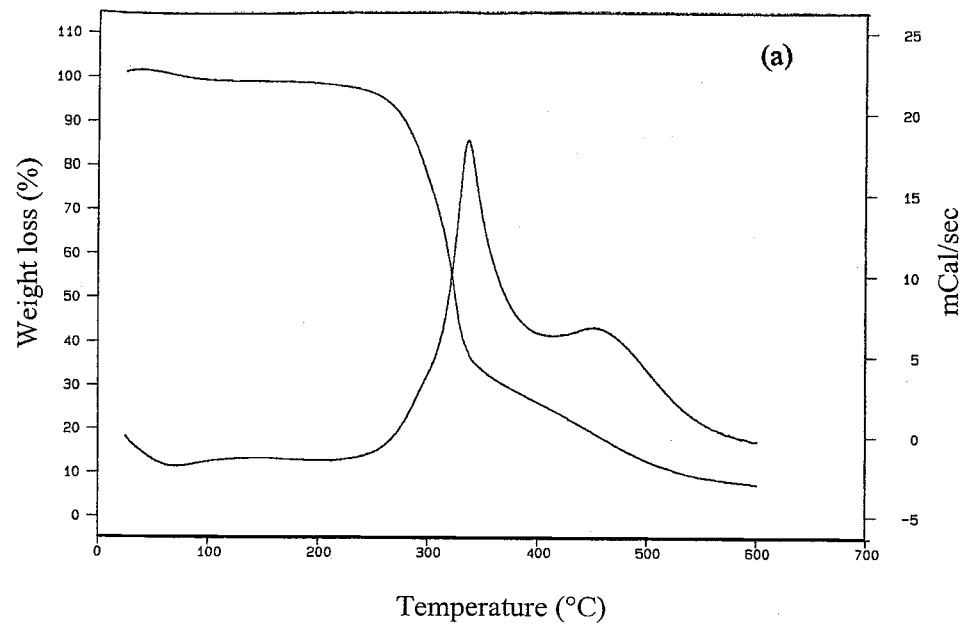
Figure 5 The thermograms of native sugarcane bagasse (a) and acetylated bagasse samples prepared at 80°C for 2.0 h with 0.5% NBS (b, sample 9) and 1.5% NBS (c, sample 11) as a catalyst.

SCB sample 11. This decreasing trend of decomposition temperature implies that the thermal stability of the acetylated SCB is lower than that of the un-modified SCB, but the thermal stability of the acetylated SCB over to 200°C is satisfactory.

In general, DSC is used to investigate the possibility of interaction between both components and measure the extent of disruption of the hydrogen bonds as well as quantify the heat energy flows [27]. As illustrated in Fig. 5, the exothermic peak, which represents heat released from the sample, was observed at a maximum temperature of 341°C for both un-modified SCB and two acetylated SCB samples due to the disintegration of intramolecular interactions and the decomposition of the polymer. It should be noted that the occurrence of asymmetric exothermic peaks in all of the samples were probably due to overlapping endothermic responses from both unreacted SCB and the reaction product [28].

3.5. Oil absorptivity

Acetylation of SCB resulted in a significant increase in acetyl groups. The esterified SCB was, therefore, significantly hydrophobic and did not wet with water in the absence of an organic solvent. The oil absorptivity of the acetylated SCB materials was examined using machine oil and the data are given in Table I. The oil was suspended in water and treated with acetylated SCB. It was found that the machine oil in water was immediately absorbed by the acetylated SCB, which did not absorb water. The capacity of oil absorbence of the samples 2–14 prepared using NBS as a catalyst, was 11.4–18.8 g/g of acetylated SCB, which is, in general, proportional to the degree of acetylation as shown by the WPG values. As expected, the oil sorption capacities of the acetylated SCB were higher than those of the synthetic sorbents such as polypropylene fiber (∼10 g oil/g synthetic material) [13]. In addition, it was found that the sorbed machine oil can be recovered from the acetylated SCB products by a simple mechanical action such as a simple squeezing operation and the sorbents can be reapplied several times for oil cleanup. The acetylated SCB when used as absorbents have the characteristics of low cost, high capacity, quick uptake, and are easy to desorb. This suggested that a total or partial substitution of commercial synthetic oil sorbents by acetylated SCB materials could be beneficial in the oil spill cleanup operation by improving the efficiency of oil sorption and by incorporation other advantages such as biodegradability. These novel oil sorption-active materials could be used effectively to recover oil spilled in bodies of refining or heavy industrial waste water, and the water such as in lakes, rivers, and oceans. Further studies to elucidate the mechanism of oil absorption by the acetylated SCB are necessary.

4. Conclusions

In short, the acetylation of the free hydroxyl groups in the cell walls of SCB fiber with acetic anhydride using NBS as a catalyst in a solvent free system represents a convenient and effective method for the preparation of SCB fiber acetates having a more hydrophobic characteristic. The use of NBS instead of DMAP as an acetylation catalyst is advantageous because the NBS catalyst is an inexpensive and commercial available reagent. It is very likely that NBS is a novel and highly effective catalyst for acetylation of SCB fibres under extremely mild conditions such as at 30°C. The weight percent gain increased with increments of reaction time and temperature and NBS concentration from 0.5 to 1.5%. Under a mild reaction condition (80°C, 2.0 h, 1.0% NBS), a higher WPG value of 18.7% was obtained in the solvent free system. The thermal stability of acetylated SCB fiber was slightly lower than that of the unmodified SCB fiber, but a thermal stability over to 200°C is satisfactory. More importantly, Acetylation significantly increased the oil sorption capacity of SCB fibre. It was shown that with the aid of suitable mechanical retrieval equipment, sorbed oil can be recovered from the modified SCB fibre so that the sorbents can be recycled several times for oil spill cleanup. These results indicated that a total or partial substitution of commercial synthetic oil sorbents by acetylated SCB fibre could be beneficial in the oil spill cleanup operation by improving the efficiency of oil sorption and the sorbents' biodegradability.

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