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Esterification of cellulose from sugarcane bagasse by some long- chain acid chlorides

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Abstract

In recent years there is a growing urgency to develop renewable biodegradable materials for various applications, and to replace petroleum-based materials. This study aimed to extract cellulose as raw material from Sudanese sugarcane bagasse (SCB) to prepare cellulose esters. The (SCB) sample was collected, grounded, dewaxed, delignified and purified. The pure cellulose was solubilized using N,N-Dimethylacetamide / Lithium Chloride (DMA/LiCl) solvent system at 160 °C. Cellulose esters were prepared by the reaction of solubilized cellulose with long chain acid chlorides namely myristoyl (C_{14}), palmitoyl (C_{16}) and oleoyl (C_{18}) which is unsaturated, in the presence of triethylamine for proton capture at optimum reaction condition. The produced cellulose esters were characterized using different instruments and methods. Elemental analysis was carried out to confirm the degree of substitution (DS), the results shows that the DS value increases as the chain length increases. Fourier transfer Infra-Red spectroscopy (FT-IR) provide evidence of acylation by the presence of ester carbonyl groups and decrease of the band of the hydroxyl group. Thermogravimetrical analysis (TGA) was used to study the thermal stability of prepared cellulose esters which showed that the prepared esters have different thermal stability depending on DS value and chain length at the substitution position. The results show significant changes occur in the structure and thermal stability of cellulose by esterification and the produced esters can be more useful than pure unmodified cellulose.

Keywords: sugarcane bagasse, cellulose esters, delignification, dissolution and esterification

1. Introduction

Nature has provided a wide variety of materials to help improve and sustain the health of all living things either directly or indirectly. Naturally occurring polymeric materials have advantages over synthetic ones and they can be modified in different ways (Jani *et al*., 2009) [3].

The reutilization of natural organic residues to obtain an applicable product is a very useful practice that has many advantages. There has been an increasing trend towards more efficient utilization of agro-industrial residues, such as sugarcane bagasse (SCB) as raw materials for industrial applications (Silva *et al*., 2012) [7].

Sugarcane is the common name of a species of herb belonging to the grass family. The official classification of sugarcane is Saccharum officinarum, and it belongs to the family Gramineae (Nigam and Pandey, 2009) [6]. Sugarcane bagasse (SCB) is a residue produced in large quantities by the sugar industry, it is the fiber left over after the juice has been squeezed out of sugarcane stalks, it is the major by-product of the sugarcane industry. For each 10 tons of sugarcane crushed sugar factory's produces nearly three tons of wet bagasse that may causes environmental problems. (SCB) is a very promising raw material for the production of glucose, xylose, ethanol and methane (Guilherme *et al*., 2015) [1].

Lignocellulosic biomass including (SCB) is the most abundant organic material in the world and it has the potential to be a very promising alternative source of fuels and chemicals (Maitan *et al*., 2015) [5]. About 40 – 50% of sugarcane bagasse is the glucose polymer cellulose, much of Which is in a crystalline structure. Another 25 – 35% is hemicelluloses, an amorphous polymer usually composed of xylose, arabinose, galactose, glucose, and mannose. The remainder is mostly lignin (18– 24%) plus lesser amounts of mineral (1– 4%), wax (<1%), and other compounds (Sun *et al*., 2004) [8] (Wirawan *et al*., 2012) [11].

Cellulose is an unbranched polymer composed of glucose monomer linked by β-1,4 glycosidic bonds (Figure (1)). The fundamental and derived properties of cellulose derivatives are presented concomitantly with applications in various fields. Cellulose derivatives have been widely used as coatings, optical films, fibers, molded objects, and matrices for controlled release (Zheng, 2014) [13].

Esterification cellulose is one of the most important methods to functionalize cellulose. Cellulose esters are commonly obtained by esterification of cellulose with a carboxylic acid, acid anhydride, or acyl chloride in the presence of a catalyst (Hegner *et al*., 2010) [2].

The formation of ester cross-links in cellulosic or lignocellulosic composite materials during drying and heating is of interest for production of paper and wood composite boards, for wood modification and in giving cotton materials improved characteristics (Pantze, 2006). Cellulose esters are widely produced as commercial products (Yuan *et al*., 2005) [12].

The longer-chain saturated and unsaturated fatty acids esters of cellulose have been previously prepared. However, little characterization of these materials has been presented with respect to their plastic and physical properties (Wang and Tao, 1995) [10].

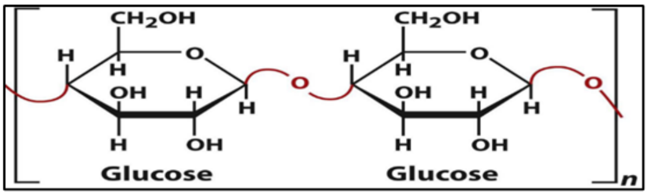


Fig 1: The structure of Beta (1-4) glycosidic Bond

2. Materials and Methods

2.1 Materials

2.1.1 The sample

The sample of this study was sugarcane bagasse (SCB) collected from Guneid Sugar Factory, Gezira state, Sudan. The (SCB) sample was washed with water, dried and cut into small pieces and grounded.

2.1.2 Reagents and Solvents

The reagents used in this study were hydrogen peroxide, triethylamine from Central Dug House (P) Ltd (CDH). Myristoyl chloride ($CH_3(CH_2)_{12}COCl$), Palmitoyl chloride ($CH_3(CH_2)_{14}COCl$), Oleoyl chloride ($CH_3(CH_2)_7$ CH = CH $(CH_2)_7COCl$), were obtained from Sigma Aldrich, USA.

The solvent system used in this study was N, N-Dimethylacetamide (DMA) (obtained from Merck KGaA, Darmstadt, Germany) / Lithium Chloride (LiCl) obtained from Oxford Lab Chem. Ethanol absolute obtained from CARLO.ERBA Milan, Italy.

2.1.3 Elemental Analysis

Elemental analysis (EA) was used for the DS determination of cellulose esters was carried out using LECO CHNS- 932 elemental analyzer in the Petroleum Laboratories Research and Studies (PLRS) Khartoum, Sudan.

2.1.4 Fourier Transfer Infra-Red Spectra (FT-IR)

FT-IR spectra were performed for determination of the structures of cellulose and cellulose esters using Shimadzu FT-IR 8400 S. CE instrument using potassium bromide (KBr) discs, at the Central Research Laboratory, University of Khartoum, Sudan.

2.1.5 Thermogravimetrical Analysis (TGA)

TGA was performed in a TGA Linseys PT 1000 Simultaneous Thermal Analyzer. Measurements of thermal stability of cellulose myristate, cellulose palmitate and cellulose oleoate were carried out at ramp 2.00 ^{O}C ⁄ min to 600 ^{O}C⁄ min using a platinum pan, the sample gas was oxygen flow was 60 ml ⁄min^{-1} and the balance gas flow was nitrogen 50 ml/min. All samples were at the powdered form. Measurements were carried out in the laboratory of chemistry, Faculty of Science. Al-Neelain University, Sudan.

2.2 Methods

2.2.1 Dewaxing of sugarcane bagasse (SCB)

20 g of the dried powder of sugarcane bagasse (SCB) was dewaxed using a Soxhlet apparatus with toluene/ethanol (2:1, V/V) for 6 h, then, it was dried in an oven at 60 °C for 16h.

2.2.2 Delignification and Purification of Sugarcane Bagasse (SCB)

The method of delignification of sugarcane bagasse (SCB) described by (Sun, 2010) [9] was followed. The sample of dewaxed sugarcane bagasse (SCB) was treated with 2.0% H_2O_2 at pH of 11.8 at 48^{o}C for 16 h with stirring. After filtration, the insoluble residue (delignified cellulose) was purified with a mixture of 80% acetic acid and 70% nitric acid (1:1, V/V) at 100^{o}C for 20 min, then it was washed with 95% ethanol, and distilled water until neutralization (detected by litmus red paper). Delignified, purified cellulose was dried in an oven at 60^{o}C for 16 h.

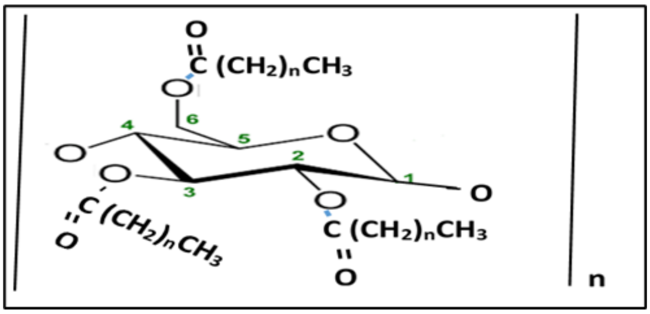
2.2.3 Dissolution of Cellulose

0.25 g of delignified and purified cellulose was placed in a 250 ml conical flask and 25 ml of N, N-Dimethylacetamide (DMA) were added. The mixture was heated at 160°C with stirring for 2 h using hot plate with magnetic stirrer. Then, the temperature was adjusted to 100°C, and 2 gm of lithium chloride (LiCl) were added under stirring for an hour. Then the mixture was cooled and left with stirring at room temperature for several hours (about 9 hours) until dissolution was completed.

2.2.4 Preparation of Cellulose Esters

2 ml of trimethylamine for proton capture were added to (1%) cellulose solution in N, N-Dimethylacetamide/Lithium chloride (DMA/LiCl). Then, 2 ml of the acid chloride (myristoyl chloride, palmitoyl chloride and oleoyl Chloride) were added to the cellulose solution flask, and the mixture was stored for 24 hours to complete the reaction. All these steps were completed under stirring at room temperature.

The product of each cellulose myristate, cellulose palmitate as shown in Figure (2) and cellulose oleoate as shown in Figure (3) were precipitated into about 500 ml ice water and it was washed with ethanol, acetone and distilled water, and was kept at room temperature for three days and then was dried in an oven at 50°C for 10 hours. The amount yield and percentage of cellulose esters are shown in Table (1).



Note: n = 14 or 16

Fig 2: Structure of Theoretical Full Substitutional Cellulose Esters

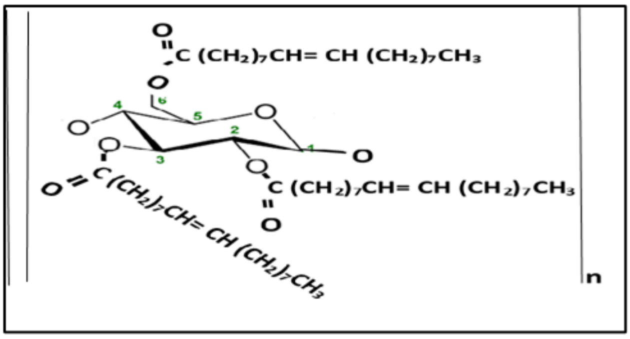


Fig 3: Structure of Theoretical Full Substitutional Cellulose Oleoate

Table 1: The Degree of Substitution, Amount

Cellulose Ester	Amount Yield(g)	Yield %
Cellulose Myristate	0.28	23.33
Cellulose Palmitate	0.31	23.84
Cellulose Oleoate	1.25	83.33

3. Results

The prepared cellulose esters (myristate, palmitate and oleoate) were subjected to elemental analysis, fourier transfer infra-red (FT-IR) spectroscopy, thermal analysis and solubility tests.

3.1 Results of Elemental Analysis and Determination of the Degree of Substitution

Dry ground samples of cellulose esters (myristate, palmitate and oleoate) were characterized by the elemental analyzer for the determination of the percentage of carbon in each molecule. The degree of substitution (DS) of cellulose esters were determined depending on carbon atoms percentage measured by elemental analysis and calculated (theoretical) percentage. The results shown in Table (2)

Table 2: Results of elemental analysis and the degree of substitution (DS) values of cellulose esters.

Cellulose esters	Measured (C%) value	Theoretical (C%) value	DS- value
cellulose myristate	49.42	63.16	2.75
cellulose octanoate	49.85	66.67	2.83
cellulose decanoate	56.91	69.23	2.66

3.2 Results of FT-IR Spectrum of Cellulose Myristate

Figure (2) shows FT-IR spectrum of cellulose myristate and Table (3) shows the resulting bands.

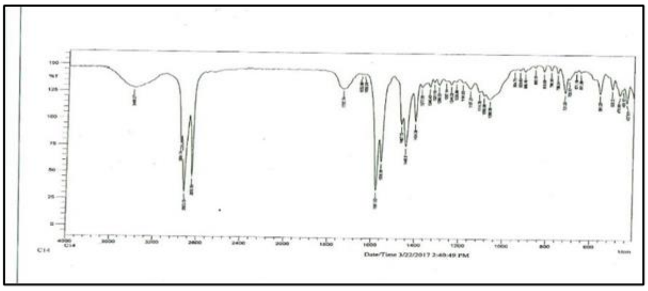


Fig 2: FT-IR Spectrum of Cellulose Myristate Ester

Table 3: Characteristic FT-IR Absorption Frequencies of Cellulose Myristate

The Functional Group	Type of Vibration	Absorption cm^{-1}	Peak Intensity
O-H	Stretching	3400.27	V, weak
CH_2 and CH_3	Stretching	2954.74 to 2850.58	Strong- sharp
C=O	Stretching	1737.74 1581.52	Weak, broad Strong, sharp
C-C	Stretching	1244.00	V, weak
four linearly connected –$(CH_2\text{-})_n$	Stretching	721.33	weak
C-O	Stretching	1157.21	medium

3.3 Results of FT-IR Spectroscopy of Cellulose Palmitate

Figure (3) shows FT-IR spectrum of cellulose palmitate and Table (4) shows the Characteristic FT-IR Absorption Frequencies.

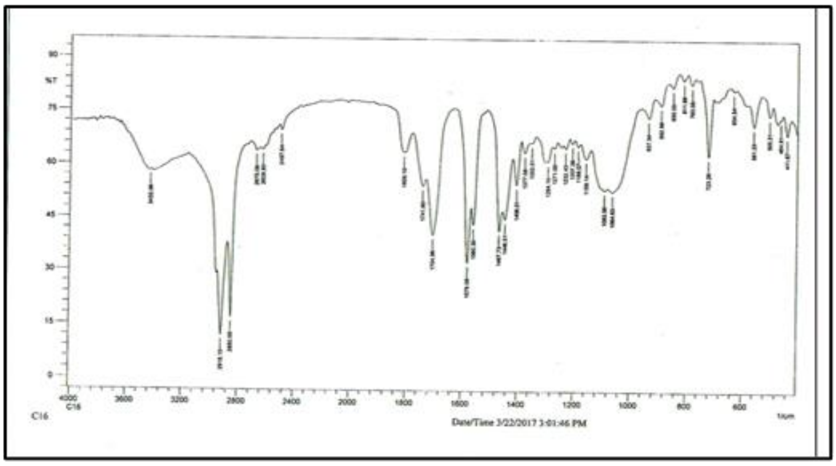


Fig 3: FT-IR Spectrum of Cellulose Palmitate Ester

Table 4: Characteristic FT-IR Absorption Frequencies of Cellulose Palmitate

The Functional Group	Type of Vibration	Absorption cm^{-1}	Peak Intensity
O-H	Stretching	3433.06	V, weak
CH_2 and CH_3	Stretching	2918.10 - 2850.50	Strong- sharp
C=O	Stretching	1704.96 1741.60 1579.59	Strong, sharp
C-C	Stretching	1232.34	V, weak
four linearly connected –$(CH_2\text{-})_n$	Stretching	723.26	Strong, sharp
C-O	Stretching	1188.07	weak

3.4 Results of FT-IR Spectrum of Cellulose Oleoate

Figure (4) shows FT-IR spectrum of cellulose oleoate and Table (5) shows the Characteristic FT-IR Absorption Frequencies

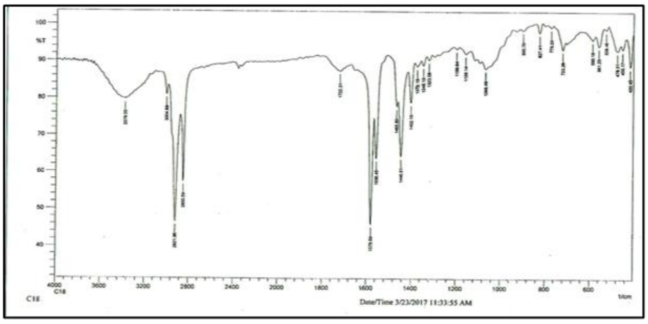


Fig 4: FT-IR Spectrum of Cellulose Oleoate Ester

Table 16: Characteristic FT-IR Absorption Frequencies of Cellulose Oleoate

The Functional Group	Type of Vibration	Absorption cm^{-1}	Peak Intensity
O-H	Stretching	3379.05	V, weak
=CH-	Stretching	3004.89	Weak
CH_2 and CH_3	Stretching	2921.96 to 2850.59	Strong- sharp
C=O	Stretching	1722.31 and 1579.59	Weak and Strong, sharp
C-C	Stretching	1232.34	V, weak
four linearly connected -CH_2-	Stretching	723.26	Strong, sharp
C-O	Stretching	1159.14	Weak

3.5 Results of TGA for Prepared Cellulose Esters

Figures from (5) to (7) and Table (6) show the results of TGA of prepared cellulose esters.

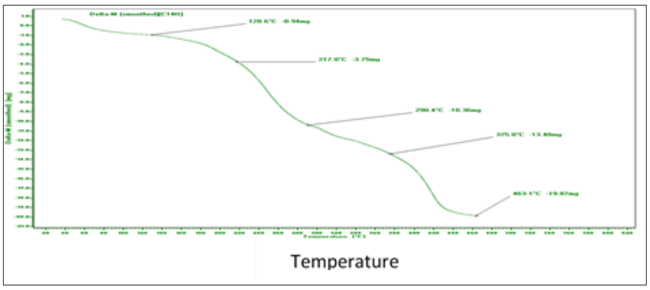


Fig 5: TGA Curve of Cellulose Myristate

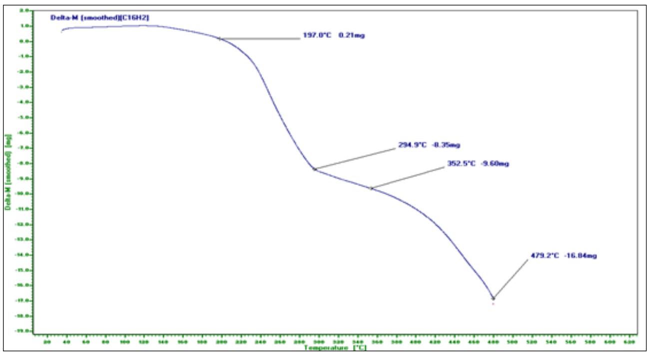


Fig 6: TGA Curve of Cellulose Palmitate

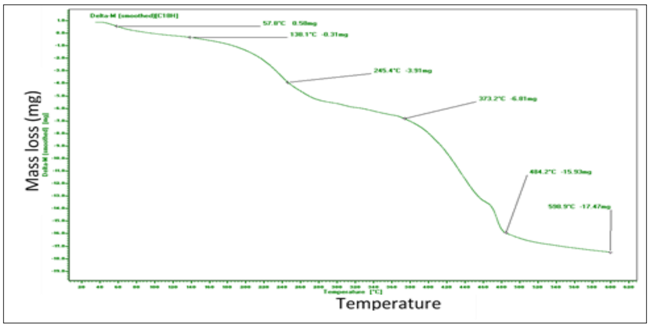


Fig 7: TGA Curve of Cellulose Oleoate

Table 6: shows the results of TGA of prepared cellulose esters

Ester	t(C⁰) of water loss and volatiles	t(C⁰) of decomposition	t(C⁰) of degradation	Mass loss (mg)	Mass loss (%)	DS-value
Cellulose myristate	128.5	217.0	375.0	13.40	67.00	2.75
Cellulose palmitate	197.0	294.9	352.5	09.60	48.00	2.83
Cellulose oleoate	138.1	245.4	373.2	6.81	34.05	2.66

4. Discussion

The results of elemental analysis show an increase of DS-value from cellulose myristate to cellulose palmitate as the number of carbon atoms increase, and the decrease of DS-value of cellulose oleoate with increasing number of carbon atoms (2.66), this may due to the double bond. DS- value of all three esters was high, indicates that esterification was efficient sines the maximum DS is (3).

The results of FT-IR spectroscopy of cellulose myristate shows relative efficiency of acylation compared with the spectrum of unmodified pure cellulose. The absorption intensity of hydroxyl group (OH) stretching characteristic band was decreased indicates that a large amount of hydroxyl group was substituted. The absorption bands from 2954.74 cm-1 to 2850.58 cm-1 are related to CH2- and CH3- groups associated to the myristoyl group. The characteristic peak around 1737.74 cm-1 and 1581.52 cm-1 gives evidence to presence of ester carbonyl absorption. The absorption at 1244.00 cm-1 is related to the stretching of (C-C) bonds. The peak at 1157.21cm-1 is characteristic of (C-O) stretching. The peak at 721.33 cm-1 is characteristic of at least four linearly connected –CH2-. That means fatty acid constituent have been directly connected to cellulose.

The results of FT-IR spectrum of cellulose palmitate show a very weak peak absorption for hydroxyl group stretching as expected for high degree of acylation. The absorption bands from 2918.10 cm-1 to 2850.50 cm-1 are related to methyl and methylene groups associated to the palmitoyl group. The absorption at 1704.96 cm-1, 1741.60 cm-1 and 1579.59 cm-1 shows an intense band of carbonyl (C=O) which indicated the formation of the ester group of high degree of substitution. The absorption at 1232.34 cm-1 is related to the stretching of (C-C) bonds. The peak at 1188.07 cm-1 is characteristic of (C-O) stretching. The peak at 723.26 cm-1 is characteristic of at least four linearly connected –CH2-. That means fatty acid constituent have been directly connected to cellulose in additional proof of the successful esterification of cellulose.

The FT-IR spectrum of cellulose oleoate shows a very weak peak absorption for hydroxyl group stretching as expected for high degree of acylation. The absorption bands from 2921.96 cm-1 to 2850.59 cm-1 are related to methyl and methylene groups associated to the oleoate substitution group. The absorption at 1722.31 cm-1 and 1579.59 cm-1 shows the band of carbonyl (C=O) which indicated the formation of the ester group. The peak at 1159.14 cm-1 is characteristic of (C-O) stretching. The peak at 3004.89 cm-1 is characteristic of (CH=CH-) stretching. The peak at 723.26 cm-1 is characteristic of at least four linearly connected –CH2-. That means fatty acid constituent have been directly connected to cellulose in additional proof of the successful esterification of cellulose.

The result of TGA of cellulose myristate indicated that its thermal stability is less than that of pure unmodified cellulose. Thermal stability of long- chain cellulose esters increases as the chain length increases, this fact known via the thermal decomposition temperature of cellulose palmitate. Cellulose oleoate shows less thermal stability than unmodified pure cellulose but it shows high thermal stability than cellulose palmitate. this is due to the lowest DS, unsaturation of the side chain and the chain length.

5. Conclusion

Cellulose polymer obtained from sugarcane bagasse can modified to prepare chemical compound used for deferent purposes. Significant changes occur in the structure and thermal stability of cellulose by esterification and the produced esters can be more useful than pure unmodified cellulose.

6. Acknowledgement

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7. References

1. Guilherme AA, Dantas PVF, Santos ES, Fernandes FAN, Macedo CR. Evaluation of composition, characterization and enzymatic hydrolysis of pretreated sugar cane bagasse, Brazilian J of Chem. and Eng. 2015; 32(1):32-33.
2. Hegner J, Pereira KC, DeBoef B, Lucht BL. Conversion of cellulose to glucose and levulinic acid via solid-supported acid catalysis. J Tetra. Lett. 2010; 51(17):2356-2358.
3. Jani GK, Shah DP, Prajapati VD, Jain VC. Gums and mucilages: versatile excipients for pharmaceutical formulations. Asian J of Pharm. Sci. 2009; 4(5):309-323.
4. Jandura P, Riedl B, Kokta BV. Thermal degradation behavior of cellulose fibers partially esterified with some long chain organic acids. Polymer Degradation and Stability. 2000; 70(3):387-394.
5. Maitan AGP, Visser EM, Alfenas RF, Nogueira BRG, DeCampos GG, Milagres AF, *et al*. The influence of pretreatment methods on saccharification of sugarcane bagasse by an enzyme extract from Chrysoporthe cubensis and commercial cocktails: a comparative study. J of Biores. And Tech. 2015; (192):670-676.
6. Nigam PSN, Pandey A. (Eds.)., Biotechnology for agro-industrial residues utilisation: utilisation of agro-residues. Springer Science and Business Media, 2009.
7. Silva AJP, Lahr FAR, Christoforo AL, Panzera TH. Properties of sugar cane bagasse to use in OSB. Intern. J of Mater. Eng. 2012; 2(4):50-56.
8. Sun JX, Sun XF, Zhao H, Sun RC. Isolation and characterization of cellulose from sugarcane bagasse. Polymer degradation and stability. 2004; 84(2):331-339.
9. Sun R. Cereal straw as a resource for sustainable biomaterials and biofuels: chemistry extractives, lignins, hemicelluloses and cellulose. 1st edition, Elsevier, 2010.
10. Wang P, Tao BY. Synthesis of cellulose-fatty acid esters for use as biodegradable plastics. J. of Poly. and The Enviro. 1995; 3(2):115-119.
11. Wirawan R, Sapuan SM, Yunus R, Abdan K. Density and water absorption of sugarcane bagasse-filled poly (vinyl chloride) composites. Polymers & Polymer Composites. 2012; 20(7):659.
12. Yuan H, Nishiyama Y, Kuga S. Surface esterification of cellulose by vapor-phase treatment with trifluoroacetic anhydride. Cellulose journal. 2005; 12(5):543-549.
13. Zheng X. Regioselective Synthesis of Cellulose Esters. Dissertation for (Ph. D) faculty of the Virginia Polytechnic Institute and State University, 2014.