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Hemicelluloses addition to improve the physical and mechanical properties of different pulps as a green procedure

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ABSTRACT

One of the most effective ways to prevent generation of wastes is to make sure that insofar as possible all materials involved in making a product should be incorporated into the final product[1]. In this work we use new trend "green Chemistry" which we isolate hemicellulos from agriculture waste and renewable feedstock as Bagasse and Cotton Stalks to prevent pollutions, use less hazardous chemical, saver solvents and auxiliaries. The aim of this work was to investigate the extent to which hemicelluloses and different fillers additives can be improved by mechanical and physical properties in both paper and viscose pulp. Hemicelluloses are extracted by aqueous alkali. Hemicelluloses extracted from holocellulose and from acid hydrolysis liquor (Liquor of Prehydrolysis). Viscose grade pulp from depithed bagasse; barked and debarked cotton stalks were prepared after prehydrolysis and pulping with NaOH. Bagasse, barked and debarked cotton stalks viscose grade pulps were bleached with green procedure and classical bleaching agents as well as the mechanical and physical properties were studied. The doses of bleaching agent in case of depithed bagasse pulp is lower than cotton stalks pulp. This is due to the higher lignin content in cotton stalks pulp. The addition of hemicellulose, during the beating process, to both viscose and paper grade pulps improved the physical and mechanical properties of produced paper sheets, where the breaking length increases from 2490 to 3050 m, Burst factor increases from7.6 to13.6 and Tear factor also increase 15.7 to 35.1 in viscose grade pulp (Low Hemicellulose content). We study the effect of adding different fillers such as Oxidized starch, polymer (polymin SK) and $CaCO_3$ to bleached bagasse paper grade pulp and the Physicomechanical properties of paper sheets will studied.

KEYWORDS

Green Chemistry;
Hemicelluloses addition;
Improved the physical and mechanical properties of paper sheets.

INTRODUCTION

Fibrous raw material

Bagasse has more heterogeneous structure than wood. It contains about 65%of its weight central and vascular bundles, which are composed of fiber and vessel elements. It contains also 25% of its weight pith cells and 10% soluble matters.

Adepithing step is, therefor, usually applied and prior to pulping process in order to eliminate these" non fibrous" materials. Pulping of bagasse was carried with soda[2] or with Kraft cooking liquor[3] and by batch or continuous system. Comparing with softwood, bagasse has lower ?-cellulose and higher pentosans. Nonwood raw materials account for 5-7% of the worldwide production of paper pulp[4]. The production of this type of pulp has increased more rapidly than that of pulp from wood in last two decades. By a factor of about two in Latin America and three in Africa and the middle East[5]. In Egypt no forests. Cotton Stalk is one of the agricultural residues available for pulping and papermaking[6]. Cotton Stalks are available in large quantities in several parts of the world. The stalks contain a substantial percentage of pith cells which together with the dark-colored outer bark, create problems in both pulping and papermaking processes. Fibrous raw material such as wood or agricultural residues consists of three dominating polymers; cellulose, hemicelluloses and lignin, so it called as lignocellulosic material. Hemicelluloses are any of several polysaccharides that are more complex than a sugar and less complex than cellulose, i.e. intermediate in complexity between sugar and cellulose that hydrolyze to mono-saccharides more readily than cellulose. It was found in plant cell walls and produced commercially from grain hulls, DP range from 50-300. Hemicellulose is class of plant cell wall polysaccharide that can be extracted by aqueous alkali. Includes xylan, glucuronoxylan, arabinoxylan, arabinogalactan II, glucomannan, xyloglucan and galactomannan part of the cell wall matrix a polysaccharide found in plant cell walls. Previous studies[7]. Have demonstrated a relationship; between the degradation of hemicellulose components, such as arabinose and mannose, and wood strength losses. The significant reduction in strength observed during incipient decay is therefore likely to be due to hemicellulose decomposition. In softwoods there are two principal hemicelluloses: galactogluco-mannan (70% mannan), which makes up approximately 60% of the total hemicellulose content, and arabino-4-O-methylglucuronoxylan (65% xylan), which constitutes the remaining 40%. Thus the amount of galactose/mannan and arabinan/xylan can be used to estimate the quantities of the major and minor, respectively, hemicellulose component of the wall[8-9]. Some monomers of hemicellulose are shown in the sketch, which show that hemicellulose consists mainly of sugars and sugar acids. Usually, all of the pentoses are present. There may even be small amounts of L-sugars. Note that there are hexoses as well as acids formed by oxidation of sugars. Mannose and mannuronic acid tend to be present, and there can be galactose and galacturonic acid. The pentoses are also present in rings (not shown) that can be 5-membered or 6-membered. Xylose is always the sugar present in the largest amount. In contrast to cellulose that is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base, but nature provides an arsenal of hemicellulase enzymes for its hydrolysis. These enzymes are commercially important because they open the structure of wood for easier bleaching, and older methods of bleaching consume larger amounts of chemicals such as chlorine that are bad for the environment

Effects of fillers

There are several reasons why fillers are used in papermaking. The main reasons are their low cost compared to fibre and their ability to improve optical properties in the final product. Fillers can also improve surface properties of paper and by that have a positive effect on the printability of the final product. The use of fillers however brings also many challenges in papermaking. Fillers have poor binding capacity which limits their use. Poor binding results in lower strengths in paper[10]. Perhaps the most important reason to use fillers is the lower cost compared to fibre raw material. The price of bleached chemical fibre is roughly five to seven times as much as filler prices. Even recycled and deinked pulp (DIP) is more than twice as expensive as common fillers. The great price advantage of filler easily makes a papermaker to think possibilities on how to use more filler instead of fibres[11].

Fillers improve the optical properties of paper or paperboard in many ways. They improve such properties as opacity, brightness and colour. Opacity is increased because of filler particles scatter light well. Amount of light scattering is dependent on the size and shape of the filler particles, the refraction index of filler and the amount of pigmentair interfaces present in the product. Therefore e.g. very small and flat filler particles are optimal for obtaining opacity. With the use of fillers brightness and colour of the final product can be controlled. The brightness and colour values of fillers typically beat the values of fibres as most of the fillers are almost 100% white or at least nearly white. Fillers also have a smoothening effect on the paper surface. As small filler particles settle in between of fibres they together form a smooth paper surface. A smooth surface is required for example in rotogravure printing. High use of fillers in rotogravure printed SC-paper might be explained by this theory. Although fillers are needed for a smooth surface and a good printing image, excessive amount of filler will compromise the paper surface strength. The loose particles and fibres will lint during converting and final quality will suffer[12]. Recently focus has fallen on the development of "green" additives in order to decrease the carbon foot print and improve the environmental impact of the pulp and paper industry. Development of additives from natural biomass sources are being chosen over the conventional synthetic/plastic or mineral additives[13]. One of the natural biomass additive groups that are getting much attention are native and modified hemicellulose based additives. Hemicelluloses are the second most abundant plant polysaccharide next to celluloses[14-18]. These polysaccharides are attractive as "green" additives because they are already present in the initial biomass that enters the pulp and paper mill[18]. They should only be liberated from the biomass prior to pulping.

The biomass that is used to produce paper consists of five major components; cellulose, hemicelluloses, lignin, extractives and ash. The cellulose is used to produce paper, thus the remaining components need to be removed. During delignification in the Kraft pulping phase, the hemicellulose fraction of the biomass is degraded into isosaccharinic acids. These isosaccharinic acids end up in the black liquor and are burned in the recovery furnace. This is not the most efficient use of isosaccharinic acids due to their low calorific value. Burning of the hemicelluloses can be avoided by extracting them prior to pulping. There are a number of advantages to the pre-extraction of hemicelluloses at a pulp and paper mill. These advantages have only recently been applied to large scale industrial applications[19]. The economic value of hemicelluloses is the driving force behind the recent interest in this biopolymer. When the isosaccharinic acids are burnt with the black liquor the value is R 350 per ton of hemicellulose. If it is pre-extracted and converted to value added products, such as biopolymers, the worth increases to between R 3000 and R 21 000 per ton of hemicellulose[20-21]. This is a considerable increase in value, which will improve existing pulp and paper mill economics.

Hemicelluloses as strength additives

Recently there is a growing interest in using hemicelluloses as biodegradable polymers in similar ways such as cellulose and starch. Unfortunately, hemicellulose is not available in its pure extracted form for industrial use. Woody biomass contains approximately 40-45 wt. % cellulose, 25-30 wt. % lignin, and 20-30 wt. % hemicelluloses[18, 22]. This indicates that there are large quantities of hemicelluloses present in woody biomass that can be utilised as films, coatings, pharmaceuticals, food and other industries applications, as well as additives for the papermaking industry[23].

Hemicelluloses are heterogeneous, non-cellulosic polysaccharide polymers which are interconnected in the cell wall of woody biomass by covalent bonds and secondary forces[24]. Hemicelluloses consist of both hexose and pentose sugar monomers which are linked together and can be branched in some cases. Some hemicelluloses may contain uronic acids such as 4-O-methyl-â-D-glucuronic acid and galacturonic acid in the side chains[25]. Hemicelluloses are the most complex polysaccharides in the cell wall of woody biomass. The covalent bonds that they form with lignin, as well as the extensive hydrogen bonding between the individual polysaccharide cell wall components, restrict the removal of hemicelluloses. Over the last decade, research has been done on many methods of hemicellulose extraction. Some of these methods include alkaline, alkaline peroxide, and steam explosion extraction. There is however no method that can liberate 100% pure hemicellulose from woody biomass. The reason for the interest in using hemicelluloses as strength additives is due to the many free hydrogen and hydroxyl groups available in their chemical structure. When the hemicelluloses are adsorbed onto the cellulose fibres these free hydrogen and hydroxyl groups provide more hydrogen bonding sites. The more hydrogen bonding sites there are available on the cellulose fibres, the more tightly bonded the paper web will be[22,26]. Hemicelluloses are naturally interwoven in wood's micromolecular structure, which indicates a strong relationship between hemicelluloses and cellulose[27]. The molecular weight distribution of the hemicelluloses also plays an important role in the extent to which paper strength is improved[28]. It is known that higher molecular weight hemicelluloses are more effective than low molecular weight hemicellulose additives[29]. Research has shown that the presence of hemicelluloses in the paper web increase the strength properties of the paper because of the above mentioned properties[30-31]. Research indicates that the adsorption of hemicelluloses is favoured by papers produced by Kraft pulping[32].

EXPERIMENTAL

Material

The raw materials used in this work are depithed bagasse which delivered from Edfo Paper Mell, Egypt and cotton stalks which are delivered from farm in Zagazig, Egypt. All Reagents used for this study were obtained from Merk-schudardt (analytical grade). the composition of raw materials are summarized in TABLE 1

From Table, it is clear that the depithed bagasse has a higher hemicellulose and lower lignin than cotton stalks. Debarked cotton stalks have a higher lignin than barked cotton stalks.

Prehydrolysis

of raw material was carried out before soda pulping process using 1.5% H_2SO_4 for 2hrs. at 110Ë%C in autoclave under pressure equal 15psi.

Pulping of bagasse

(a) Soda pulping: Raw material was cooked by using 20% NaOH solution using (6:1) liquor ratio, at 160Ë%C for 2 hours in autoclave under pressure equal 35psi. (b) Peroxyacid pulping method: Raw material was cooked in polyvinyl acetate bag using 16% peroxyacid and 7:1 liquor ratio at 85Ë%C for 2hrs.

Bleaching

Bleaching by alkaline hydrogen peroxide[33-34]:

In this work, the substance that pose hazards to human and environment such as ClO_2 should be replaced by the alkaline hydrogen peroxide bleaching procedure that was applied as follows:

1) An oven dry weight of the sample under investigation was prepared and mixed with distilled water to give consistency of 20%.
2) Sodium hydroxide 2% (based on pulp) and magnesium sulphate 0.1% (based on pulp) used as an act ivator were prepared. And 1% sodium silicate which has a buffering effect causing stabilization of hydrogen peroxide.
3) The required sodium hydroxide, sodium silicate and magnesium sulphate were dissolved quietly in the water of consistency.
4) In polyethylene bag, the required weight of pulp was put and the solution of step 3 was added followed by addition of hydrogen peroxide 2%

TABLE 1 : Chemical analysis of different raw materials

Raw Material	α- Cellulose %	Lignin%	Hemicellulose %	Ash %	Alcohol-toluene extract%
Depithed bagasse	46.66	21.09	26.07	2.00	1.20
Barked Cotton Stalks	50.22	25.96	20.85	2.30	1.42
Debarked Cotton Stalks	50.17	26.22	19.22	1.90	1.13

(based on pulp) and then the bag was tightly sealed and put into water bath of temperature 70°C- 80°C for one hour under hand fluctuation from outside of the sealed bag.

5) At the end of bleaching, the pulp was filtered and washed thoroughly till neutrality with distilled water.
6) The produced bleached pulp was applied to another one hour of alkaline H_2O_2 bleaching under the same conditions of steps from 2 to 5.

Bleaching by alkaline hydrogen peroxide followed by sodium chlorite ($NaClO_2$) bleaching ($NaClO_2$ sequence)[35]:

Bleaching via alkaline H_2O_2 technique (except that, the hydrogen peroxide concentration was 2% and the time of reaction was one hour) followed by bleaching by sodium chlorite with the same procedure of hollocellulose estimation, except that, the concentration of $NaClO_2$ will be 8% (based on pulp weight) of two to three portions for one hour.

Chemical analysis

Lignin, á-cellulose, hemicelluloses, and ash content was estimated by Tappi standard method (T13 wd-74), (T203 OS-61), (T19 wd-71)[36].

Degree of polymerization

(D.P) of the produced bleached pulp was determined by dissolving the cellulose sample in a copper ammonium hydroxide, Cu concentration 13 g/l and ammonia concentration 200 g/l. By determining the viscosity of this solution, the average degree of polymerization can be easily found by applying Schulz and Blaschke, (1941) expanded Staudinger equation[37].

Isolation of hemicellulose from plant materials

The plant materials were cut into small pieces then finely ground (40-60 mesh). It was then extracted with 2:1 toluene ethanol mixture and air dried.

Alcohol-toluene solubility

Usually alcohol benzene is used. But we avoided benzene which is one of the most toxic solvents (Carcinogenic substance) and replace it by toluene which less hazardous substance. A clean dry soxhlet extraction flask was weighted to nearest milligram. From the air dry sample, a specimen equivalent to 2+ 0.1g of moisture free sample was weighted. The crucible and specimen were placed in position in the soxhlet apparatus. A small wire of fine mesh screen wire was place placed in the top of the crucible to prevent any loss of specimen. The apparatus was assembled and the extracted was carried out with 200ml of (2: 1) toluene ethanol mixture for 6 hours. The solvent was evaporated from the extraction flask which was then dried to constant weight at 105+2^{o}C. and weighted.

Extraction of hemicellulose from holocellulose

Holocellulose was extracted by shaking with a deoxygenated 10% NaOH solution for 20h; at room temperature, liquor ratio 1:20. the hemicellulose was precipitated by acidification to PH 4.5 – 4.7, with 50%aqueous acetic acid and then poured in 3 volumes of 95% ethanol. And left over night. The heavy white precipitate was filtered through cloth, and washed with 75% ethanol, 95% ethanol and then ether, then dried under vacuum over $CaCl_2$.

Extraction of hemicellulose from acid hydrolysis liquor

The acid Hydrolysis Liquor (Liquor of Prehydrolysis) was then poured in 3 volumes of 95% ethanol. And left over night. The heavy white precipitate was filtered through cloth, and washed with 75% ethanol, 95% ethanol and then ether, then dried under vacuum over $CaCl_2$.

Instrumental analyses

Brightness of paper was measured by Carl Zeiss El Reph Tester. The intensity of light distinguishes the brightness of pulp as compared to the intensity of light reflected by a standard white body at the same wave length. The intensity of reflected light is measured photoelectrically.

RESULTS AND DISCUSSION

Preparation of viscose grade pulp

Viscose grade pulp from depithed bagasse, barked and debarked cotton stalks were prepared. The effect of addition of the hemicellulose to these prepared viscose grade pulp on the mechanical strength of the produced sheets were studied, as

TABLE 2 : Chemical analysis of viscose grade pulp produced from depithed bagasse, barked and debarked cotton stalks

Pulp	α-Cellulose%	Lignin %	Hemicellulose %	Ash %	Yield %	$KMnO_4$ no.	Bleach required g/l
Depithed bagass	96.07	0.13	2.90	0.05	31.90	6.50	2.98
Barked C.S	91.45	0.80	6.68	0.08	35.80	13.90	6.94
Debarked C.S	93.26	0.93	6.76	0.06	33.90	13.30	6.64

C.S: Cotton stalks

TABLE 3 : Some properties of the produced pulp after bleaching with different bleaching agents

Pulp	Bleaching condition	α- Cellulose%	Brightness%	D.P
	2%H-2%P-1%H	96.9	90.7	596
Dipithed bagasse	2%H-2%P	94.6	89.4	650
	2%H-2%H	95.8	90.1	615
	6%H-2%P-2%H	93.3	91.0	630
Barked cotton stalks	6%H-2%P	89.3	88.3	710
	6%H-2%H	91.2	90.2	680
	6%H-2%P-2%H	93.8	92.7	610
Debarked Cotton stalks	6%H-2%P	91.4	90.6	680
	6%H-2%P	92.5	91.3	640

H: Hypochlorite, P: Hydrogen peroxide

shown in TABLE 2.

Viscose grade pulp was prepared by prehydrolysis of raw materials with 1.5% H_2SO_4 at 110 ^{0}C under pressure equal 15psi for 2hrs. Pulping of the hydrolyzed bagasse was carried out using 20% NaOH at 160 ^{0}C under pressure equal 35psi for 2hrs,and 22% NaOH (based on raw material) for cotton stalks at 170 ^{0}C for 2hrs because it has more lignin content than bagasse.Bagasse, barked and debarked cotton stalks were bleached with different bleaching agents and physical properties were studied, as shown in TABLE 3.

From TABLE 3, it is clear that the dose of bleaching agent in case of depithed bagasse pulp is lower than cotton stalks pulp. This is due to the higher permanganate number due to the higher lignin content in cotton stalks pulp. The brightness is nearly the same in case of bleached bagasse and cotton stalks pulps. Although the dose of bleaching agent in case of bagasse pulp is lower than in case of cotton stalks pulp. On the other hand, the degradation in bagasse pulp during bleaching is higher than that in case of cotton stalks pulp. This can be due to that the produced pulp from cotton stalks is not flexible as in case bagasse pulp, which decreases the penetration of chemicals through the pulp. So, it is also clear from the table that the degree of polymerization of produced viscose grade from cotton stalks is higher than that in case of bagasse pulp. The bleaching with hypochlorite- hypochlorite for bagasse and cotton stalks pulps produced good pulps with high brightness as indicated above.

The mechanical properties

The mechanical properties of produced paper sheets from bagasse and cotton stalks viscose grade pulp are compared in TABLE 4.

From TABLE 4, it is clear that, the mechanical properties of cotton stalks viscose grade pulp paper sheets have a higher value than the depithed bagasse viscose grade pulp paper sheets. This can be due to the higher fiber length of cotton stalks pulp than bagasse fiber pulp. Also the fiber degradation of viscose grade pulp cotton stalks during pulping and bleaching processes is less than that in case bagasse pulp.

Effect of addition of hemicellulose on the properties of bagasse paper and viscose grade pulps

To study the effect of hemicelluloses on the me-

TABLE 4 : Mechanical and physical properties of different bleached viscose grade pulps

Bleached Pulp	S.R^0	Basis weight g/cm^2	Breaking length(m)	Burst factor	Tear factor	Brightness	H.C
Bagasse viscose grade pulp 2%H-2%H	40	58.3	2415	10.4	21.6	90.0	2
Barked C.S. Viscose grade pulp 6%H-2%H	42	60.1	2473	13.5	35.5	90.1	4.5
Debarked C.S. Viscose grade 6%H-2%H	50	61.1	2800	15.1	34.5	91.2	4.1

H.C: Hemicellulose content

TABLE 5 : Effect of added hemicellulose % on the bleached bagasse paper grade and viscose grade pulp

Amount of hemicellulose %(based on weight paper sheet)	Breaking length(m)		Burst factor		Tear factor		Brightness%		Opacity%	
	P.P	V.P	P.P	V.P	P.P	V.P	P.P	V.P	P.P	V.P
0	3985	2490	19.87	7.6	55.4	15.7	78.6	90.6	82.1	93.5
10	3365	2637	18.77	10.1	53.1	19.2	78.3	90.5	82.1	93.6
20	3260	2920	18.90	11.9	56.0	30.1	78.0	90.5	81.7	93.5
30	3060	3050	18.96	13.6	40.2	35.1	77.0	90.2	81.3	93.3

P.P: Paper pulp, V.P: Viscose pulp

chanical properties of paper sheets. A comparison was carried out between produced paper sheets from viscose grade pulp (low hemicellulose content)with paper sheets produced from viscose grade pulp after addition hemicellulose with different concentrations (based on weight of paper sheet),as indicates in TABLE 5.

From TABLE 5 it is clear that addition of hemicellulose to the pulp during beating process increases the mechanical strength of the pulp beside it improves the physical properties of the paper sheets. Where the breaking length increases from 2490 to 3050 m, Burst factor increases from7.6 to13.6 and Tear factor also increase 15.7 to 35.1 in viscose grade pulp (Low Hemicellulose content). This can be attributed to that hemicellulose accelerates the fiber swelling according to their sTABLE and location in the fibers of the pulp. On the other hand, presence of hemicellulose acts in the capacity of the protective colloids and as such gives rise to interchain hydrogen bonds during drying. Also, hemicellulose acts as adhesion material between cellulose fibers in paper sheets. Hemicellulose enhances the fiber bonding. Moreover, presence of hemicellulose in the pulp enhances from the beating process to its swelling in water and consequently increases from the strength properties of paper. The aim of presence of hemicellulose in the pulp is to develop the potential bonding area in the fiber by increasing its swelling capacity. Although the hemicellulose assists fiber swelling, a compromise must be sought between inherent fiber strength, D.P, and hemicellulose content, according to the sheet properties must desired. High hemicellulose concentration reduces Sheet strength. From the same table, the mechanical properties of paper sheets increases by increasing the quantity added of hemicellulose.

From TABLE 5, it is clear that addition of hemicellulose to the pulp (paper grade) decreases the mechanical properties of produced paper sheets from it due to the increase of the percent of hemicellulose which increases the bonding strength between fibers of paper sheets beside increase the adhesion force between paper sheets fiber, this increase the hardening of fiber in paper sheets and becomes brittle. In case of addition of hemicellulose to the bagasse pulp (viscose grade). The mechanical properties of produced paper sheets increase due to the increase of interchain hydrogen bonds during drying and adhesion force between paper sheets fibers.

Effect of addition of hemicellulose on the properties of paper and viscose grade pulps of debarked cotton stalks

TABLE 6 : Effect of addition of hemicellulose on the mechanical and physical properties of bleached debarked cotton stalks

Amount of hemicellulose %	Breaking length(m)		Burst factor		Tear factor		Brightness %		Opacity %	
	P.P	V.P	P.P	V.P	P.P	V.P	P.P	V.P	P.P	V.P
0	5422	2824	28.8	10.5	56.3	15.8	75.7	92.7	91.1	94.9
10	5574	3005	30.6	12.8	55.2	18.6	75.8	92.7	91.3	94.5
20	5701	3420	30.8	16.7	53.4	20.4	75.3	92.5	90.8	94.8
30	5340	3820	29.8	20.1	46.8	23.3	75.1	92.4	90.6	95.1

P.P: Paper pulp, V.P: Viscose pulp

TABLE 7 : Mechanical and physical properties of debarked and barked cotton stalks viscose grade pulp after addition of hemicelluloses

Amount Of hemicellulose added %	Breaking length (m)		Burst factor		Tear factor		Brightness %		Opacity %	
	B.C.S	D.C.S	B.C.S	D.C.S	B.C.S	D.C.S	B.C.S	D.C.S	B.C.S	D.C.S
0	2473	2800	9.5	10.5	13.6	15.8	91.4	92.7	94.4	94.9
10	2660	3005	11.3	12.8	16.5	18.6	91.1	92.7	94.2	94.5
20	2840	3420	11.5	16.7	17.6	20.4	91.03	92.5	94.2	94.8

B.C.S: Barked cotton stalks, D.C.S: Debarked cotton stalks

The effect of addition of hemicellulose on the mechanical and physical properties of bleached debarked cotton stalks is shown in TABLE 6.

TABLE 6 shows, the effect of addition of hemicellulose on the mechanical and physical properties of paper and viscose grade pulp of bleached debarked cotton stalks. From the table it is clear that, the addition of hemicellulose to paper grade debarked cotton stalks increase the mechanical and physical properties of produced paper sheets. The increase in the mechanical properties increases by the addition of hemicelluloses till 20% (based on pulp) and increasing this concentration more than 20%, the mechanical properties decreases.

This can be attributed to the increase of the adhesion force between paper sheets fibers and hemicellulose, this increase causes an increase in the hardening of paper sheets causing a brittleness of the paper sheets fibers. Comparing the excess in the mechanical properties %, due to the addition of hemicelluloses, between produced paper sheets from bagasse pulp and debarked cotton stalks pulp. It has a high percent in case of bleached debarked cotton stalks sheets. This is due to the percent in hemicellulose of debarked cotton stalks is lower than that in case of bagasse pulp (cf.TABLE1).This shows the effect of hemicellulose addition on the strength properties of debarked cotton stalks paper sheets.

On the other hand, although the percent of hemicellulose in bleached debarked paper grade pulp is lower than that in case of bleached bagasse paper grade pulp. The mechanical properties of the debarked cotton stalks paper sheets is higher than that in case of bagasse. This is due to higher fiber length and hydrogen bonding between the fiber in case of cotton stalks than bagasse. On the other hand, the increase in the mechanical properties % of the bleached debarked cotton stalks viscose grade pulp due to the addition of hemicellulose is higher than that in case of bleached debarked cotton stalks paper grade pulp.

Comparison between barked and debarked cotton stalks viscose grade pulps

A comparison between the mechanical and physical properties of barked and debarked cotton stalks viscose grade pulps after addition of hemicellulose is shown in TABLE 7.

From TABLE 7, it is clear that the increase in the mechanical properties due to the addition of hemicellulose is higher in case of debarked cotton stalks viscose grade pulp than the barked cotton stalks viscose grade pulp. This is attributed to that the pres-

TABLE 8 : Physical properties of paper sheets produced from depithed bleached bagasse paper grade pulp

Pulp		Basis weight g/cm^2	B.L (m)	B.F	T.F	Brightness %	Opacity %	Porosity	Retained filler%
Blank without additives		59.24	3264	19.87	55.40	78.60	82.10	170	
Bagasse with4% oxidized starch.		60.60	3449	18.23	49.50	78.90	83.90	195	---
Bagasse with4% Polymin SK		59.20	3266	19.6	50.50	73.50	83.50	120	---
Bagasse with Rosin and Alum.		60.80	2522	14.2	52.60	71.70	87.60	230	---
oxidized starch.	5% $CaCO_3$	59.60	3244	19.23	45.45	80.10	84.50	200	65%
Polymin SK		60.06	3080	19.8	51.20	74.80	85.60	190	78%
Rosin and Alum.		---	---	---	---	---	---	---	---
oxidized starch.	10% $CaCO_3$	61.97	3012	16.3	47.30	80.70	86.20	270	55%
Polymin SK		60.10	2914	15.8	45.30	76.70	89.40	280	60%
Rosin and Alum.		59.70	2010	8.7	42.90	77.40	90.50	200	35%
oxidized starch.	20% $CaCO_3$	57.50	2580	15.1	50.10	84.70	86.80	510	42%
Polymin SK		60.80	2083	14.2	46.50	82.60	89.70	230	44%
Rosin and Alum.		---	---	---	---	---	---	---	

ence of bark decrease the penetration of hemicelluloses through the pulp fiber and consequently the quantity of hemicellulose in the barked cotton stalks is decreased and this cause a decrease in the adhesion force between paper sheet fibers. Also, presence of bark decrease the penetration of chemical during pulping and bleaching process which decrease the flexibility and elasticity of fiber which decrease the inter and intra fiber bond between the fibers.

Effect of addition of different fillers on the properties of bagasse paper grade pulp

Different fillers such as Oxidized starch, polymer (polymin SK) and $CaCO_3$ were added to bleached bagasse paper grade pulp and the Physicomechanical properties of paper sheets would illustrated in TABLE 8.

TABLE 8, shows the physical properties of paper sheets produced from depithed bleached bagasse paper grade pulp after addition different fillers e.g.:[Oxidized starch, polymer (polymin SK) and $CaCO_3$].

From TABLE 8, it is clear that, the addition of polymeric materials to the pulp increases the mechanical properties of produced paper sheets except in case of rosin addition which decreases the mechanical properties of produced paper sheets. This is attributed to the acidity properties of the rosin which causes degradation of the fiber and consequently the mechanical properties. On the other hand the breaking length of the produced sheet after addition of oxidized starch is higher than that in case of addition of polymin SK. Moreover, the brightness of paper sheet after addition of oxidized starch is higher than that in case after addition of polymin SK and rosin. The porosity and opacity of paper sheets produced after addition rosin and alum is higher than that after addition of oxidized starch and polymin SK. This is due to the homogenous distribution of rosin through the fiber of paper sheets which then precipitated on the fiber of papers by alum solution.

It is also seen that the retained of fillers was highly affected by addition of polymer. So, the retained of $CaCO_3$ on the fiber of the produced paper sheets is lower than that in case of addition polymer. This can concluded that addition of polymer acts as adhesion and consequently that inter chain of fiber increase which decreases the loss of fillers with the water. On the other hand, due to the loss of retained filler in paper sheets, causes a decrease in the physical properties of paper sheets as, porosity and opacity. Although the addition of fillers improves the physical properties of paper sheets e.g. porosity, brightness and opacity, it decreases the mechanical properties of paper sheets. This is due to that the filler causes a decrease in crossing and inter chains between fibers of paper sheets. And consequently the inter fiber bonding and adhesion forces between fibers in paper sheets. This can be confirmed by the increase in opacity (which is highly affected by the porosity of paper sheets).

So, the addition of fillers is mainly used for certain properties in paper sheets production e.g. improve the printability and writing paper as well as books paper. Also, it is used for decrease from cellulosic fibers to increase the production of paper sheets.

From the previous table, it is clear that retained filler percent decreases by increasing the weight of filler added. On the other hand, the physical properties are highly improved. It is seen also, that the use of rosin and alum as retention aid for $CaCO_3$ fillers is not effective as in case of oxidized starch and polymin SK. This is due to that the rosin acid which react with $CaCO_3$ and so, the aim of use it as filler decreases.So, the best retention aid is the polymer which is not acidic.

CONCLUSION

Addition of greener fillers to pulp to improve economics, printability and optical properties. Bagasse has a higher hemicelluloses and lower lignin than cotton stalks, so the dose of bleaching agent in bagasse is lower than cotton stalks., Debarked cotton stalks has a higher lignin than barked one due to presence of waxes and others that reduce actual weight. The degree of polymerization in case of cotton stalks viscose grade pulp is higher than bagasse viscose grade pulp. So, the mechanical properties of cotton stalks viscose grade pulp paper sheets have higher value than bagasse viscose grade pulp paper sheets. In case of viscose pulps (low hemicelluloses content) the addition of hemicellulose to pulp during beating process increases the mechanical strength and physical properties of the pulp. While in case of paper grade pulp (High hemicelluloses content), the addition of hemicelluloses decrease the mechanical properties of produced paper sheets due to increase hardening of fiber in them and became brittle. The mechanical properties due to addition of hemicelluloses are higher in case of debarked cotton stalks viscose grade pulp than that in barked cotton stalks.

The addition of polymeric materials to bagasse paper pulp increase the mechanical properties of produced paper sheets except in case of rosin addition which decrease the mechanical properties., addition of oxidized starch increase the breaking length and brightness than adding polymin SK and rosin. While porosity and opacity of paper after adding rosin is higher than oxidized starch and polymin SK. The retained of fillers was highly affected by addition of polymer. Although the addition of fillers improve the physical properties of paper sheets e.g. :(porosity, brightness, and opacity), it decrease the mechanical properties of produced paper sheets.

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