

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

# Some Crystallographic Properties of Cellulose I as Affected by Cellulosic Resource, Smoothing, and Computation Methods

Sherif S. Z. Hindi

Department of Arid Land Agriculture, Faculty of Meteorology, Environment and Arid Land Agriculture,  
King Abdullaziz University, P.O. Box 80208, Jeddah 21589, Saudi Arabia

**Abstract:** Seed flosses of *Calotropis procera* and *Ceiba pentandra*, recycled writing papers (RWP), recycled newspapers (RNP), and recycled cardboards (RCB) were characterized, delignified, purified, and subjected to X-ray analysis. The crude data (unsmoothed) were fitted using Savitzky-Golay, Gauss, and loess methods. Crystallinity index (CI) was determined using the peak height method (PHM), Jayme-Knolle method (JKM), and modified Ruland-Vonk method (MRVM). Crystallite size (CS), full width at half maximum (FWHM), and lattice spacing (LS) were also estimated. The CI computed by MRVM was the highest, while PHM gave the lowest value. The recycled materials had higher CI and CS values and lower FWHM and LS than those for both seed flosses. The CI computed from crude data was higher than those for smoothed data. The CS from crude data was the lowest for both seed flosses as well as RNP and vice versa for RWP. The CI of cellulose was related directly to both holocellulose content and CS and inversely proportional to total extractives content, FWHM, and LS values.

**Keywords:** Gauss, Loess, Savitzky-Golay, Crystallinity index, Crystallite size, Spacing.

### I. INTRODUCTION

Natural cellulosic fibers (NCF) have been attracting much attention because of their novel properties, such as biodegradability, wide availability, environmental friendliness, easy handling and processing, suitable physico-mechanical properties, and possibility of blending in different composite materials [1](Thakur and Thakur 2014). Seed flosses extracted from mature pods of milkweed (*Calotropis procera*) shrubs and kapok (*Ceiba pentandra*) trees are additional cellulosic resources. Except for cotton, most seed flosses must be treated to remove impurities such as lignin, pectin, wax [2, 3, 4, 5]. The seed flosses are characterized by the presence of long fibers (Hindi 2013, 2014), and this property was found to be positively correlated with the mechanical properties, whereby longer fibers are generally stronger than shorter ones and *vice versa* [6].

Writing papers, newspapers, and cardboards are manufactured from wood fibers, either from hardwoods, termed deciduous or angiosperms, or softwoods, known as conifers or gymnosperms. Softwoods commonly have longer fiber lengths (3 to 5 mm) than hardwoods (1 to 2 mm). For the fiber width, softwood produces wider fibers (30 to 40  $\mu\text{m}$ ) than hardwoods (10 to 20  $\mu\text{m}$ ), as reported by Rothbard [7]. To recycle these fibrous products, all additives that were added to the fibers during manufacturing must be removed. These additives include bonding agents (dry-strength additives) added to improve bonding, sizing agents used to impart water resistance to paper, and fillers, including mineral pigments, added to improve smoothness and optical properties. The content of alpha cellulose in the final fibrous product depends on the pulping process applied. Chemical pulping gives the highest purity of cellulose, whereas mechanical pulping gives fibrous products with high lignin content, although it leads to the highest product yield.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

Cellulose is a straight chain polymer composed of D-glucopyranose units conjugated by 1,4- $\beta$ -glycosidic linkages. The cellulosic chains are constructed from repeating cellobiose units that generate diverse architectures, reactivity, and functions, increasing its importance [8]. A single cellulosic chain may be composed of 10,000 glucopyranose subunits [9] or more. In biosynthesis, cellulose polymers aggregate to form microfibrils (0.1 to 1  $\mu\text{m}$  in width and 5 to 50  $\mu\text{m}$  long), which in turn aggregate to form cellulose fibers having a micro- or nano-substructure [10, 11]. The nanofibrils have diameters ranging from 1 to 100 nm, while the fibrils have diameters ranging from less than 100 nm to more than 0.1  $\mu\text{m}$  [12]. Hydroxyl groups present in the cellulose matrix are involved in a huge number of intra- and intermolecular hydrogen bonds, which offer vast ordered crystalline structures [13]. The attraction between cellulosic chains in such regions by hydrogen bonds creates a regular pattern of crystallites [14].

Seven crystalline allomorphs, namely celluloses I $_{\alpha}$ , I $_{\beta}$ , II, III $_{\text{I}}$ , III $_{\text{II}}$ , IV $_{\text{I}}$ , and IV $_{\text{II}}$ , have been identified by XRD and  $^{13}\text{C}$ -NMR analyses. Cellulose I is the most abundant form found in nature [13, 15]. It consists of two distinct crystalline forms, the triclinic (I $_{\alpha}$ ) and monoclinic (I $_{\beta}$ ) forms, which have been verified by solid state  $^{13}\text{C}$ -NMR [16]. The monoclinic crystalline form (I $_{\beta}$ ) is dominant in higher plants [16]. Cellulose II can be synthesized from cellulose I by either mercerization or chemical regeneration. Celluloses I and II can be transformed into celluloses III $_{\text{I}}$  and III $_{\text{II}}$ , respectively, by ammonia (liquefied or gas) treatment [17]. The later allomorphs can be transformed thermally into IV $_{\text{I}}$  and IV $_{\text{II}}$ , respectively [18]. The microfibrils constitute crystalline cellulose (60% to 70%) and amorphous cellulose (30% to 40%) as indicated by Nisizawa [19] and Thygesen *et al.* [20]. The crystalline region of cellulose is estimated to be 3 nm in width and 30 nm in length [20]. The amorphous component of the microfibril exhibits a regular structure with a lack of the hydrogen bonds [21].

Hemicelluloses have a less ordered structure than cellulose, while lignin is an amorphous material with a high molecular weight [7]. The fiber properties are strongly influenced by its chemical composition, internal structure, microfibril angle, cell dimensions, and defects, which differ within a plant as well as between plants [22].

X-ray diffraction is a rapid, non-destructive method for determination of the crystalline portion of cellulose as well as the conformation and structure of cellulosic microfibrils [23, 24, 25]. This method can detect the interference-spaced crystalline cellulose planes encountered by the X-ray [21]. A diffraction pattern results from the contributions of all cellulose crystallites in the sample crossed by the X-ray beam. The position of the diffracted spot depends on the orientation of the crystallite, termed the sample texture [26]. This texture has been reported to be influenced by the nature of the crystallites, the synthesis method, and the preparation of the sample for the XRD test [20]. There are three major effects controlling the XRD: diffractogram shape, namely material structure, spectral distribution of the X-ray source, and instrumentation effects [27].

A rectangular model explaining the structure of the cellulosic microfibrils with 24 chains has been proposed, where the disorder in chain packing and hydrogen bonding was found to increase outward from the microfibril center [28]. The Meyer and Misch model of cellulose I was constructed with the aid of X-ray diffraction and molecular modeling [29, 30]. Furthermore, the microfibrils are proposed to be agglomerated in parallel groups of 36 cellulosic chains each [31]. The suggested Sponser and Dore unit of cellulose I illustrates the molecular arrangement of sheets constricting cellulose I along the 002-plan and parallel to the b-molecular axis [30, 32, 33]. For the pure crystalline materials with a large crystallite size, scattering is sharp without or with minimum diffusion. Furthermore, isolating amorphous reflections from small crystallite size (2 to 5 nm) would no longer be trivial because of the serious overlaps [20, 34, 35].

The XRD scans consist of a wide series of counts, which are the number of photons that are diffracted in a certain direction during a certain period, with numerical values obeying Poisson distribution. These scans are often smoothed and the  $K\alpha_2$  component is removed [36]. There are different factors that may produce noise with respect to the true counts during the measurement of the signal, depending on detector type, exposure time, and number of photons. Accordingly, smoothing and differentiation are necessary in signal and imaging processing, analytical chemistry, and spectroscopic analysis [37] to separate the true effects of the X-ray on a material's molecules.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

A Savitzky–Golay filter is a digital smoothing procedure (convolution) applied to a set of digital data points for fitting them to increase the signal-to-noise ratio without clear distortion of the signal. This is done by fitting successive subsets of adjacent data points with a low-degree polynomial by the method of linear least squares [37].

Gaussian smoothing is a procedure for blurring a diffractogram by a Gaussian function to reduce its noise. This method is also used as a pre-processing step in computer vision algorithms to enhance the image structures at different scales. Mathematically, it is a convolution process for the diffractogram termed a two-dimensional Weierstrass transform. Wang and Zhou [38] have derived a general model of smoothing-induced distortions of an XRD peak theoretically by convoluting a Savitzky–Golay polynomial filter with the Gaussian, Lorentzian, and pseudo-Voigt curves. Based on the assumption that an XRD peak consists of five main and two additional parameters, they indicated that flattening and broadening arise as a result of smoothing without distortion in the peak area.

Loess is a powerful and simple analysis method for smoothing curves of empirical data depending on the ordinary least-squares methods. Although it is used most frequently as a scatterplot smoother, Loess can be generalized very easily to multivariate data. The crystallinity index (CI) has been used for a long time to investigate changes in the cellulosic structure [20, 39, 40]. It is a measure of the relative amount of crystalline material and varies notably with the selected measuring method [13, 20, 39, 40], X-ray method, and experimental mode (transmission or reflection geometries) used [41]. Materials with highly crystalline cellulose content give a sharp peak with a high intensity, whereas those with large amounts of amorphous components such as lignin, hemi-celluloses, pectin, and amorphous cellulose give a broad peak with a low intensity [42, 43, 44]. It can be investigated by various techniques and computation methods using XRD,  $^{13}\text{C}$ -nuclear magnetic resonance ( $^{13}\text{C}$ -NMR), Fourier transform infra-red (FTIR), and Raman spectroscopies [13, 41, 45].

Using FTIR to measure CI is simple but gives only relative rather than absolute values because the spectrum always contains both crystalline and amorphous contributions [39, 46, 47]. Measuring the CI of cellulose by XRD provides a qualitative or semi-quantitative evaluation of the amounts of amorphous and crystalline cellulosic components in a sample. Developing a truly quantitative determination of the CI of cellulose is laudable but would need to proceed along the principles established for quantitative XRD phase analysis [48, 49]. There is a lack of suitable cellulose standards available to calibrate the crystallinity measurements [13].

It was found by Hindi [4] that X-rayed seed floss of *Ceiba pentandra* and *Calotropis procera* showed a broad peak at  $2\theta$  of  $18^\circ$  for amorphous components and a sharp one at approximately  $22^\circ$  related to crystalline materials. In addition, the CI of seed floss of *Calotropis procera* was found to be 65.5%, which approaches that for wood pine (70%) found by Borysiak and Doczekalska [20] and lies within the CI range (41.5% to 95.5%) found by Park *et al.* [13] and that (56% to 78%) by Terinte *et al.* [41] for different celluloses with different measuring techniques. The higher crystallinity investigated by the wide angle-XRD for *Calotropis procera* seed floss (46.2%) than that for *Ceiba pentandra* (39.7%) reflects lower amorphicity for the former resource in its fiber wall nanostructure, which offers an additional mechanism for the latter to sorb more fluids [5]. The CI of Avicel cellulose differs significantly, from 39% to 67%, according to the measurement technique used [20]. The ranges of the reported CI were 56% to 78%, 65% to 83%, and 37% to 93% for cotton linters, microcrystalline cellulose, and Avicel PH – 101, respectively [41].

There are several methods for calculating CI from XRD data, including the peak height method (PHM), Jayme-Knolle method (JKM), and modified Ruland-Vonk method (MRVM). The PHM developed by Segal *et al.* (1959) is the most popular method and a time saving empirical measure of the relative CI of cellulose, allowing the rapid comparison of cellulosic samples without quantifying the crystalline and amorphous components of cellulose. It produces values significantly higher than those from the other methods [13, 41].

The JKM depends on two X-ray methods, namely the Hermans-Weidinger method by using different correction factors and Segal and co-worker's method [50] to estimate the apparent crystallinity of cellulose [41, 51]. The RVM is an earlier development to measure the CI of polymeric materials [35]. This method involves the separation of crystalline peaks apart from those of amorphous components. Then, the reflections are sealed down below the crystalline peaks

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

and the portion of the integrated intensity of the crystalline component are excluded from the total intensity of the XRD diffractogram [35].

The crystallite size (CS) is the crystallite thickness determined by the Scherrer equation when the crystals are smaller than 100 nm [52]. Because the crystallite size of cellulose I is generally small (5 nm in width), the resolution of the XRD pattern is not adequate to give exact information about the crystal lattice of the cellulose structure [13].

The mean lateral dimensions of cellulosic microfibrils can be estimated from the full width at half maximum (FWHM) of the X-ray Bragg peaks. The 002 plane has the clearest reflection among the 101, 101 $\bar{1}$ , 021, 002, and 040 reflections, with the highest capability to determine these dimensions. In addition, the microfibril size is dependent on the botanical source of the fibers [53].

The lattice spacing of cellulosic microfibrils is a measure of the distance between successive cellulose monomers within a microfibril [54]. Cellulose axial lattice spacing ( $d_{004}$ ) at mechanical equilibrium depends on the lateral size of the crystallite [55]. In addition, by comparing the XRD of various cellulosic resources, it was determined that a larger crystal size leads to a larger  $d_{004}$  [55]. No difference in crystallite size or lattice spacing was detected for *Pinus radiata* (a softwood) and *Castanea sativa* (a hardwood), although they are different genetically and structurally. As reported by Montero *et al.* (2012), the lattice spacing can be calculated using Bragg's equation, which links the wavelength of the X-ray source to the lattice spacing  $d$  and the scattering angle ( $\theta^\circ$ ).

The objectives of this study were therefore as follows:

- 1) Find the best smoothing algorithm for the XRD data by comparing the crude data with those smoothed by the Savitzky-Golay, Gauss, and loess methods.
- 2) Find the most accurate computation method for the CI of cellulose I by comparing three different methods, namely peak height, Jayme-Knolle, and modified Ruland-Vonk.
- 3) Characterization of the crystallographic properties of cellulose I isolated from five CRs, namely seed flosses of *Calotropis procera* and *Ceiba pentandra*, and three recycled materials (RWP, RNP, and RCB).
- 4) Determine the relationships between the crystallographic properties of cellulose I and the chemical properties of the crude parent precursor.

## II. EXPERIMENTAL

### Raw Material

Five fibrous resources, namely seed floss of each of milkweed (*Calotropis procera* (Ait.) Ait. F.) and kapok (*Ceiba pentandra* (L.) Gaertn.), recycled writing paper (RWP), recycled newspaper (RNP), and recycled cardboard (RCB), were used in the present investigation.

### Seed Flosses

Four shrubs of *Calotropis procera* were selected randomly from Hada Al-Sham village (Saudi Arabia) in a sandy site (21° 46'.839N and 39° 39.911E) and 206 m above sea level during May-June 2013-2014. In addition, four trees of *Ceiba pentandra* were assigned from those grown at the campus of King Abdullaziz University (21.4939° N, 39.2503° E) in Jeddah (Saudi Arabia). Reference plants were identified using flora of the Kingdom of Saudi Arabia (KSA) [57]. Four mature pods were taken randomly from each assigned plant and were air-dried. Accordingly, 16 samples were collected to represent each of the seed flosses of *Calotropis procera* and *Ceiba pentandra*. Before the over mature stage and self-opening of the pods, the flosses were separated manually from the seeds, mixed, and stored in a relatively dry atmosphere in a sealed container.

### Recycled Cellulosic Resources

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

The recycled materials (RWP, RNP and RCB) were collected by the Scientific Endowment of King Abdullaziz University (KAU) at four different times from the specified disposal boxes of the Faculty of Meteorology, Environment and Arid Land Agriculture; each of the four times was considered statistically as one replicate. Accordingly, four replicates were assigned for testing each of the RWP, RNP, and RCB. From each replicate, four samples were taken randomly. Accordingly, 16 samples were collected to represent each of the recycled cellulosic resources. Collected samples were sorted and converted into scraps. The scraps were softened by cold distilled water, over-saturated by hot distilled water, and blended to obtain gelatinous liquor. Fibers were vacuum-filtered and washed adequately to remove any additives added while manufacturing, such as calcium carbonate, clay, polymers, blenders, and dyes. The resulting cellulosic samples were air-dried for 24 h at  $103\pm 2$  °C. Subsequently, approximately 100 g of air-dried sample from each replicate was converted into a cellulosic meal using a suitable grinder. Then, the cellulosic meal was sieved using different sieves, depending on the standard methods applied for the characterization.

## Characterization

### Anatomical Measurements

The anatomical properties studied were fiber length (FL), using optical microscopy; fiber width (FW), using scanning electron microscopy; and fiber yield (FY).

### Optical Microscopy (OM)

Optical microscopy was used only to measure the FL of RWP, RNP, and RCB. The FL of both seed flosses were measured by an ordinary ruler. A drop of gelatinous fibrous liquor was mounted on a slide and was stained with 1% aqueous safranin. The fibers were speculated using a light microscope (CE-MC200A) with a suitable visualization and photography system (OPTIKA PRO 5 Digital Camera-4083.12, OPTIKA, Italy) and a calibrated eyepiece at 10X magnification [58]. One slide was specified to represent each of the four replicates. Twenty five fibers were taken randomly and measured from each slide. Accordingly, 2000 fibers were measured for the investigation.

### Scanning Electron Microscopy (SEM)

The SEM study was employed to characterize the surface morphology and anatomical features of the floss fiber as well as to measure the FW of each of the five cellulosic resources, according to Hindi and Abohassan [58]. Approximately ten fibrous flosses were placed on a double-sided carbon tape on an Al stub and dried in air. Before examination, all samples were sputtered with a 15-nm-thick gold layer (JEOL JFC- 1600 Auto Fine Coater, JEOL, Tokyo, Japan) in a vacuum chamber. The specimens were examined with a Quanta FEG 450 SEM (FEI, Netherlands). The microscope was operated at an accelerating voltage ranging from 5 to 20 kV.

### Chemical Analysis

The chemical properties studied were holocellulose content (HC), lignin content (LC), ash content (AC), total extractives content (TEC), and wax content (WC). From each of the 16 samples selected for each of the five cellulosic resources, three sub-samples (2 g each) were assigned for each of HC, AC, and WC. Each of the three samples specified for the TEC determination was reused for the subsequent LC analysis. Accordingly, 48 samples were used for the determination of the HC, AC, and WC of the five cellulosic resources. In addition, another 48 samples were assigned for the determination of both TEC and LC.

For the crude seed floss, the determination of wax content was done using a Soxhlet apparatus in a manner similar to that described by ASTM [59] for the preparation of extractive-free wood, with diethyl ether substituted for the solvents specified [4]. The extracted free-seed floss samples were divided into two equal portions. One portion was used to determine lignin content, and the other one was used for the determination of holocellulose content (HC). The lignin content of each seed floss as well as RNP and RCB was determined according to ASTM [60] using  $\text{H}_2\text{SO}_4$  (72%). The holocellulose content (HC) of the cellulosic resources was determined according to Viera *et al.* [61] as follows: a 5 wt% fiber solution was prepared in a round-bottom flask. Then, 0.5 mL of glacial acetic acid and 0.75 g of sodium chlorite were added. The flask was top sealed to prevent the loss of gas released during the reaction process. Then, the contents

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

were placed in a water bath at 75 °C. After each hour, 0.5 mL of acetic acid and 0.75 g of sodium chlorite were added to the flask, repeating this step twice. The system was then cooled to 10 °C, and the contents were filtered and washed with distilled water at 5 °C until the fibrous residue became whitish. The funnel containing the fibrous residue was then dried in an oven at 105 ± 5 °C for 6 h. Afterward, the residue was cooled to room temperature in a desiccator and then weighed to quantify the holocellulose. To measure the ash content for each of the five cellulosic resources, air-dried samples were ignited at 600 °C until all carbon was eliminated [62].

### X-Ray Diffraction (XRD)

Because the sample texture is drastically influenced by the relative intensities of the diffraction peaks, subsequently influencing the CI values, the XRD samples must be prepared carefully to eliminate or minimize the texture effect to avoid a texture-biased CI. The wide-angle XRD spectra of the five cellulosic resources were acquired using an XRD 7000 Shimadzu diffractometer (Japan) according to the method of Park *et al.* [13] and Hindi [4]. The system used contained a rotating anode generator with a copper target and wide-angle powder goniometer. The system was operated using CuK $\alpha$  radiation generated at 30 kV and 30 mA. The CuK $\alpha$  radiation consists of K $\alpha$ 1 (0.15406 nm) and K $\alpha$ 2 (0.15444 nm) components, and the resultant XRD data has both components. The CuK $\alpha$  radiation was filtered out from the data using a single-channel analyzer on the output from the semiconductor detector and did not influence the data. Each of the divergence and scatter slits was 1°, and the receiving slit was 0.15 mm at the same radius. Dried cellulose samples (approximately 0.5 g) were mounted onto a quartz substrate using several drops of diluted glue. This glue is amorphous when it is dry and adds almost no background signal. All samples were scanned in a 2 $\theta$  range varying from 10° to 30°. All experiments were performed in the reflection mode at a scan speed of 4°/min in steps of 0.05°.

### Data Handling and Processing

When the cellulosic sample was X-rayed, a stream of crude data representing x- and y-coordinates (2 $\theta$  and I, respectively) of all points representing the XRD diffractometer was obtained. The XRD data were processed using curve table-software either for crude (unsmoothed) data or for smooth ones fitted by the Savitzky-Golay, Gauss, or Loess algorithms.

### Computational Methods for Crystallinity Index (CI)

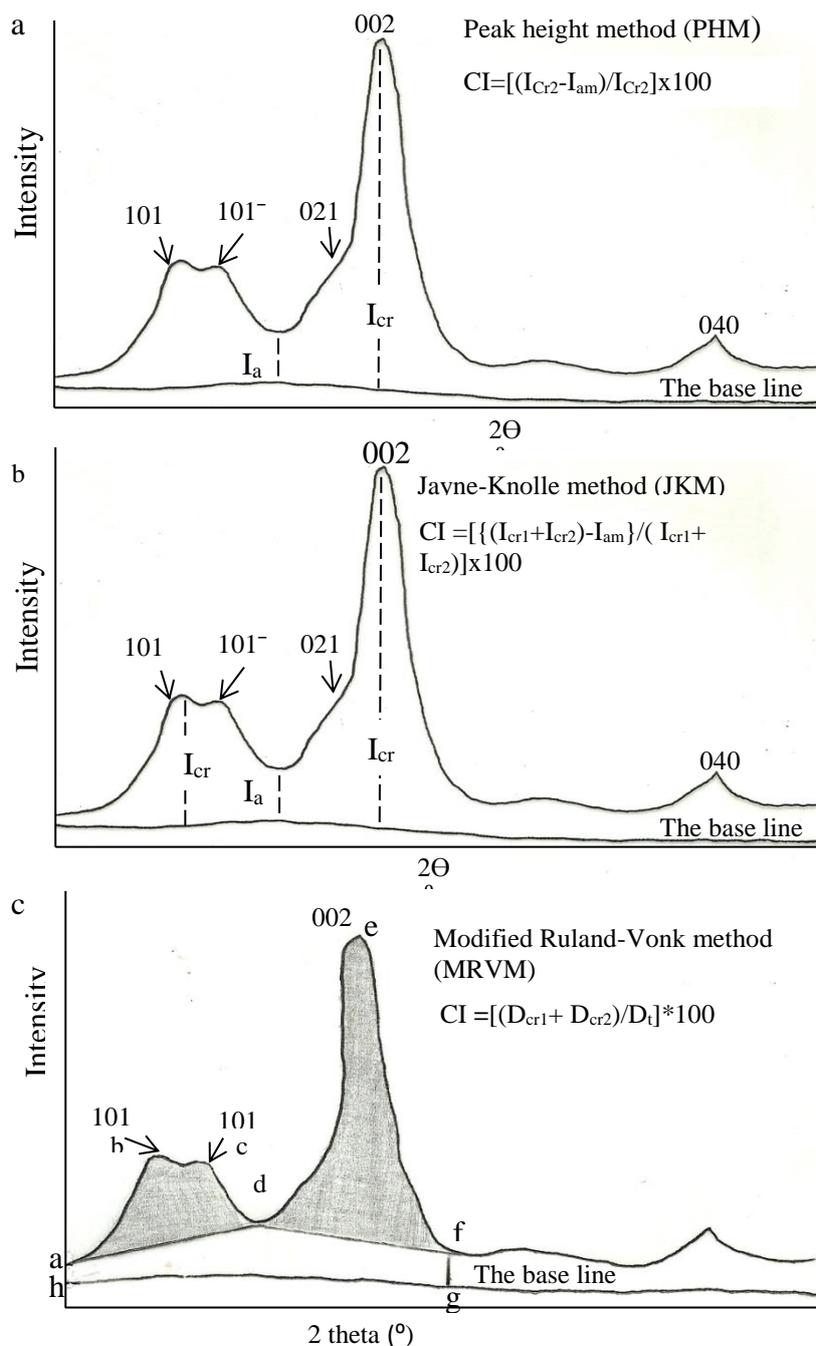
A representative diagram of the X-ray diffraction of cellulose I is presented in Fig. 1. The diagram shows the most common crystallographic planes for X-rayed cellulose I (101, 101 $\bar{1}$ , 021, 002, and 040). Three sharp and clear XRD peaks were considered in the present investigation, at 101, 101 $\bar{1}$ , and 002.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017



**Fig. 1.** Representative diagrams of the X-ray diffraction spectra of cellulose-I at the 101, 101<sup>-</sup> and 002 planes and the three CI computations

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

The CIs of cellulose I isolated from the five cellulosic resources (CRs) were computed by the peak height method (PHM), Jayne-Knolle method (JKM), and modified Ruland-Vonk method (MRVM) for both crude and smoothed data fitted by Savitzky-Golay, Gauss, and Loess algorithms.

### Peak Height Method (PHM)

The CI of cellulose I was calculated based on the PHM method after subtracting the background signal [4, 12, 13, 38, 63] using the following equation (Fig. 1a):

$$CI = [(I_{Cr2} - I_{am}) / I_{Cr2}] \times 100 \quad (2)$$

Where  $I_{Cr2}$  is the intensity of the crystalline peak from hemicellulose and alpha-cellulose, corresponding to the crystallographic plane of 002, and  $I_{am}$  is the intensity of the amorphous peak from lignin, hemicellulose, pectin, and amorphous cellulose.

### Jayne-Knolle Method (JKM)

The CI was calculated according to the JKM [13] using the following equation (Fig. 1b):

$$CI = \{[(I_{Cr1} + I_{Cr2}) - I_{am}] / (I_{Cr1} + I_{Cr2})\} \times 100 \quad (3)$$

Where  $I_{Cr1}$  is the intensity of the 1<sup>st</sup> crystalline peak from hemicellulose and alpha-cellulose, corresponding to the crystallographic planes  $I_{101\&101^-}$ ;  $I_{Cr2}$  is the intensity of the crystalline peak from hemicellulose and alpha-cellulose, corresponding to the crystallographic plane 002; and  $I_{am}$  is the intensity of the amorphous peak from amorphous components such as lignin, hemicellulose, pectin, and amorphous cellulose.

### Modified Ruland-Vonk Method (MRVM)

Individual crystalline peaks were first extracted by a curve-fitting process from the diffraction intensity profiles [13, 53, 64]. The CI was calculated by dividing the diffractogram area of crystalline cellulose by the total area of the original diffractogram (Fig. 1c) using the following equation:

$$CI = [(D_{Cr1} + D_{Cr2}) / D_t] \times 100 \quad (4)$$

where  $D_{Cr1}$  is the area under the 1<sup>st</sup> crystalline peak (abcd), corresponding to the 101 and 101<sup>-</sup> planes;  $D_{Cr2}$  is the area under the 2<sup>nd</sup> crystalline peak (def), corresponding to the 002 plane; and  $D_t$  is the area under the total diffractogram (abcdefgh).

The area under the curve was estimated by summing of adjacent trapezoids using Excel (Microsoft, USA) with the following equations:

$$\text{Trapezoid area} = \Sigma(X_2 - X_1)(I_2 + I_1) / 2 \quad (5)$$

where  $X_1$  and  $X_2$  are the x-coordinates ( $2\theta$ ) of two subsequent points of a diffractogram boundary, and  $I_1$  and  $I_2$  are their y-coordinates (intensities).

The modification done for this method was restricted to the following: a) calculation of the area under the curve by summing the adjacent trapezoids using Excel; and b) specifying base lines for crystalline and amorphous peaks.

### Characteristics of Crystalline Lamella

#### Crystallite size (CS)

The CS was calculated by the Scherrer equation as follows [52, 65]:

$$CS = (57.3k\lambda) / (\beta \cos\theta) \quad (6)$$

where CS is the mean diameter of the crystal,  $k$  is the shape factor of the crystal (0.94),  $\lambda$  is the wave length of X-ray incident upon the crystal (0.1542 nm),  $\beta$  is the full width at half maximum (FWHM) of the crystalline peak

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

corresponding to the crystallographic plane 002, and  $\theta$  is the Bragg angle corresponding to the (002) plane. A factor of 57.3 was used to convert  $\beta$  from degrees to radians.

## Lattice Spacing (LS)

The  $d$ -spacings were calculated using the Bragg equation as follows:

$$d = n \lambda / 2 \sin \theta \quad (7)$$

where  $n$  is an ordinal number with a value of 1 for diffractions with the strongest intensity [66],  $\lambda$  is the wavelength of X-rays incident on the crystal (0.1542 nm), and  $\theta$  is the Bragg angle corresponding to the (002) plane.

## Statistical Design and Analysis

Three different statistical designs were used in the present investigation:

1. A randomized complete block design was used for FL, FW, FY, HC, LC, AC, and WC of the five fibrous resources.
2. A split split-plot design in three replicates was used for the crystallinity index (CI).

Statistical analysis of the recorded data was performed using Statistical Analysis System (SAS, USA) program for the analysis of variance (ANOVA) procedure and least significant difference test (LSD) at 0.05 according to Dancy and Reidy [67].

## III. RESULTS AND DISCUSSION

### Fiber Characterization

#### Anatomical Characteristics

The fiber length (FL) and fiber width (FW) of the five cellulosic resources were determined by optical and scanning electron microscopies, respectively and presented in Table 1.

**Table 1.** Mean Values<sup>1,2</sup> of fiber length (FL), fiber width (FW), fiber yield (FY), holocelluloses content (HC), lignin content (LC), ash content (AC), total extractives content (TEC), and wax content (WC) of the Five Cellulosic Resources.

Fibers <sup>3</sup>	FL <sup>4</sup> (mm)	FW <sup>4</sup> ( $\mu$ m)	FY <sup>5</sup> ,%	HC <sup>5</sup> ,(%)	LC <sup>5</sup> ,(%)	AC <sup>5</sup> ,(%)	TEC <sup>5</sup> ,(%)	WC <sup>5</sup> ,(%)
CPSF <sub>1</sub>	43.99 <sup>b</sup>	11.48 <sup>c</sup>	51.1 <sup>d</sup>	61.42 <sup>bc</sup>	20.09 <sup>a</sup>	4.97 <sup>b</sup>	9.24 <sup>b</sup>	4.28 <sup>a</sup>
CPSF <sub>2</sub>	65.94 <sup>a</sup>	17.23 <sup>a</sup>	51.4 <sup>d</sup>	68.19 <sup>b</sup>	12.98 <sup>b</sup>	0.76 <sup>d</sup>	17.76 <sup>a</sup>	0.31 <sup>b</sup>
RWP	1.21 <sup>c</sup>	9.09 <sup>d</sup>	83.01 <sup>a</sup>	86.41 <sup>a</sup>	3.24 <sup>d</sup>	10.35 <sup>a</sup>	Nil <sup>c</sup>	Nil <sup>c</sup>
RNP	2.68 <sup>c</sup>	14.08 <sup>b</sup>	74.83 <sup>b</sup>	83.22 <sup>a</sup>	7.19 <sup>c</sup>	9.59 <sup>a</sup>	Nil <sup>c</sup>	Nil <sup>c</sup>
RCB	0.72 <sup>c</sup>	17.54 <sup>a</sup>	67.5 <sup>c</sup>	84.65 <sup>a</sup>	12.64 <sup>b</sup>	2.71 <sup>c</sup>	Nil <sup>c</sup>	Nil <sup>c</sup>

<sup>1</sup>Means within the same column followed by the same letter are not notably different according to LSD at 0.05.

<sup>2</sup> As a percentage of the oven-dried precursor, except for FL and FW.

<sup>3</sup> CPSF<sub>1</sub> is *Calotropis procera* seed floss, CPSF<sub>2</sub> is *Ceiba pentandra* seed floss, RWP is recycled writing paper, RN is recycled newspaper, and RCB is recycled cardboard.

<sup>4,5</sup>Each value is the average of 400 and 48 observations, respectively.

It is clear from Table 1 that the FLs of both seed flosses of *Calotropis procera* and *Ceiba pentandra* were higher (65.94 and 43.99 mm, respectively) than those for the recycled materials (RWP, RNP, and RCB), which ranged from 0.72 to

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

2.68 mm. In addition, the seed floss of *Ceiba pentandra* and RCB had the highest FW values (17.23 and 15.54  $\mu\text{m}$ , respectively). On the other hand, PWP had the lowest FW (9.09  $\mu\text{m}$ ). The FWs of RNP and RCB resemble that for cotton, which ranges from 15 to 20  $\mu\text{m}$  [68]. This difference in fiber length and width may be due to the genetic difference between fibrous plants [69]. It is worth mentioning that the length of fiber greatly affects the strength of pulp and the paper made from it [70]. Accordingly, fibrous products made from species with long fibers are expected to show higher quality than those with shorter fibers [3]. The fiber yield (FY) values obtained from the three recycled materials were higher than those for both seed flosses examined (Table 1) in this study. This finding can be attributed to the higher contents of LC and TEC in the seed flosses studied compared with the recycled materials. The higher fiber productivity of the recycled materials will increase the interest in the recycling process for such materials.

## Chemical Characteristics

Holocellulose content (HC), lignin content (LC), ash content (AC), total extractives content (TEC), and wax content (WC) for the five cellulosic resources (CRs) are presented in Table 1. It is clear from Table 1 that the CRs examined had notably different chemical properties.

The HC, the sum of alpha cellulose and hemicellulose, was found to be higher for the recycled materials than for both seed flosses. This is because the former materials were previously delignified, while the latter ones are crude fibrous materials.

The LC of the seed floss of *Calotropis procera* was the highest (20.09%) followed by that for *Ceiba pentandra* and RCB (12.98% and 12.64%, respectively). The differences in the LC of the three recycled materials can be attributed to the pulping procedure applied (mechanical, chemical, or semi-chemical) as well as the botanic origin of the parent wood. A low lignin content for a lignocellulosic material reduces the pulping time and chemical charge compared with those of other non-wood raw materials [71, 72]. Furthermore, higher contents of lignin are predicted to consume more chemicals in the pulp industry [73]. The present results are in agreement with those of Lopez *et al.* [72].

For the AC of the parent CRs, both RWP and RNP had the highest values (10.35% and 9.59%, respectively). On the other hand, the seed floss of *Ceiba pentandra* had the lowest AC (0.76%). In industry, high contents of AC will negatively impact the chemical recovery process and therefore could constitute a serious drawback [74].

It can be seen from Table 1 that TEC and WC were present only in seed flosses in the crude form without any pretreatments. The seed floss of *Ceiba pentandra* had higher TEC (17.76%) than that for *Calotropis procera* (9.24%). In addition, the WC in seed floss of *Calotropis procera* was higher (4.28%) than that for *Ceiba pentandra* (0.31%). The difference between the seed flosses of *Calotropis procera* and *Ceiba pentandra* can be attributed to the difference in their botanical origin. The presence of high extractives content in the lignocellulosic tissues is unpreferred for industrial applications because of the interference of such extractives with maceration reagents used to separate the fibers, which also will add additional cost to the industry [3]. However, the chemical parameters show a decrease in the fibrous quality of *Calotropis procera* and *Ceiba pentandra* compared with the recycled materials because of their high contents of TEC, LC, AC, and the presence of waxes in their structures. More chemical reagents are required to remove such compounds, which will negatively impact the chemical recovery process and therefore constitute a serious drawback [4, 74]. The present results are in agreement with those from other literature [3, 4, 5, 71, 72, 75, 76, 77].

## Characterization of Cellulose I

### X-Ray Diffraction (XRD)

The crude and smoothed XRD data obtained from cellulose I isolated from each of the five cellulosic resources (Appendix 1) were used for the determination of crystallographic properties. These properties were crystallinity index (CI), crystallite size (CS), and lattice spacing (LS).

### Crystallinity Index (CI)

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

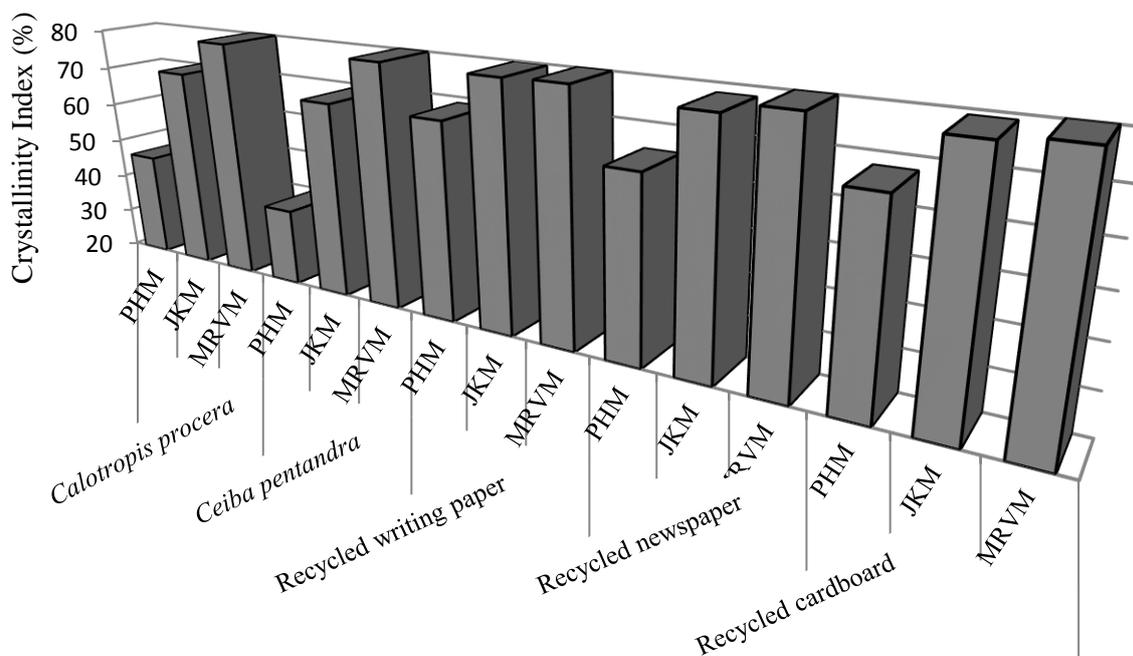
Vol. 6, Issue 1, January 2017

The CIs of cellulose I isolated from the five cellulosic resources and computed by the peak height method (PHM), Jayme-Knolle method (JKM), and modified Ruland-Vonk method (MRVM) are presented in Fig. 2.

Comparison of the CI within the CRs reveals that the MRVM led to the highest CI value. This is can be attributed to the dependence of this method on the area under the peaks, which includes all features of the XRD diagram without excluding any data except for those related to the noise (Figs. 1c and 2). On the other hand, the PHM led to the lowest CI value by considering only the intensity at the crystalline peak 002 ( $I_{cr2}$ ) and that at the amorphous peak ( $I_{am}$ ), as shown in Figs. 1a and 2. However, this trend was observed for all five CRs. In between, the JKM led to a CI value higher than that of the PHM for all the CRs studied and approaching that for the MRVM for the recycled materials (Fig. 2). Accordingly, the JKM can enhance the PHM by considering the average intensities of both crystalline peaks, namely 101 and 101<sup>-</sup>, in its computation (Fig. 1b).

Based on this result, the MRVM is the best computation method for the CI, followed by JKM and PHM. The latter method is not recommended because it cannot give an absolute value of the CI and is not suitable except for fast comparisons between different resources.

Regardless of the computation method, comparisons between the CRs indicated that RWP, PNP, and RCB had higher CI values than the seed flosses (Fig. 2). The CI differences between the CRs can be attributed to the differences in their chemical composition. Because fibers with higher extractives content have lower crystallinity and lower cellulose crystallite size [65], the lower CI values for the seed flosses of *Calotropis procera* and *Ceiba pentandra* can be attributed to their higher TECs (9.24% and 17.76%, respectively). This is confirmed by the highly significant positive correlation relationship ( $R^2=0.931$ ) found between the TEC and the CI (Table 2). In addition, HC can be used to illustrate the difference in crystallinity between species. Higher HC leads to higher CI. This finding was confirmed by the highly notably positive correlation equation ( $R^2=0.849$ ) presented in Table 2.



**Fig. 2.** Crystallinity index (CI) of cellulose I isolated from the five cellulosic resources (CRs) and computed by peak height method (PHM), Jayme-Knolle method (JKM), and modified Ruland-Vonk method (MRVM).

## International Journal of Innovative Research in Science, Engineering and Technology

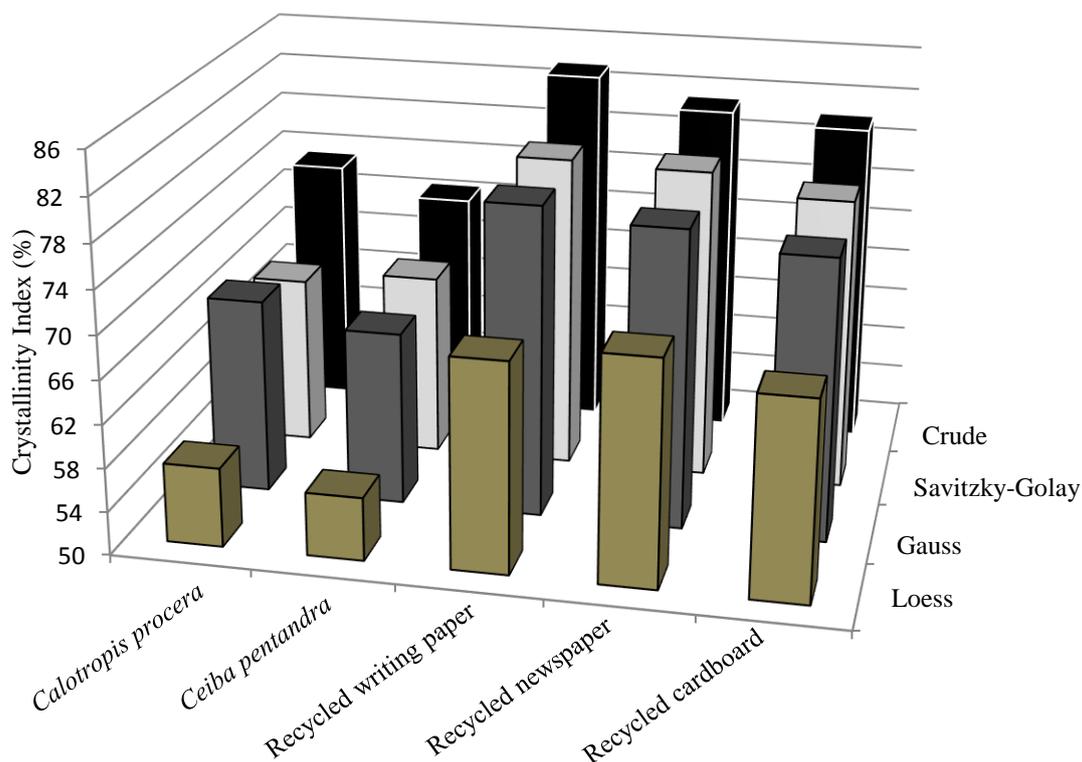
(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

The CIs of cellulose I isolated from the five cellulosic resources determined by crude XRD data and the three smoothing algorithms (Savitzky-Golay, Gauss, and Loess) are presented in Fig. 3. For smoothing algorithms, the CI computation using crude XRD data gave the highest value. On the other hand, using the data smoothed by the Loess method gave the lowest CI value. In between, the Savitzky-Golay and Gauss methods gave median CI values (Fig. 3). This trend of decreasing the CI from crude, Savitzky-Golay and Gauss, to Loess was observed for all the CRs. The highest CI obtained using the crude data (without smoothing) can be attributed to the conservative nature of this method, in which no XRD counts were excluded and subsequently peak height was not decreased by excluding terminal points of the peaks. On the other hand, Loess was the most aggressive smoothing technique because it excludes more terminal XRD counts along the height axis of the crystalline peak. The aggressive smoothing of Loess was followed by Gauss and, finally, by Savitzky-Golay among the algorithms examined.

Considering the cellulosic resources, RNP had the highest CI value among the CRs for all four smoothing algorithms. On the other hand, seed flosses of *Calotropis procera* and *Ceiba pentandra* had the lowest CIs (Fig. 3).



**Fig. 3.** Crystallinity index (CI) of cellulose I isolated from the five cellulosic resources (CRs) for crude XRD data and the three smoothing algorithms (Savitzky-Golay, Gauss, and loess)

### Crystallite Size (CS)

For CS, presented in Fig. 4, the CS resulting from crude data was the lowest for both the seed flosses as well as RNP. However, this trend was reversed for that estimated for the RWP. Comparisons between the CRs lead to the fact that the CS from the recycled materials (RWP, RNP, and RCB) were higher than those produced from the seed flosses (Fig. 5). Because fibers with higher extractives contents have lower cellulose crystallite sizes [65], the TEC can be used to illustrate the differences in the CI. This is logical because of the well-known amorphicity of such organic extractives.

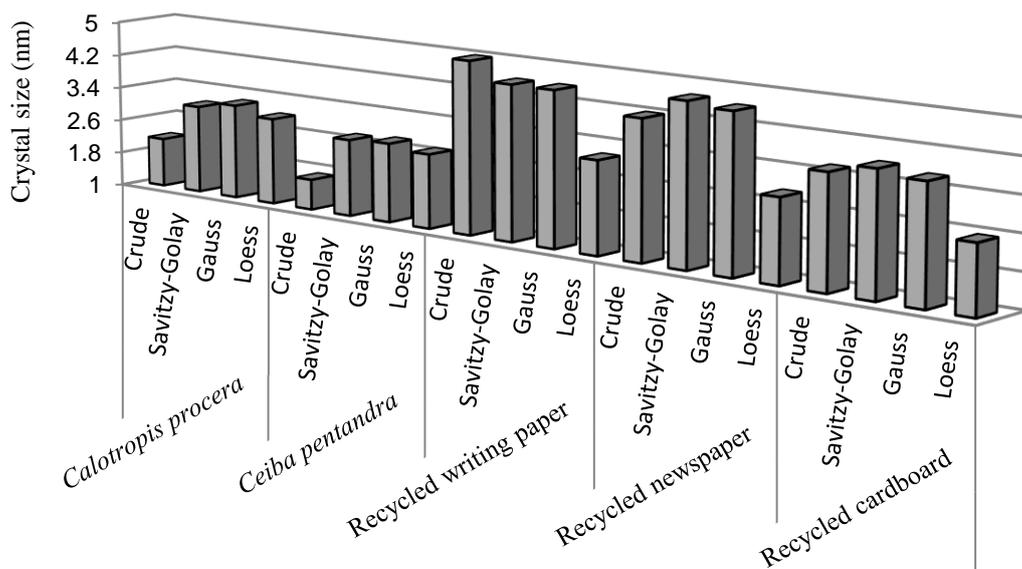
## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

Furthermore, this illustration was confirmed by the positive correlation relationship ( $R^2=0.931$ ) found between the TEC and the CI (Table 2). Based on these findings, cellulosic resources such as seed flosses of *Calotropis procera* and *Ceiba pentandra* that contain high TEC will have a lower CS than those with lower TEC, such as the recycled cellulosic resources (RWP, RNP, and RCB). Furthermore, a direct relationship was found between the AC of the CRs and the CS ( $R^2=0.814$ ), as shown in Table 2. It is not logical that the AC can contribute to any altering of the CS of cellulose. However, the XRD crossed the inorganic minerals of the AC, which interfered with those diffracted by the crystalline cellulose because these minerals have their own crystallinity. Accordingly, this enhancement in the CS from the AC can be considered a false effect. Furthermore, a direct relationship was found ( $R^2=0.894$ ) between the CS of the cellulosic sample and its CI. Accordingly, RWP, RNP, and RCB, with higher CI, possess bigger crystallites than those from the seed flosses of *Calotropis procera* and *Ceiba pentandra*. An inverse relationship was found between the FWHM of the cellulosic material and both the CS ( $R^2=0.971$ ) and CI ( $R^2=0.945$ ), as shown in Table 2. Crystalline materials are characterized by their large CS, leading to a sharp peak with a small FWHM, and *vice versa* for amorphous materials. Accordingly, the FWHM can be used simply as an indicator for both CI and CS.



**Fig. 4.** Crystallite size of cellulose I estimated from crude XRD data and the three smoothing algorithms (Savitzky-Golay, Gauss, and loess) for the five cellulosic resources (CRs).

### Lattice Spacing (LS)

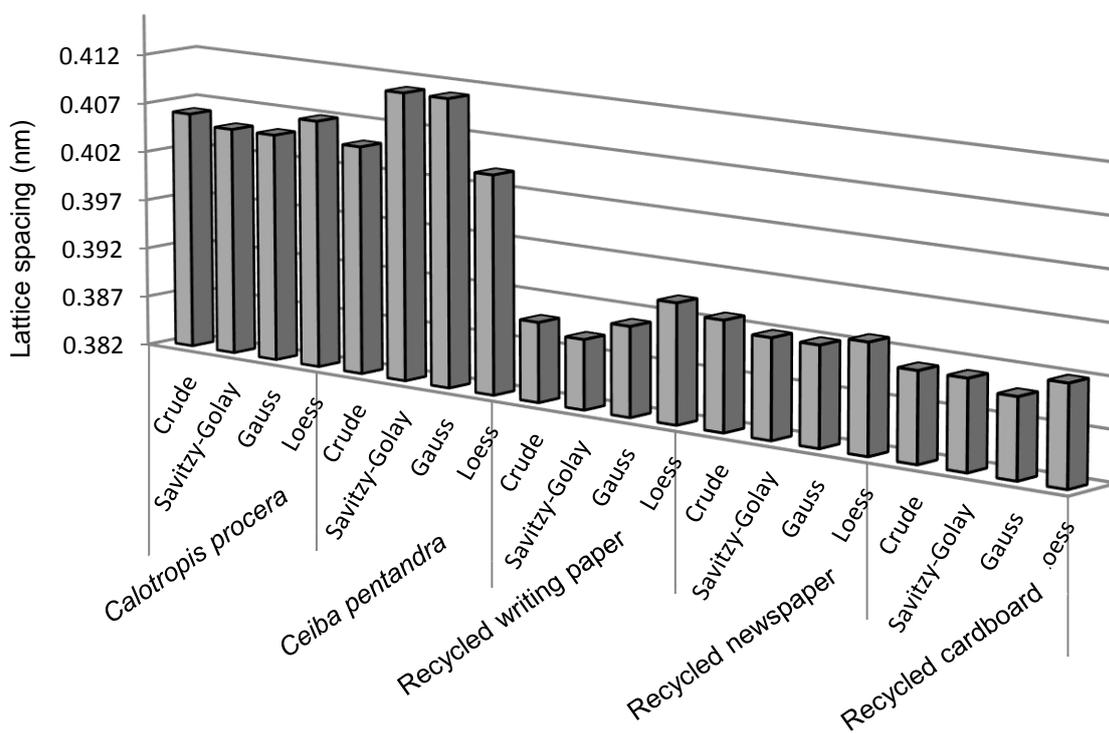
For the LS of cellulosic samples, no notable differences in the LS were observed for the smoothing algorithms within the CRs (Fig. 5). In addition, the LS for the crystallite regions within both seed flosses of *Calotropis procera* and *Ceiba pentandra* were higher than those from recycled materials (RWP, RNP, and RCB). The correlation analysis revealed that both the HC and TEC of the cellulosic samples influence the LS (Table 2). Accordingly, samples containing higher HC and lower TEC have increased distances between crystallite lamellae, or LS. The effect of the HC and TEC on the LS may be restricted to their influence on the crystallinity and FWHM. Increasing the HC enhances the CI and subsequently reduces the FWHM, and *vice versa* for the TEC because of the amorphicity of the extractives. This is confirmed by the direct relationships found between the FWHM and the LS of the cellulosic samples and that stated between the TEC and the FWHM, as well as the negative correlation between the LS and the CI (Table 2).

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017



**Fig. 5.** Lattice spacing of cellulose I estimated from crude XRD data and the three smoothing algorithms (Savitzky-Golay, Gauss, and Loess) for the five cellulosic resources (CRs).

**Table 2.** Equations, Standard Error of Estimate (SEE) and Regression Coefficient ( $R^2$ ) for Relationships between Crystallinity Index (CI), Full Width at Half Maximum (FWHM), Crystallite Size (CS), Lattice Spacing (LS), and Chemical Properties, namely Holocellulose content (HC), Ash Content (AC), and Total Extractives Content (TEC) of the Five Cellulosic resources.

Equation	SEE <sup>1</sup>	$R^2$	Equation	SEE <sup>1</sup>	$R^2$
CI=29.311+0.554HC	2.352	0.849**	CS=2.491+0.169AC	0.303	0.814*
CI=77.334-0.888TEC	1.6	0.931**	CS=4.061-0.098TEC	0.281	0.840**
CI=99.502-10.419FWHM	1.413	0.945**	CS=6.714-1.228FWHM	0.316	0.971**
CI=43.78+8.126CS	1.969	0.894**	LS=0.452-0.0007HC	0.002	0.910**
CI=386.15-790.6LS	1.099	0.967**	LS=0.391+0.001TEC	0.003	0.867**
FWHM=2.138+0.083TEC	0.141	0.944**	LS=0.365+0.012FWHM	0.003	0.847**

<sup>1</sup>Number of observations = 48, \* Significant at 5% level, \*\* Significant at 1% level

## IV. CONCLUSIONS

1. The modified Ruland-Vonk method gave the highest crystallinity index, while the peak height method had the lowest one, with similar trends among the five cellulosic resources studied.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

2. Recycled writing paper, newspaper, and cardboard had higher crystallinity index values than those for seed flosses of both *Calotropis procera* and *Ceiba pentandra*.
3. The crystallinity index computed using the crude data gave the highest value, while that smoothed by the Loess method gave the lowest value.
4. The recycled newspapers had the highest crystallinity index value among the cellulosic resources for all four types of smoothing.
5. The crystallinity index of cellulose was related directly to both holocellulose content and crystallite size, and inversely proportional to total extractives content, full width at half maximum, and lattice spacing.
6. The full width at half maximum of the crystalline peak corresponding to the crystallographic plane of 002 estimated from crude data was the highest for both seed flosses, while Loess gave the highest value for the three recycled materials. Fitting X-ray diffraction-data by the Savitzky-Gollay method gave higher full width at height maximum than that for Gauss in all the cellulosic resources, except for the recycled newspaper.
7. The crystallite size from crude data was the lowest for both seed flosses as well as recycled newspapers and *vice versa* for recycled writing paper.
8. No notable differences in the lattice spacing were observed for the smoothing algorithms within the cellulosic resources.
9. The recycled materials had higher crystallinity index and crystallite size, and lower full width at height maximum and lattice spacing, than both seed flosses.
10. The crystallite size was directly related to the ash content of the cellulosic resources and inversely related to total extractives content and full width at height maximum of the crystalline peak corresponding to the crystallographic plane of 002.

### V. ACKNOWLEDGMENTS

This project was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah under grant no. 115/155/1432. The authors therefore acknowledge with thanks the DSR for technical and financial support.

### VI. REFERENCES

1. Thakur, V. K. and Thakur, M. K., "Processing and characterization of natural cellulose fibers/thermoset polymer composites", Carbohydrate Polymers, Vol. 109, 102-117, 2004. DOI: 10.1016/j.carbpol.2014.03.039.
2. Borysiak, S. and Doczekalska, B., "X-ray diffraction study of pine wood treated with NaOH", Fibers and Textiles in Eastern Europe, Vol. 5(53), 87-89, 2005.
3. Hindi, S. S.; Bakhshwain, A. A., and El-Feel, A., "Physico-chemical characterization of some Saudi lignocellulosic natural resources and their suitability for fiber production", Journal of King Abdulaziz University, Vol. 21(2), 45-55, 2011. DOI: 10.4197/Met.21-2.4.
4. Hindi, S. S. Z., "*Calotropis procera*: The miracle shrub in the Arabian Peninsula", International Journal of Science and Engineering Investigations, Vol. 2(16), 48-57, 2013.
5. Hindi, S. S. Z., "Characteristics of some natural fibrous assemblies for efficient oil spill cleanup", International Journal of Science and Engineering Investigations, Vol. 2(16), 89-96, 2014.
6. Azzouz, B.; Ben Hassen, M. and Sakli, F., "Adjustment of cotton fiber length by the statistical normal distribution: Application to binary blends", Journal of Engineered Fibers and Fabric, Vol. 3(3), 35-46, 2008.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

7. Rothbard, D. R., "Electron Microscopy for the Pulp and Paper Industry", Technical Paper Series Number 911, Institute of Paper Science and Technology (IPST), Atlanta, GA, 2001.
8. Klemm, D., Heublein, B., Fink, H. P., and Bohn, A., "Cellulose: Fascinating biopolymer and sustainable raw material", *Angewandte Chemie International*, Vol. 44(22), 3358-3393, 2005. DOI: 10.1002/anie.200460587.
9. Zabel, R. A., and Morrell, J. J., "Wood Microbiology: Decay and Its Prevention", Academic Press, San Diego, CA, 1992.
10. Chakraborty, A., Sain, M., and Kortschot, M., "Reinforcing potential of wood pulp derived microfibrils in a PVA matrix", *Holzforschung*, Vol. 60(1), 53-58, 2006. DOI: 10.1515/HF.2006.010.
11. Frone, A. N., Panaitrscu, D. M., and Donescu, D., "Some aspects concerning the isolation of cellulose micro- and nano-fibers", *University Politehnica of Bucharest Scientific Bulletin Journal Series B*, Vol. 73(2), 133-152, 2011.
12. Wang, S, Cheng, Q., Rials, T. G., and Lee, S. H., "Cellulose microfibril/nanofibril and its nanocomposites", paper presented at the 8th Pacific Rim Bio-Based Composites Symposium, 20-23 November, Kuala Lumpur, Malaysia, 2006.
13. Park, S., Baker, J. O., El-Himmell, M., Parilla, P. A., and Johnson, D. K., "Cellulose crystallinity index: Measurement techniques and their impact on interpreting cellulase performance", *Biotechnology for Biofuels* Vol. 3, 10, 2010. DOI: 10.1186/1754-6834-3-10.
14. O'Sullivan, A. C., "Cellulose: The structure slowly unravels", *Cellulose*, Vol. 4(3), 173-207, 1997. DOI: 10.1023/A:1018431705579
15. Habibi, Y., Lucia, L. A., and Rojas, O. J. "Cellulose nanocrystals: Chemistry, self-assembly, and applications", *Chemical Reviews*, Vol. 110(6), 3479-3500, 2010. DOI: 10.1021/cr900339w
16. Atalla, R., and Vanderhart, D. L., "Native cellulose: A composite of two distinct crystalline forms", *Science*, Vol. 223(4633), 283-285, 1984. DOI: 10.1126/science.223.4633.283.
17. Hayashi, J., Sufoka, A., Ohkita, J., and Watanabe, S., "The confirmation of existence of cellulose III<sub>I</sub>, III<sub>II</sub>, IV<sub>I</sub>, and IV<sub>II</sub> by X-ray method", *Journal of Polymer Science: Polymer Letters Edition*, Vol. 13(1), 23-27, 1975. DOI: 10.1002/pol.1975.130130104.
18. Gardiner, E. S., and Sarko, A., "Packing analysis of carbohydrates and polysaccharides. The crystal-structures of cellulose IV<sub>I</sub> and cellulose IV<sub>II</sub>", *Canadian Journal of Chemistry*, Vol. 63(1), 173-180, 1985. DOI: 10.1139/v85-027
19. Nisizawa, K., "Mode of action of cellulases". *Journal of Fermentation Technology*, 51(4), 267-304, 1973.
20. Thygesen, A., Oddershede, J., Lilholt, H., Thomsen, A. B., and Ståhl, K., "On the determination of crystallinity and cellulose content in plant fibres", *Cellulose*, Vol. 12(6), 563-576, 2005. DOI: 10.1007/s10570-005-9001-8.
21. Howell, C., Hastrup, A. C. S., and Jellison, J., "The use of X-ray diffraction for analyzing biomodification of crystalline cellulose by wood decay fungi", *International Research Group on Wood Preservation: 38th Annual Meeting*, Vol. IRG/WP 07 IRG/WP 07-10622, 2007, Jackson Hole, WY.
22. Dufresne, A., "Cellulose-based composites and nanocomposites", in: *Monomers, Polymers and Composites from Renewable Resources*, A. Gandini and M. N. Belgacem (eds.), Elsevier, Oxford, UK, pp. 401-418, 2008.
23. Cullity, B. D., "Elements of X-Ray Diffraction", 2<sup>nd</sup> ed., Wesley Publishing Company, Reading, MA, 1978.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

24. Cave, I. D., "Theory of X-ray measurement of microfibril angle in wood", *Wood Science and Technology*, Vol. 31(3), 143-152, 1997. DOI: 10.1007/BF00702610.
25. Lichtenegger, H., Muller, M., Paris, O., Riekel, C., and Fratzl, P., "Imaging of the helical arrangement of cellulose fibrils in wood by synchrotron X-ray microdiffraction", *Journal of Applied Crystallography*, Vol. 32, 1127-1133, 1999. DOI: 10.1107/S0021889899010961.
26. Clair, B., Almeras, T., Pilate, G., Julline, D., Sugiyama, J., and Riekel, C., "Maturation stress generation in poplar tension wood studied by synchrotron radiation micro-diffraction", *Plant Physiology*, Vol. 152(3), 1650-1658, 2010. DOI: 10.1104/pp.109.149542.
27. Taupin, D., "A powder-diagram automatic- indexing routine", *Journal of Applied Crystallography*, Vol. 6(2), 380-385, 1973. DOI: 10.1107/S0021889873008915.
28. Fernandes, A. N., Thomas, L. H., Altaner, C. M., Callow, P., Forsyth, V. T., Apperley, D. C., Kennedy, C. J., and Jarvis, M. C., "Nanostructure of cellulose microfibrils in spruce wood", *Proceedings of the National Academy of Sciences*, Vol. 108(47), E1195-E1203, 2011. DOI: 10.1073/pnas.1108942108
29. Sarko, A., "Cellulose Structure, Modification and Hydrolysis", R. A. Young, R. M. Rowell, and W. R. Goynes (eds.), John Wiley & Sons, New York, NY, p 29, 1986.
30. Zugenmaier, P., "Crystalline Cellulose and Cellulose Derivatives", Springer-Verlag, Berlin, Germany, p 11, 2008.
31. Delmer, D. P., and Armor, Y., "Cellulose biosynthesis", *Plant Cell*, Vol. 7(7), 987-1000, 1995. DOI: 10.1105/tpc.7.7.987.
32. Preston, R.D., "Cellulose Structure, Modification and Hydrolysis", R. A. Young, R. M. Rowell, and W. R. Goynes (eds.), John Wiley & Sons, New York, NY, p 3, 1986.
33. Ford, E. N. J., Mendon, S. K., Thames, S. F., and Rawlins, J. W., "X-ray diffraction of cotton treated with neutralized vegetable oil- based macromolecular crosslinkers", *Journal of Engineered Fibers and Fabrics*, Vol. 5(1), 10-20, 2010.
34. Kasai, N., and Kakudo, M., "X-ray diffraction by macromolecules", Springer Series in Chemical Physics. New York, 504pp, 2005.
35. Brijwani, K., and Vadlani, P. V., "Solid state fermentation of soybean hulls for cellulolytic enzymes production", In: *Soybean Applications and Technology*, Tzi- Bun Ng (ed.), InTech, Rijeka, Croatia, 2011. DOI: 10.5772/14369.
36. De Rooi, J. J., van der Pers, N. M., Hendriks, R. W. A., R. Delhez, R., Böttger, A. J., and Eilers, P. H. C., "Smoothing of X-ray diffraction data and  $K(\alpha)^2$  elimination using penalized likelihood and the composite link model", *Journal of Applied Crystallography*, Vol. 47(3), 852-860, 2014. DOI: 10.1107/S1600576714005809.
37. Luo, J., Ying, K., and Bai, J., "Savitzky-Golay smoothing and differentiation filter for even number data", *Signal Processing*, Vol. 85(7), 1429-1434, 2005. DOI: 10.1016/j.sipro.2005.02.002.
38. Wang, H., and Zhou, H. (2000). "Data smoothing and distortion of X-ray diffraction peaks. I. Theory", *Journal of Applied Crystallography*, Vol. 33(4), 1128-1135, 2000. DOI: 10.1107/S0021889800006932.
39. Evans, R., Newman, R. H., Roich, U. C., Suckling, I. D., and Wallis, A. F. A., "Changes in cellulose crystallinity during kraft pulping. Comparison of infrared, X-ray diffraction and solid state NMR results", *Holzforschung*, Vol. 49(6), 498-504, 1995. DOI: 10.1515/hfsg.1995.49.6.498.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

40. He, J., Cui, S., and Wang, S.-Y., "Preparation and crystalline analysis of high-grade bamboo dissolving pulp for cellulose acetate", *Journal of Applied Polymer Science*, Vol. 107(2), 1029-1038, 2008. DOI: 10.1002/app.27061
41. Terinte, N., Ibbett, R., and Schuster, K. C., "Overview on native cellulose and microcrystalline cellulose I structure studied by X-ray diffraction (WAXD): Comparison between measurement techniques", *Lenzinger Berichte*, Vol. 89, 118-131, 2011.
42. Mwaikambo, L.Y., and Ansell, M. P., "Chemical modification of hemp, sisal, and kapok fibers by alkalization", *Journal of Applied Polymer Science*, Vol. 84(12), 2222-2234, 2002. DOI: 10.1002/app.10460.
43. Jayaramudu, J., Guduri, B. R., and Rajulu, A. V., "Characterization of new natural cellulosic fabric *Grewia tilifolia*", *Carbohydrate Polymers*, Vol. 79(4), 847-851, 2010. DOI: 10.1016/j.carbpol.2009.10.046.
44. Reddy, K. O., Maheswari, C. U., Reddy, D. J. P., Guduri, B. R., and Rajulu, A. V., "Properties of ligno-cellulose *Ficus religiosa* leaf fibers", *International Journal of Polymers and Technologies*, Vol. 2(1), 29-35, 2010.
45. Schenzel, K., Fischer, S., and Brendler, E., "New method for determining the degree of cellulose I crystallinity by mean of FT Raman spectroscopy", *Cellulose*, Vol. 12(3), 223-231, 2005. DOI: 10.1007/s10570-004-3885-6.
46. Kataoka, Y., and Kondo, T., "FT-IR microscopic analysis of changing cellulose crystalline structure during wood cell formation". *Macromolecules*, Vol. 31(3), 760-764, 1998. DOI: 10.1021/ma970768c.
47. Akerholm, M., Hinterstoisser, B., and Salmen, L., "Characterization of the crystalline structure of cellulose using static and dynamic FT-IR spectroscopy", *Carbohydrate Research*, Vol. 339(3), 569-578, 2004. DOI: 10.1016/j.carres.2003.11.012.
48. Klug, H. P., and Alexander, L. E., "X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials", 2<sup>nd</sup> ed., John Wiley & Sons, New York, NY, 1974.
49. Jenkins, R. and Snyder, R. L., "Introduction to X-Ray Powder Diffractometry", John Wiley & Sons, Hoboken, NJ, 1996.
50. Segal, L., Creely, J. J., Martin Jr., A. E., and Conrad, C. M., "An empirical method for estimating the degree of crystallinity of native cellulose using X-ray diffractometer", *Textile Research Journal*, Vol. 29(10), 786-794, 1959. DOI: 10.1177/004051755902901003.
51. Jayme, G., and Knolle, H., "Introduction to empirical X-ray determination of crystallinity of cellulose materials", *Das Papier* 18(8), 249-255, 1964.
52. Ciupina, V., Zamfirescu, S., and Prodan, G., "Evaluation of mean diameter values using Scherrer equation applied to electron diffraction images", In: *Nanotechnology-Toxicological Issues and Environmental Safety*, NATO Science for Peace and Security Series, 231-237, 2007. DOI: 10.1007/978-1-4020-6076-2\_15.
53. Garvey, C. J., Parker, I. H., and Simon, G. P., "On the interpretation of X-ray diffraction powder patterns in terms of the nanostructure of cellulose I fibres", *Macromolecular Chemistry and Physics*, Vol. 206(15), 1568-1575, 2005. DOI: 10.1002/macp.200500008.
54. Clair, B., Almeras, T., Yamamoto, H., and Okuyama, J., "Mechanical behavior of cellulose microfibrils in tension wood, in relation with maturation stress generation", *Biophysics Journal*, Vol. 91(3), 1128-1137, 2006. DOI: 10.1529/biophysj.105.078485.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

55. Davidson, T., Newman, R. H., and Ryan, M. J., "Variations in the fibre repeat between samples of cellulose I from different sources", *Carbohydrate Research*, Vol. 339(18), 2889-2893, 2004. DOI: [10.1016/j.carres.2004.10.005](https://doi.org/10.1016/j.carres.2004.10.005).
56. Montero, C., Clair, B., Almeras, T., Van Der Lee, A., and Gril, J. "Relationship between wood elastic strain under bending and cellulose crystal strain", *Composite Science and Technology*, Vol. 72(2), 175-181, 2012. DOI: [10.1016/j.compscitech.2011.10.014](https://doi.org/10.1016/j.compscitech.2011.10.014).
57. Chaudhary, S. A., and Al-Jowaid, A. A., "Vegetation of the Kingdom of Saudi Arabia", Ministry of Agriculture and Water, Riyadh, Saudi Arabia, 1999.
58. Hindi, S. S. Z. and Abohassan, R. A., "Cellulose triacetate synthesis from cellulosic wastes by heterogeneous reactions", *BioResources*, Vol. 10(3), 5030-5048, 2015. DOI: [10.15376/biores.10.3.5030-5048](https://doi.org/10.15376/biores.10.3.5030-5048).
59. ASTM D1105-84, "Standard method for preparation of extractive-free wood", ASTM International, West Conshohocken, PA, 1989.
60. ASTM D 1106-84, "Standard test method for acid-insoluble lignin in wood", ASTM International, West Conshohocken, PA, 1989.
61. Viera, R. G. P., Filho, R. G., de Assuncao, R. M. N., Meireles, C. da S., Vieira, J. G., and de Oliveira, G. S. (2007). "Synthesis and characterization of methylcellulose from sugar cane bagasse cellulose", *Carbohydrate Polymers*, Vol. 67(2), 182-189, 2007. DOI: [10.1016/j.carbpol.2006.05.007](https://doi.org/10.1016/j.carbpol.2006.05.007).
62. ASTM-D 1102-84 (1989). "Standard test method for ash in wood", ASTM International, West Conshohocken, PA, 1989.
63. Cao, Y., and Tan, H., "Study on crystal structures of enzyme-hydrolyzed cellulosic materials by X-ray diffraction", *Enzyme and Microbial Technology*, Vol. 36(2-3), 314-317, 2005. DOI: [10.1016/j.enzmictec.2004.09.002](https://doi.org/10.1016/j.enzmictec.2004.09.002)
64. Hult, E. L., Iversen, T., and Sugiyama, J., "Characterization of the supramolecular structure of cellulose in wood pulp fibers", *Cellulose*, Vol. 10(2), 103-110, 2003.
65. Poletto, M., Ornaghi, H. L. and Zattera, A. J., "Native cellulose: Structure, characterization and thermal properties", *Materials*, Vol. 7(9), 6105-6119, 2014. DOI: [10.3390/ma7096105](https://doi.org/10.3390/ma7096105).
66. Krassing, H. A., "Cellulose". CRC Press, Boca Raton, FL, 1993.
67. El-Nakhlawy, F.S., "Principles of statistics, biostatistical experimental design and analysis". KAU Pub. Center. KSA, 2008.
68. Parker, J., "All about cotton: A fabric dictionary and swatchbook". Fabric Reference Series, Vol. 2, Rain City Publishing, Seattle, WA, 1998.
69. Barsa, A., "Cotton Fibers: Developmental Biology Quality Improvement and Textile Processing", Food Products Press, Binghamton, NY, 1999.
70. Kaila, K. A., and Aittamaa, J., "Characterization of wood fibers using fiber property distribution", *Chemical Engineering and Processing*, Vol. 45(7), 246-254, 2006. DOI: [10.1016/j.cep.2005.12.003](https://doi.org/10.1016/j.cep.2005.12.003).
71. Diaz, M. J., Garcia, M. M., Eugenio, M. M., Tapias, R., Fernandez, M., and Lopez, F., "Variations in fiber length and some pulp chemical properties of leucaena varieties", *Industrial Crops and Products*, Vol. 26(2), 142-150, 2007. DOI: [10.1016/j.indcrop.2007.02.003](https://doi.org/10.1016/j.indcrop.2007.02.003).

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

72. Lopez, F, Garcia, M. M., Yanez, R., Tapias, R., Fernandez, M., and Diaz, M. J., "Leucaena species valoration for biomass and paper production in 1 and 2 year harvest", *Bioresource Technology*, Vol. 99(11), 4846-4853, 2008. DOI: 10.1016/j.biortech.2007.09.048.
73. Khristova, P., Kordsachia, O. and Khider, T. "Alkaline pulping with additives of date palm rachis and leaves from Sudan", *Bioresource Technology*, Vol. 96(1), 79-85, 2005. DOI: 10.1016/j.biortech.2003.05.005.
74. Khiari, R., Mhenni, M. F., Belgacem, M. N., and Mauret, E., "Chemical composition and pulping of date palm rachis and *Posidonia oceanica*- A comparison with other wood and non-wood fiber sources", *Bioresource Technology*, Vol. 101(2), 775-780, 2010. DOI: 10.1016/j.biortech.2009.08.079.
75. Ververis, C., Georghiou, K., Christodoulakis, N., Santas, P., and Santas, R., "Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production", *Industrial Crops and Products*, Vol. 19(3), 245-254, 2004. DOI: 10.1016/j.indcrop.2003.10.006.
76. Amaducci, S., Amaducci, M. T., Benati, R., and Venturi, G. "Crop yield and quality parameters of four annual fibre crops (hemp, kenaf, maize and sorghum) in the North of Italy", *Industrial Crops and Products*, 11(2-3), 179-186, 2000. DOI: 10.1016/S0926-6690(99)00063-1
77. Lopez, F, Garcia, J. C., Perez, A., Garcia, M. M., Feria, M. J., and Tapias, R., "*Leucaena diversifolia* a new raw material for paper production by soda-ethanol pulping process", *Chemical Engineering Research and Design*, Vol. 88(1), 1-9, 2009. DOI: 10.1016/j.cherd.2009.06.016.

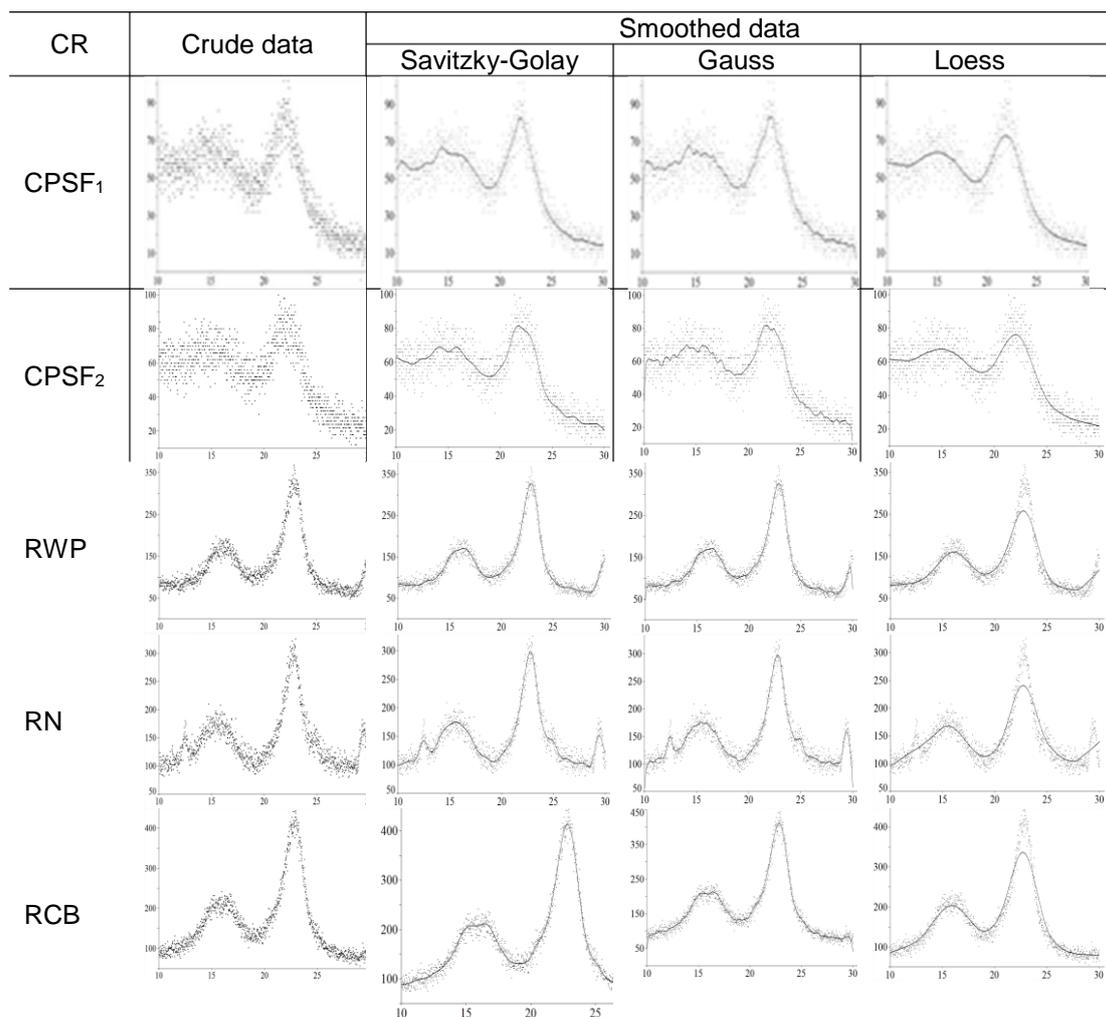
# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

## APPENDIX



**Appendix 1.** X-ray diffraction spectra for crude data and those smoothed by Savitzky-Golay, Gauss, and Loess algorithms for the five cellulosic resources: CPSF<sub>1</sub> (*Calotropis procera* seed floss), CPSF<sub>2</sub> (*Ceiba pentandra* seed floss), RWP (recycled writing paper), RN (recycled newspaper), and RCB (recycled cardboard).