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Comparison of crystallinity index computational methods based on lignocellulose X-ray diffractogram

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Abstract. Crystallinity index (CrI) obtained from X-ray diffraction (XRD) technique is often utilized as a characterization parameter of lignocellulosic biomass. There exist a few methodologies to calculate CrI but the respective merit as lignocellulose characterization parameter is not very clear. Here four commonly employed CrI computational methods were applied to raw and torrefied biomasses (palm kernel shell and sugarcane bagasse), cellulose- and lignin-added raw biomasses and artificial mixtures of cellulose, hemicellulose and lignin in order to compare the effect of the composition of lignocellulosic biomass toward CrI calculated from X-ray diffractogram. Calculated CrI systematically showed larger value than the weight percentage of cellulose contained in the samples. Among the four computational methods compared, Segal (single peak height ratio) method and Ruland-Vonk (two-peak area ratio) method appeared to give reasonable CrI numbers although they are still overestimating the cellulose weight ratio. The Ruland-Vonk method consistently gave the lowest CrI values among the methods examined.

Introduction

Crystallinity is one of the primary parameters in describing the nature of lignocellulose. The degree of crystallinity could be made an indicator to predict the rate of cellulose hydrolysis by cellulase in bioethanol production [1] or the strength of biocomposite material [2]. Furthermore, crystallinity is often utilized to monitor the effect of various treatments on lignocellulosic biomass [3-6]. Due to its importance, various methodologies have been proposed to yield a measure of crystallinity in lignocellulosic biomass [7], including X-ray diffraction, Fourier-transform infrared spectroscopy, Raman spectroscopy and solid state ^{13}C nuclear magnetic resonance. X-ray diffraction (XRD) is one of the most popular among those proposed methodologies for the quantification of crystallinity of lignocellulosic biomass, partly due to its wide availability and straight-forward data interpretation.

Crystallinity of lignocellulosic biomass is commonly expressed in the form of crystallinity index (CrI), which is intended to reflect the fraction (could be weight, volume or molar) of crystalline cellulose within the lignocellulosic biomass sample. When XRD is employed to derive CrI of a lignocellulose sample, first powder X-ray diffractogram of the sample is obtained, which constitutes a few diffraction peaks from the crystalline part of its cellulose and a single broad peak (called halo) from the amorphous parts of the sample. There exist a few methodologies to calculate CrI from the powder X-ray diffractogram: Segal peak height method [8], Jayme-Knolle method [9], Ruland-Vonk method [10,11] and peak deconvolution method [12]. The first two methods utilize peak heights to calculate CrI, while the third method employ peak area rather than peak

height. The more recent entry to the field, peak deconvolution method, deconvolutes the diffractogram peaks using standard distribution function to obtain respective peak contributions.

Comparison of these methodologies has been attempted in the past [13,14]. However, those comparisons were done on a fixed sample like powder cellulose (Avicel PH-101) along with literature data analysis on the same sample. Park et al. [13] reports that in their literature compilation of 18 measurements, CrI of Avicel PH-101 reported varied from ca. 50 % to 91.7 %. The present paper took a different approach for CrI computational methodology comparison by preparing samples with systematic change of lignocellulose compositions: (1) through torrefaction of raw palm kernel shell and sugarcane bagasse, (2) through addition of pure cellulose and lignin to those raw biomasses and (3) through synthesis of a series of artificial lignocellulose samples by physically mixing known lignocellulosic components.

Experimental

Lignocellulosic Sample Preparation. Palm kernel shell was obtained from an oil palm plantation of FELCRA Processing & Engineering Sdn. Bhd. at Teluk Intan, and sugarcane bagasse from Lian Hup Hin Provision Sdn. Bhd., Kamunting, both in Perak, Malaysia. These raw biomass samples were washed with distilled water to remove dirt and dust, cut into small pieces (ca. 1cm in length) with a mechanical knife and left in a laboratory open atmosphere for two days before proceeding for drying in an air oven at 105 °C for 24 hours. The moisture content of the samples was measured following ASTM E871-82 protocol and was less than 10 wt%. The dried biomass was then grinded and sieved to obtain fractions of uniform particle size. The sugarcane bagasse was then undergone palletization process to increase its density due to its inherently characteristic low density.

In order to manipulate chemical composition of these raw biomasses, torrefaction was performed at 200 °C for 30 min under flowing nitrogen. Furthermore, a modified lignocellulosic biomass was prepared by mixing microcrystalline cellulose (Avicel PH-101, Sigma-Aldrich) and pure lignin (Sigma-Aldrich) to the raw biomasses. In addition, several artificial lignocellulosic biomass samples were produced by mixing microcrystalline cellulose, xylan (representative of hemicellulose) and pure lignin to simulate the changes in crystallinity in the artificial lignocellulosic sample. The amount of cellulose, hemicellulose and lignin in the raw and torrefied lignocellulosic biomass was determined following the method described by Yang et al. [15] and listed in Table 1.

Crystallinity Index Measurement. X-ray diffractogram of the above samples were obtained by using Malvern Panalytical's HighScore Plus X-ray diffractometer. The scanning ranged from 5° to 40°, with an exposure time of 0.4 s per step in steps of 0.01415° using Cu-$K_{\alpha 1}$ radiation at 1.541 Å. The extracted data were computed and analyzed using Origin Pro 8.5 software.

Table 1. Chemical Compositions of the Employed Biomass

	Cellulose [wt%]	Hemicellulose [wt%]	Lignin [wt%]	Extractives [wt%]
Sugarcane Bagasse	43	26	24	7
Torrefied Sugarcane Bagasse	36	15	44	5
Palm Kernel Shell	24	28	46	4
Torrefied Palm Kernel Shell	19	17	61	3

Results and Discussion

Crystallinity Index of Raw and Torrefied Biomass. The CrIs of raw and torrefied biomass as well as microcrystalline cellulose (Avicel PH-101) were computed from respective diffractogram using the four computational methods, viz., Segal peak height method, Jayme-Knolle method, Ruland-Vonk method and peak deconvolution method, and the results are shown in Fig. 1.

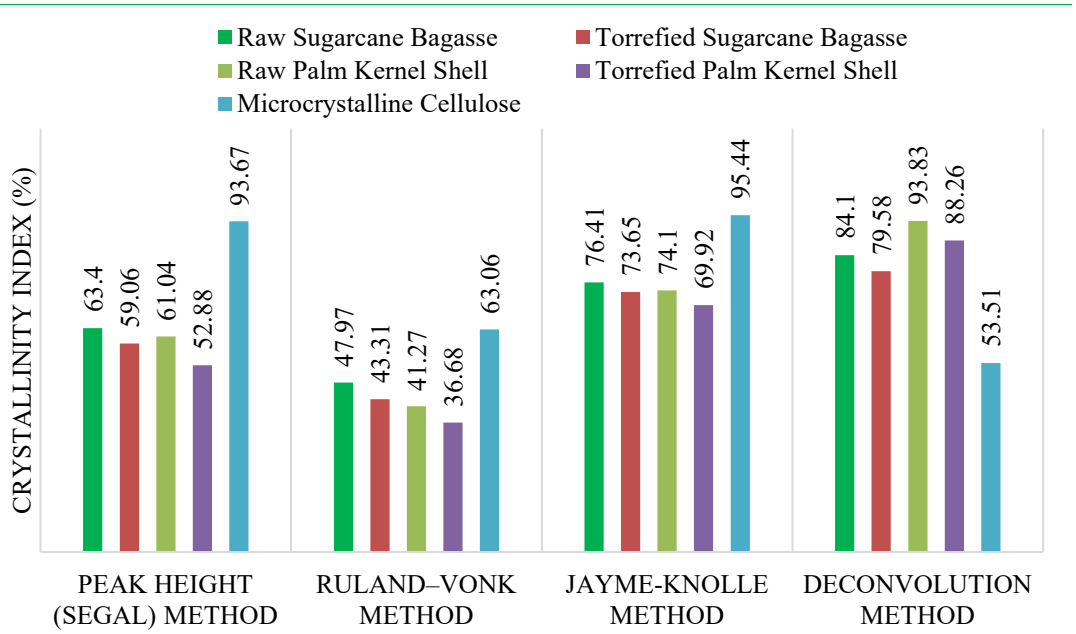

Fig. 1. Crystallinity index obtained using different computational methods

Overall comparison of the obtained CrI shown in Fig. 1 indicates that the first three computational methods listed in the figure, viz., Segal peak height method, Ruland-Vonk method and Jayme-Knolle method seems to show similar trend among the measured samples: (1) Avicel PH-101 (blue bars) shows the highest CrI within the same computational method, (2) raw sugarcane bagasse (green bars) always show higher CrI than raw palm kernel shell (olive green bars), (3) torrefaction always decrease CrI for both sugarcane bagasse and palm kernel shell. On the other hand, the last computational method, deconvolution, seems to contradict in many of these trends indicated by the first three methods.

Among the first three computational methodologies, Jayme-Knolle method gives highest overall CrI values for all the five samples, followed by Segal peak height method and then the Ruland-Vonk method. It is noted that the lowest absolute CrI values provided by the Ruland-Vonk method still seems to be higher than actual cellulose crystal contents when compared to the cellulose content of the respective samples shown in Table 1, particularly for the lower cellulose content samples such as palm kernel shell and torrefied palm kernel shell. Attentions should be paid, however, that the cellulose content in Table 1 is in the unit of wt%, while CrIs calculated and shown in Fig. 1 are the X-ray diffraction intensity ratios.

Modified Lignocellulosic Biomass Sample Analysis. In order to examine the effect of the amount of lignin and cellulose towards the measured crystallinity of lignocellulosic biomass, 10 wt%, 20 wt% and 40 wt% of microcrystalline cellulose or lignin were added into the two raw biomass samples, respectively. This translates to the actual cellulose content of 43 wt%, 48 wt%, 53 wt% and 59 wt% for Avicel-added sugarcane samples, 43 wt%, 39 wt%, 36 wt% and 31 wt% for lignin-added sugarcane samples, 24 wt%, 31 wt%, 37 wt% and 46 wt% for Avicel-added palm kernel shell samples and 24 wt%, 22 wt%, 20 wt% and 17 wt% for lignin-added palm kernel shell

samples, respectively. Obtained CrIs shown in Figs. 2 and 3 indicate that addition of cellulose monotonously increases, and addition of lignin monotonously decreases, the calculated CrIs for the three computational methods, viz., Segal peak height, Ruland-Vonk and Jayme-Knolle. Deconvolution method again fails to follow these trends, and its calculated CrIs show irregular trend with the increase of added cellulose or lignin.

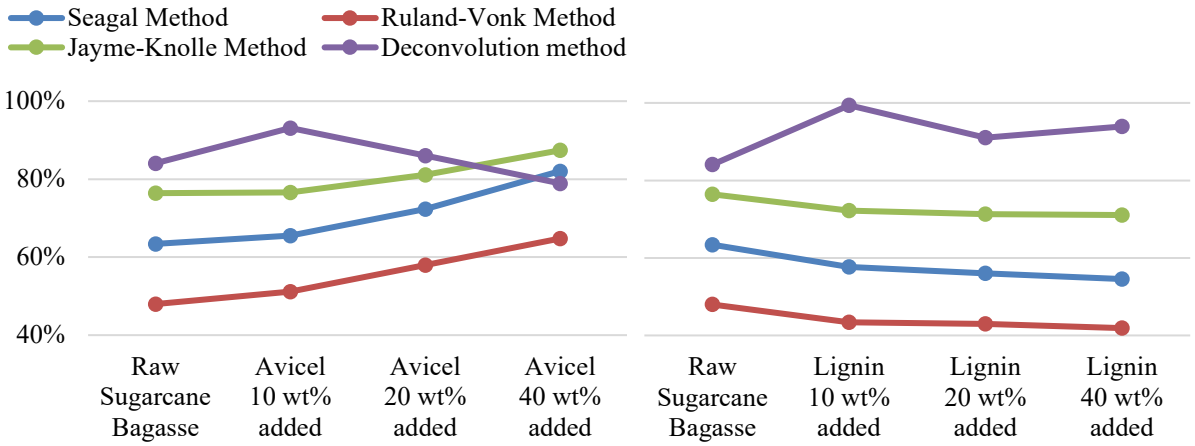

Fig. 2. Crystallinity index of raw and modified Sugarcane Bagasse

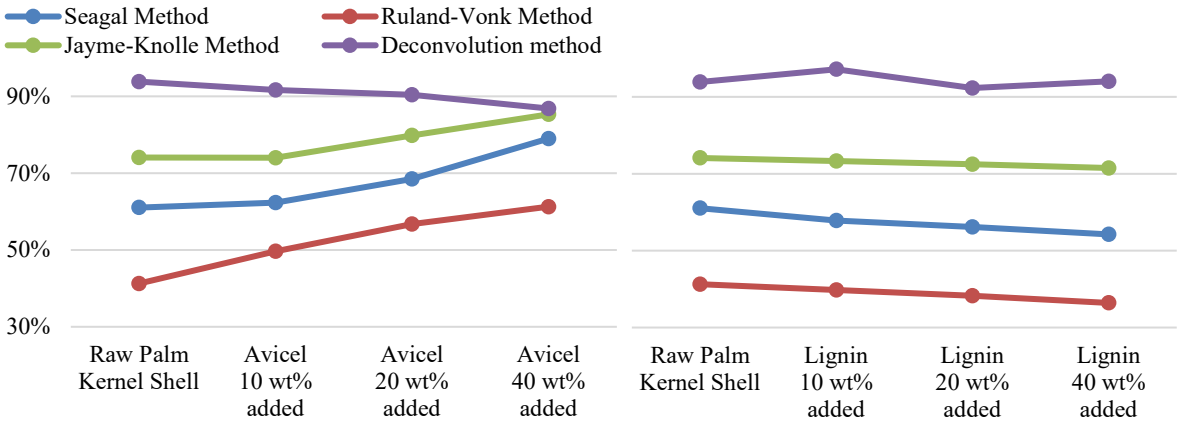

Fig. 3. Crystallinity index of raw and modified Palm Kernel Shell

Among the three computational methodologies that appear to give reasonable trend with the systematic increase (by addition of cellulose) and decrease (by addition of lignin) of cellulose amount, the absolute values of CrIs obtained are in the decreasing order of Jayme-Knolle, Segal peak height and Ruland-Vonk, in parallel with the results found in Fig. 1 for raw and torrefied biomasses. It is further noted that the two methods, Segal peak height and Ruland-Vonk, gives almost the same CrI increment when compared with raw biomass and 40 wt% Avicel (17-19 % CrI increase for sugarcane bagasse and 18-20 % for palm kernel shell). This is in good agreement with the actual increment of cellulose in those samples, 16 % and 22 %, respectively.

On the other hand, lignin addition gave much less impact on measured CrI: for the actual decrease of 12 % in cellulose content CrI decreased only 6-9 % in sugarcane bagasse, and for palm kernel shell 7 % decrease caused 5-7 % CrI decrease. Apparently, depending on the samples, non-

crystalline part of the sample contributes less for the calculation of CrI for those two calculation methods.

Artificial Lignocellulosic Biomass Crystallinity Analysis. A series of artificial lignocellulosic biomass is prepared by physically mixing microcrystalline cellulose (Avicel PH-101), xylan (representative of hemicellulose) and pure lignin. Six sets of artificial lignocellulosic biomass were produced with the compositions listed in Table 2. The compositions chosen are more or less arbitrary, except that Sample No. 1, 2, 4 and 6 mimic those of the raw and the torrefied samples found in Table 1.

Figure 4 shows the CrIs of those artificial lignocellulosic biomasses listed in the increasing order of cellulose content. As has been observed in Figs. 2 and 3, the CrIs of these samples monotonously increased with increasing cellulose content, except for the deconvolution method which is not stable and did not show the similar trend that are apparent in other three computational methods. Among the three computational methods that gave similar monotonous trend with the systematic change of the amount of cellulose, Jayme-Knolle method gave the highest absolute CrI values, followed by Segal peak height method and Ruland-Vonk method, again in line with the observation made in Figs. 1 through 3.

The two methods that gave the low absolute CrI values, Seagal and Ruland-Vonk methods, gave almost the same CrIs, although they are still higher than actual cellulose contents (in wt%) of the respective samples (abscissa). Note that in the present samples, the increment of CrI (18.7 for Ruland-Vonk and 18.0 for Seagal) between sample No. 6 and No. 1 is lesser than the increment of cellulose content (26.6 wt%).

Table 2. Chemical Compositions of the Artificial Biomass

Sample No.	Cellulose [wt%]	Hemicellulose [wt%]	Lignin [wt%]
1	46.23	27.96	25.81
2	37.89	15.79	46.31
3	35.00	25.00	40.00
4	30.00	30.00	40.00
5	25.00	28.10	46.90
6	19.59	17.53	62.89

Comparison of Computational Methods. The foregoing data obtained on three types of lignocellulose biomasses, viz., raw/torrefied, cellulose/lignin added and artificial, all points to the following conclusions: (1) Jayme-Knolle method, Segal peak height method and Ruland-Vonk method give similar tendencies of monotonous increase of CrI with increase of cellulose content, (2) the absolute value of CrI decreases in the order of Jayme-Knolle method, Segal peak height method and Ruland-Vonk method, (3) the CrI values are systematically higher than actual cellulose content expressed in wt% and (4) the deconvolution method does not seem to reflect the biomass crystallinity very accurately.

The present work indicated that the deconvolution method seems to give fluctuated results in terms of sample cellulose content. The challenge for the deconvolution method may be to identify the location of the peak, which might vary according to sample [14]. Sometimes certain diffraction peaks such as (10−1) and (021) may not be obvious in the obtained Xray diffractogram, which may cause the results of computed CrI to be rather inaccurate and unreliable.

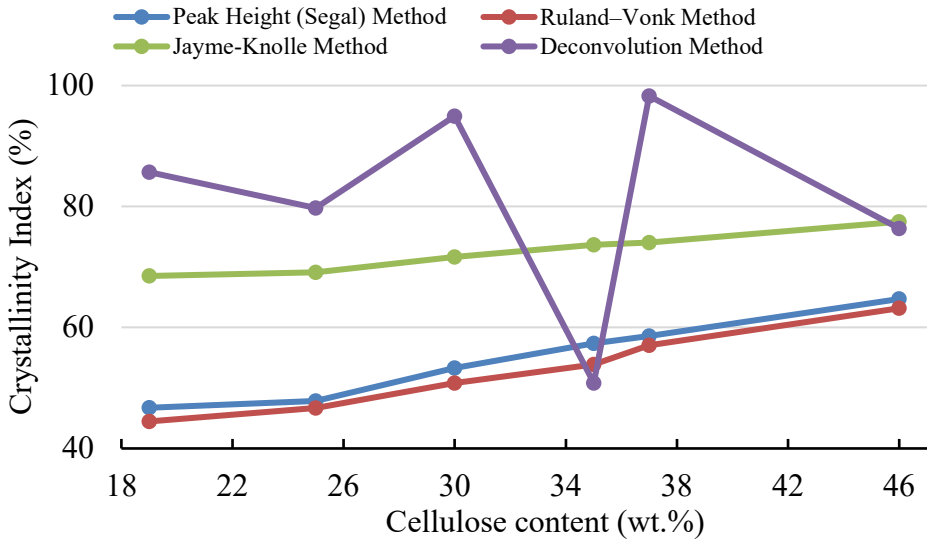

Fig. 4. Crystallinity index of artificial lignocellulosic biomass

While both Jayme-Knolle method and Seagal peak height method utilizes diffraction peak heights as calculation parameters, the former gives higher CrI than the latter due to the fact that the former incorporates (101) peak height in addition to (002) peak height while the latter uses only (002) peak. The Ruland-Vonk method, which measures peak areas rather than peak heights, led to the lowest CrI values, may be due to the fact that it considers all the amorphous region of the X-ray diffractogram without excluding any data except for the background noise.

It is interesting to note that the Segal method which utilizes simple peak heights gives CrI values closer (Figs. 1 through 3) or almost the same (Fig. 4) with Ruland-Vonk method which uses peak areas. This is also notable in view of the possibility that XRD peak height would be influenced by the cellulose crystallite sizes when they are small enough to give peak broadening [13].

Summary

Three lignocellulosic samples with systematic change of lignocellulose compositions were prepared and submitted for XRD CrI measurement. Comparison of four calculation methods showed that Jayme-Knolle method, Segal peak height method and Ruland-Vonk method give similar tendency of monotonous increase of CrI with increase of cellulose content while deconvolution method does not seem to reflect the biomass crystallinity very accurately. Among the three methods which gave a reasonable CrI trend, Segal peak height method and Ruland-Vonk method seem to be more reliable and suitable in examining the sample crystallinity. In any of the examined calculation methodologies, the amorphose part of lignocellulose samples appears to be less represented in X-ray diffractgram compared to crystalline part, giving systematically larger CrI values than actual cellulose content expressed in wt%. There also was a strong indication that CrI depends on sample composition, most likely due to its elemental composition difference which may give different X-ray scattaring characteristics among the samples.

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