In-Depth Investigation of Biomass Pyrolysis Based on Three Major Components: Hemicellulose, Cellulose and Lignin

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To better understand biomass pyrolysis, the different roles of the three components (hemicellulose, cellulose, and lignin) in pyrolysis are investigated in depth using a thermogravimetric analyzer (TGA). The pyrolysis characteristics of the three components are first analyzed, and the process of biomass pyrolysis is divided into four ranges according to the temperatures specified by individual components. Second, synthesized biomass samples containing two or three of the biomass components are developed on the basis of a simplex-lattice approach. The pyrolysis of the synthesized samples indicates negligible interaction among the three components and a linear relationship occurring between the weight loss and proportion of hemicellulose (or cellulose) and residues at the specified temperature ranges. Finally, two sets of multiple linear-regression equations are established for predicting the component proportions in a biomass and the weight loss of a biomass during pyrolysis in TGA, respectively. The results of the calculations for the synthesized samples are consistent with the experimental measurements. Furthermore, to validate the computation approach, TGA experimental analysis of the three components of palm oil wastes, a local representative biomass sample, is conducted.

1. Introduction

It is well-known that biomass consists mainly of three major components (hemicellulose, cellulose, and lignin) together with trace amount of extractives and minerals.[1,2] Normally, cellulose, hemicellulose, and lignin cover 40−60, 20−40, and 10−25 wt % of biomass materials on dry basis, respectively.[3,4] Numerous studies[5−18] based on one or all the three components have been carried out so far, and among them, several have focused on developing kinetic models for predicting the behavior of biomass pyrolysis.[6−11] Previous studies indicated that it is important to distinguish the behavior of the three components for a better understanding of the biomass pyrolysis process.[7,8]

Generally, biomass pyrolysis proceeds through a series of complex reactions. At low heating rates (<100 °C/min), biomass materials decompose in well-described stages of moisture evolution, hemicellulose decomposition, and cellulose decomposition, while lignin is decomposed very slowly and at a minor level.[14] The overall rate of biomass pyrolysis was considered as a sum of the individual rates of the three components in previous studies.[8−14] The yield of volatiles, gases, and char from pyrolysis was found to be proportional to the three components in the virgin biomass.[13,14] Other studies indicated that the global production of volatile matter corresponds to the summation of the individual contributions from the three main components.[9−13] The ratio of the three components in a biomass, which is closely related to biomass conversion, differs greatly with the source of the biomass. So far, few experimental or computing approaches for determining the contents of the three components in natural biomass have been established. Blasi et al.[1] and Li et al.[2] first used organic solvents to remove extractives in biomass, followed by the determination of the amounts of hemicellulose, cellulose, and lignin in the biomass using different experimental methods. However, these methods require several extractive steps and are generally time consuming.

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Experiments using a synthetic biomass composed of the three components were previously conducted in TGA and packed bed.[14] No interaction among these three components occurred during the pyrolysis experiments. However, natural biomass differs from the synthetic biomass, most likely because of the mineral matter in the former. It was known that mineral matter potentially has a great influence on biomass pyrolysis. Williams and Horne[19] studied the influence of metal salts (such as NaOH, Na_2CO_3, NaCl, $NiCl_2$, and $CuSO_4$) on cellulose pyrolysis; the addition of minerals lowered the temperature of cellulose pyrolysis.

In this study, cellulose, hemicellulose, and lignin were used as pure biomass components. After a full investigation of the pyrolysis characteristics of the three components, thermal degradation of the synthesized samples (a mixture of these components at different ratios) was studied. A computing approach which is capable of determining the amounts of the three main components in the biomass and also the weight loss of the biomass in TGA at specified temperature ranges was developed. To verify this computing approach, the proportions of the three main components in palm oil waste (a representative of local biomass) were determined experimentally.

2. Materials and Experimental Methods

2.1. Materials. Cellulose and lignin were purchased from Sigma-Aldrich Chemie GmbH. The former is in a powder fibrous form and the latter is alkali lignin in a brown powder form. Because commercial hemicellulose can hardly be purchased, xylan, although it might have different physical and chemical properties, has been widely used as a representative of the hemicellulose component in pyrolysis processes.[8,10,11] Here, xylan, in a yellow powder form processed from birchwood and obtained from Sigma-Aldrich Chemie GmbH, was used as hemicellulose. The particle size of hemicellulose averages ~100 μm, and those of cellulose and lignin are ~50 μm.

Palm oil waste samples, shells, fibers, and empty fruit bunches (EFB), were used as representatives of local biomass. They were ground in a laboratory-scale centrifugal mill (Rocklabs, New Zealand) and sieved in a Retsch test sieve with a 1 mm screen (Retsch, Fisher Scientific Company, USA) (i.e., all samples studied here were smaller than 1 mm). Details about the proximate and ultimate analyses of palm oil wastes can be found in our previous study.[20]

2.2. Preparation of Synthesized Biomass Samples. Biomass samples were synthesized using the three major components (hemicellulose, cellulose, and lignin), on the basis of the simplex-lattice design introduced by Scheffe.[21,22] The design is credited to be the foundation on which the theory of experimental designs for mixtures was built, and the design is still very much in use today.[23,24]

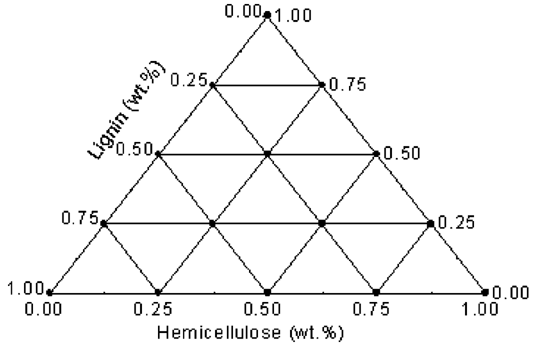

Figure 1. Proportions of hemicellulose, cellulose, and lignin in the synthetic biomass.

The component proportions of the mixture satisfy the constraints $x_i \geq 0$, $x_1 + x_2 + ... + x_q = 1.0$. Each component proportion, x_i, can take values from zero to unity, and all blends among the ingredients are possible. The key issue is to choose a representative and reproducible proportion of the three components. An ordered arrangement consisting of a uniformly spaced distribution of points on a simplex is known as a lattice. A lattice may have a special correspondence to a specific polynomial equation. To support a polynomial model of degree *m* in *q* components over the simplex, the lattice, referred to as a $\{q, m\}$ simplex lattice, consists of points whose coordinates are defined by the following combinations of component proportions: the proportions assumed by each component take the $m + 1$ equally spaced values from 0 to 1, that is

$$x_i = 0, \frac{1}{m}, \frac{2}{m}, \Lambda, 1 \qquad (1)$$

and the $\{q, m\}$ simplex lattice consists of all possible combinations (mixtures) of the components where the proportions (eq 1) for each component are used. The number of design points in the $\{q, m\}$ simplex lattice is

$$(^{q + m - 1})m = (q + m - 1)!/[m!(q - 1)!]$$

For the mixture of hemicellulose, cellulose, and lignin (three components), $q = 3$. To guarantee the accuracy and keep the computing approach simple, *m* is set to 4, so the total number of points is 15. They are shown in Figure 1 (solid dots). Only three synthesized samples involve all the three components while others involved only one or two components. The biomass samples were synthesized by dry mixing the three components according to the specific ratio. In the following text, H/C indicates the weight ratio of hemicellulose/cellulose, C/L and H/L represent those of cellulose/lignin and hemicellulose/lignin, respectively, and H/C/L is the weight ratio of a mixture of hemicellulose/cellulose/lignin.

2.3. Experimental Procedures. Pyrolysis of biomass samples (including synthesized samples and palm oil wastes) was performed in a thermogravimetric analyzer (TGA 2050, TA, USA). The experimental procedure is listed as follows. First, the sample was heated at 10 °C/min to 105 °C from the ambient temperature and kept isothermal for 5 min to remove moisture. Then, it was heated to 900 °C continuously at 10 °C/min and held for 3 min to make sure that pyrolysis was completed. The sample size was maintained at ~20 mg for every experiment, and the flow rate of carrier gas (N_2) was kept at 120 mL/min. At the selected conditions, the limitation of heat transfer inside the particles and in the external gas phase is negligible.[20]

2.4. Analysis of Hemicellulose, Cellulose, and Lignin in Palm Oil Waste. The amounts of hemicellulose, cellulose, and lignin in palm oil waste samples were determined according to the following method.[1,2] (1) To determine the amount of extractives in the biomass solvent extraction (60 mL acetone for 1 g of dried biomass sample) was used, and the temperature was held at 90 °C for 2 h. After that, the sample was dried in an oven (105−110 °C) until a constant weight was obtained. The weight difference before and after the extraction is the amount of the extractives. (2) To determine the amount of hemicellulose, 150 mL of sodium hydroxide (NaOH) solution (0.5 mol/l) was added to 1 g of extractive-free dried biomass, and the temperature was held at 80 °C for 3.5 h. After that, the sample was washed using DI water until no more Na^+ was detected (indicated by the pH value of the solution approaching 7), and then it was dried to a constant weight. The difference between the sample weight before and after this treatment is the

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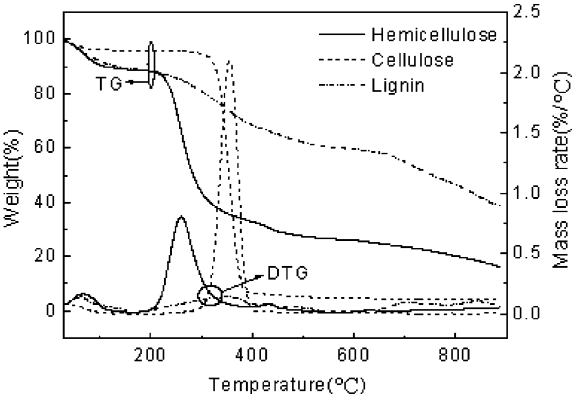

Figure 2. Pyrolysis curves of three biomass components.

hemicellulose content. (3) To determine the amount of lignin, 30 mL of 98% sulfuric acid was added for each gram sample (extractive-free dried biomass). After the sample was held at ambient temperature for 24 h, it was boiled at 100 °C for 1 h. The mixture was filtered, and then the residue was washed until the sulfate ion in the filtrate was undetectable (via titration of a 10% barium chloride solution); it was then dried to a constant weight. The weight of the residue is recorded as the lignin content. Finally, the content of cellulose is calculated by difference, assuming that extractives, hemicellulose, lignin, and cellulose are the only components of the entire biomass.

3. Results and Discussion

3.1. TG Analysis of Three Biomass Components. The pyrolysis characteristics, both TG (in weight %) and DTG (in %/°C) curves, of the three components (hemicellulose, cellulose, and lignin) are shown in Figure 2. There are obvious differences between their behaviors. The pyrolysis of hemicellulose started at 220 °C, its mass-loss rate (DTG curve) increased greatly with increasing temperature and obtained its maximum value at 260 °C. When the temperature is over 315 °C, its weight-loss rate is low, <0.099 wt %/°C, and the amount of solid residue left is high (~20 wt %). The pyrolysis of cellulose focuses at a temperature range of 315−390 °C with the maximum mass-loss rate of 2.1 wt %/°C obtained at 355 °C. At temperatures over 390 °C, its mass-loss rate is low, 0.027 wt %/°C, and the amount of solid residue remaining is low at ~7 wt %. In comparison to the sharper DTG peaks of cellulose and hemicellulose, lignin has wide and flat DTG peaks. From the ambient temperature to 700 °C, only ~40 wt % of lignin is lost at a very slow rate (<0.15 wt %/°C). It might be attributed to the slow carbonization of lignin, and carbon could be the main product; lignin is the part mainly responsible for char production. When the temperature is higher than 750 °C, its weight-loss rate increases slightly to 0.3 wt %/°C, and a total of ~67 wt % weight loss is achieved at 850 °C.

The higher activity of hemicellulose in thermal decomposition might be attributed to its chemical structure. Hemicellulose has a random amorphous structure with little strength, and it is easily hydrolyzed by dilute acid or base. In contrast, the cellulose molecule is a very long polymer of glucose units without any branches, and it is crystalline, strong, and resistant to hydrolysis. Lignin is different from cellulose and hemicellulose, which are composed of polysaccharides, because it is composed of three kinds of benzene-propane and is heavily cross-linked. The thermal stability of lignin is thus very high, and it is difficult to decompose. In terms of thermal degradation, the three components in the order of the easiest to the most difficult to degrade are hemicellulose > cellulose > lignin.

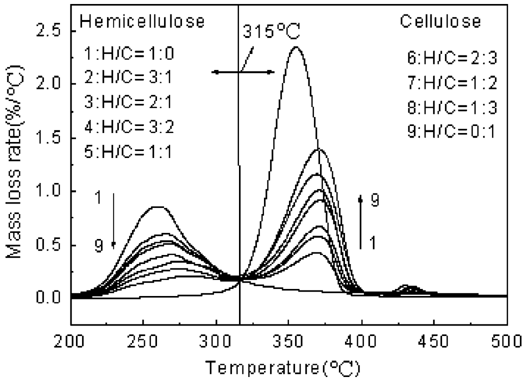

Figure 3. DTG curves of the hemicellulose/cellulose mixtures.

3.2. Pyrolysis of the Synthesized Biomass Samples. *3.2.1. Mixture of Hemicellulose and Cellulose.* The pyrolysis curves of the synthesized biomass samples of hemicellulose (H) and cellulose (C) are plotted in Figure 3. Here, the synthesized biomass samples contain not only those from the simplex-lattice (3, 4) design as given in Figure 1 (i.e., H/C = 1:0, 0.75:0.25, 0.5:0.5, 0.25:0.75, and 0:1) but also four other points (shown in Figure 3, H/C = 1:2, 2:3, 3:2, and 3:1), totaling 9 samples. In Figure 3, the DTG curves of the mixture of hemicellulose and cellulose have two separated peaks, and the cross points are located at ~315 °C. When temperature is lower than 315 °C, the mass-loss rate of pure cellulose alone (H/C = 0:1) is very low (<0.085%/°C), while that of pure hemicellulose (H/C = 1:0) is the highest (~0.8%/°C). With the ratio of H/C decreasing from case 1 to 9, the mass-loss rate also decreased. However, when temperature is higher than 315 °C, the situation is reversed. The mass-loss rate of hemicellulose alone is very low (<0.19%/°C), while that of cellulose alone is the highest (~2.4%/°C). With the ratio of H/C decreasing from case 1 to 9, the mass-loss rate increased. When the temperature is higher than 400 °C, no obvious weight loss is observed. It is reasonable to assume that the weight loss in the temperature range of 220−315 °C was mainly caused by hemicellulose and that in the range of 315−400 °C by cellulose. No obvious interaction happened between hemicellulose and cellulose pyrolysis. Moreover, if one compares the pyrolysis curve of the mixtures (cases 2−8) with the two pure components (case 1 or 9), it can be observed that the DTG peaks were shifted to a 10 °C higher temperature for both components. In the case of hemicellulose, whose pyrolysis happens at lower temperature, this may be attributed to the cellulose inhibiting the heat- and mass-transfer of hemicellulose sample. Similarly, the pyrolysis of cellulose in the mixture could also be affected by the residue from the hemicellulose pyrolysis.

3.2.2. Mixtures of Hemicellulose and Lignin and of Cellulose and Lignin. The pyrolysis of hemicellulose and lignin (L) mixtures and that of cellulose and lignin mixtures were also carried out, and the results are given in Figure 4. The ratios of the mixture were decided following the simplex-lattice (Figure 1) (i.e., both H/L and C/L are equal to 1:0, 0.75:0.25, 0.5:0.5, 0.25:0.75, and 0:1). Solid lines indicate the pyrolysis of hemicellulose and lignin mixtures at 220−315 °C, while dotted lines represent that of cellulose and lignin mixtures at 315−400 °C. The DTG curves of both mixtures (H + L and C + L) have only one peak. When the temperature is lower than 315 °C, the mass-loss rate of the cellulose and lignin mixture (cases 5−8) is very low (<0.1%/°C). Similarly, when the temperature is higher than 315 °C, the mass loss rate of the hemicellulose and lignin mixture (cases 1−4) is very low (<0.2%/°C). For both mixtures (H + L and C + L), the peak value of their mass-

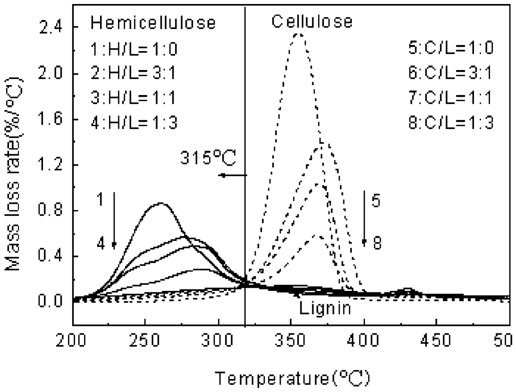

Figure 4. DTG curves of hemicellulose/lignin and cellulose/lignin mixtures.

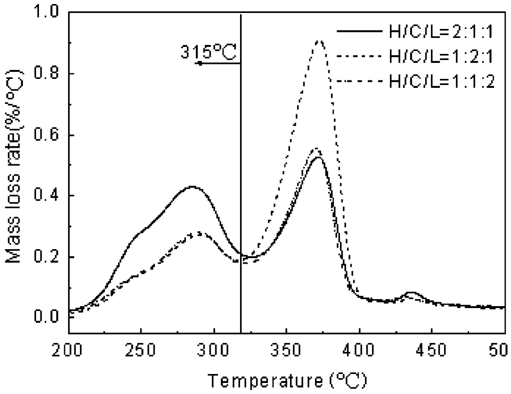

Figure 5. DTG curves of mixtures of hemicellulose, cellulose, and lignin.

loss rates decreased with the increase in lignin content, or in another words, with the decrease in hemicellulose or cellulose content. If compared to the case of the hemicellulose and cellulose mixture (Figure 3), a similar phenomenon of the DTG curve peaks of hemicellulose or cellulose shifting to a higher temperature (~10 °C) was observed, with increasing lignin.

3.2.3. Mixture of Hemicellulose, Cellulose, and Lignin at Different Ratios. According to the proportion of hemicellulose (H), cellulose (C), and lignin (L) given in Figure 1, the H/C/L ratio should be 0.5:0.25:0.25, 0.25:0.5:0.25, and 0.25:0.25:0.5. The pyrolysis curves of the synthesized samples containing the three components are plotted in Figure 5. Two distinguished peaks of DTG curves are displayed with a cross point located at ~315 °C, quite similar to the curve pattern observed in Figure 3 where only two components (hemicellulose and cellulose) are in the mixture. In Figure 5, the first peak is located at 280−290 °C, and its value increased with the increase of the hemicellulose proportion. The second peak is at ~370 °C, its value increased as the cellulose proportion increased. That is to say, in the case of mixture of three components, the weight loss happening at low (<315 °C) and high temperatures (>315 °C) is still accounted for by the decomposition of hemicellulose and cellulose, respectively. In Figure 5, the two peak values (in %/°C) are lower than those observed in Figures 3 and 4 as the absolute amounts of hemicellulose and cellulose decreased in the former because of the addition of lignin (the total weight of the synthesized biomass is fixed at ~20 mg). A comparison of Figures 5 and 3 shows that the addition of lignin into the mixture of hemicellulose and cellulose caused a larger change of the pyrolysis curve of biomass at lower temperature (<315 °C): a small shoulder peak appears before the main peak caused by the addition of lignin which decomposed slightly at lower temperature (see Figure 2). It implies that in addition to hemicellulose, lignin might also contribute to the weight loss of biomass in the lower temperature range (220−315 °C).

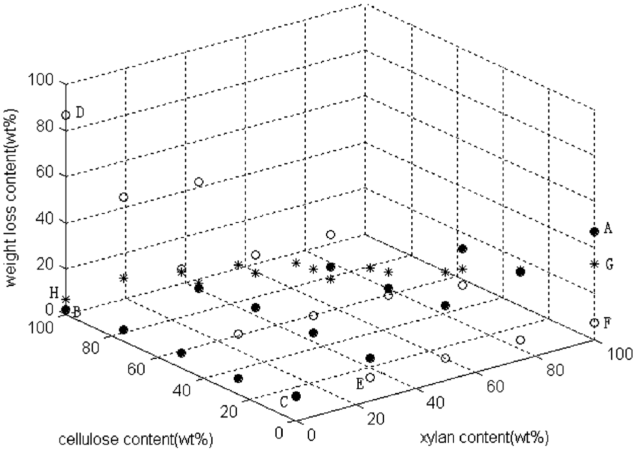

Figure 6. Relationship of weight loss and original contents in the mixture: (●) weight lost in 220−315 °C, (○) weight lost in 315−400 °C, and (*) weight left at 400 °C.

In addition to the comparison of weight loss rates, the weight loss content in the two ranges (220−315 °C and 315−400 °C) and the solid residue (weight loss happened above 400 °C) from pyrolysis of the synthetic biomass samples are plotted in Figure 6, including all the points from the simplex lattice (3, 4) design. It can be observed that the weight loss in the 220−315 °C range (indicated by ● forming a plane ABC) demonstrates a linear relationship with hemicellulose proportions (to be confirmed in the following texts) in the synthesized biomass, while the weight loss in the 315−400 °C range (indicated by ○ forming a plane DEF) also shows a similar linear relationship with cellulose proportions. Moreover, the solid residue (indicated by *), which should most likely be related to the lignin decomposition, does not show a clear relationship with the amounts of hemicellulose and cellulose.

From the above analysis, it is clear that almost no significant interaction occurs between hemicellulose, cellulose, and lignin pyrolysis, although a slight shifting of the peak to a higher temperature (10 °C) was observed, potentially, caused by the inhibition of heat and mass transfer by the addition of other biomass components with different particle sizes (100 μm and 50 μm) and chemical natures. Consequently, it could be concluded that pyrolysis of a biomass could be regarded as a simple superposition of the three components that play individual roles during biomass pyrolysis, consistent to previous studies.[8−14] The whole process of biomass pyrolysis can be divided into the following 4 ranges: <220 °C, moisture evolution; 220−315 °C, predominantly hemicellulose decomposition; 315−400 °C, cellulose decomposition; and >400 °C, mainly lignin decomposition. Nevertheless, in this study the weight loss at temperatures >400 °C is very small and, thus, is ignored and taken as the solid residue of biomass pyrolysis.

3.3. Computing Approach for Predicting the Proportions of the Three Components. A general regression function is derived to fit the data collected from the designed {3,4} simplex lattice. The polynomial equation for the three components can be rewritten as

$$w = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i \le j}^{3}\sum \beta_{ij} x_i x_j + \beta_{123} x_1 x_2 x_3 \qquad (2)$$

where x_1, x_2, and x_3 are the proportions of hemicellulose, cellulose, and lignin, respectively, in biomass and w is the weight loss of the biomass (wt %). On the basis of the previous observations, two assumptions are made: (1) there is no interaction among the three components and (2) there is a linear relationship between weight loss and the proportion of hemicellulose (or cellulose) and residues at different temperature ranges. Therefore, eq 2 can be simplified to eq 3. Here, i (1, 2, 3) refers to the temperature ranges of 220−315 °C, 315−400 °C, and >400 °C, respectively.

$$w_i = \beta_{i0} + \beta_{i1}x_1 + \beta_{i2}x_2 + \beta_{i3}x_3$$

$$1 \geq x_i \geq 0 \quad x_1 + x_2 + x_3 = 1 \quad i=1, 2, 3 \tag{3}$$

A linear multiple regression model[28] was introduced to obtain the coefficients (β_{i0}, β_{i1}, β_{i2}, β_{i3}), using the data (w, x_1, x_2, and x_3) from the synthesized biomass. The results obtained are shown in eq 4

$$w_1 = 0.4840x_1 + 0.0310x_2 + 0.1042x_3 \quad T = 220{-}315\ °\mathrm{C}$$

$$w_2 = 0.0548x_1 + 0.8051x_2 + 0.0946x_3 \quad T = 315{-}\ 400\ °\mathrm{C}$$

$$w_3 = 0.3136x_1 + 0.1111x_2 + 0.6875x_3 \quad T > 400\ °\mathrm{C} \tag{4}$$

where w_1 and w_2 are the values for the weight loss in the temperature zones of 220−315 °C and 315−400 °C, respectively, w_3 is the weight left at temperatures higher than 400 °C. The correlation coefficient R^2 was calculated using eq 5, and the results are $R_1^2 = 0.9980$, $R_2^2 = 0.9957$, and $R_3^2 = 0.9980$ for the three temperature zones, respectively.

$$R^2 = 1 - \frac{\sum (w_{\mathrm{exp}} - w_{\mathrm{calcd}})^2}{\sum w_{\mathrm{exp}}^2} \tag{5}$$

where w_{exp} is the experimentally observed weight loss and w_{calcd} is the calculated weight loss. The comparison of experimental measurements and the calculated values is plotted in Figure 7a. The calculated results for the weight loss are quite consistent with the experimental results. The maximum deviation of weight loss between all the experimental and computed results is 6.4% found in the case of 100% cellulose.

From eq 4, it can be observed that hemicellulose (x_1), with a coefficient of 0.4840, plays an important role in the weight loss at 220−315 °C, together with a partial contribution from lignin (x_3). For the weight loss at 315−400 °C, cellulose (x_2) plays a significant role, while both hemicellulose (0.0548) and lignin (0.0946) have minor contributions. Lignin is found to contribute significantly (coefficient 0.6875) in the solid residue (i.e., charcoal) (w_3) determined at temperatures greater than 400 °C, as it mainly converted to solid charcoal with a slow pyrolysis carbonization.[13] Meanwhile, at temperatures over 400 °C, hemicellulose (0.3136) also makes relatively important contribution toward the formation of char in biomass pyrolysis, similar to the previous study.[13] Equation 4 quantitatively describes the stages of biomass pyrolysis at the specified temperature ranges (220−315, 315−400, and >400 °C), which is consistent with our previous experimental observations: hemicellulose, cellulose, and lignin predominate sequentially in the three temperature ranges. This equation even tells more on the partial contribution of lignin at low temperature (220−315 °C) and also that of hemicellulose at high temperature (>400 °C) to the biomass pyrolysis. Using eq 4, the weight loss of biomass occurring at the three temperature ranges could be predicted on the basis of known proportions of the three components in a biomass.

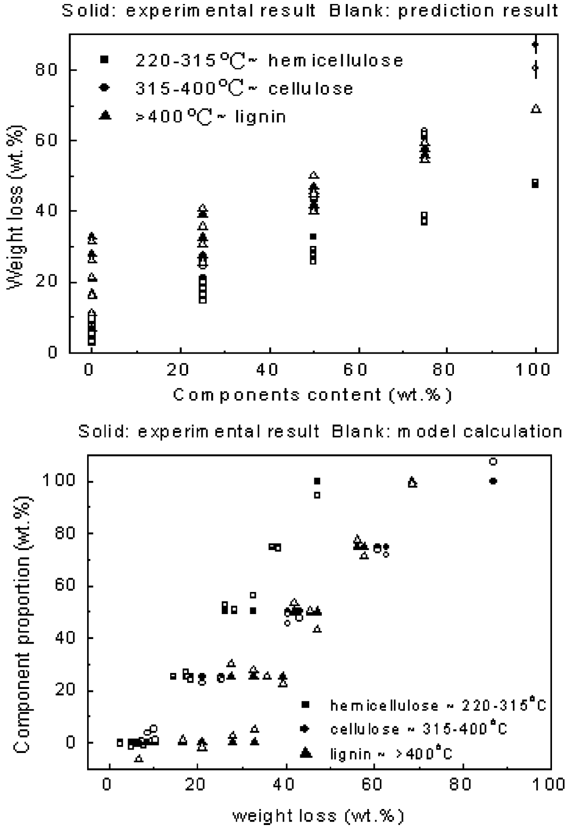

Figure 7. Comparison of predicted and experimental results. Panel a shows the predicted weight loss as a function of the proportions of the components and panel b shows the predicted proportion of the components as a function of the weight loss.

However, the proportions of the three components are generally unknown, and their measurement via the experimental approach is complicated and time-consuming (as previously described in Section 2.4). Following the previous analysis, eq 6 could be derived to calculate the proportion of hemicellulose, cellulose, and lignin in a given biomass.

$$x_1 = 0.671562 + 1.4608w_1 - 0.7387w_2 - 1.0917w_3 \qquad R^2 = 0.9954$$

$$x_2 = 1.066404 - 1.3365w_1 + 0.1488w_2 - 1.3609w_3 \qquad R^2 = 0.9927$$

$$x_3 = -\ 0.737966 - 0.1242w_1 + 0.5899w_2 + 2.4526w_3 \qquad R^2 = 0.9901 \tag{6}$$

where w_1 and w_2 are the weight loss in TGA at different temperature ranges (220−315 °C, 315−400 °C, respectively), w_3 is the solid residue at temperatures greater than 400 °C, and x_1, x_2, and x_3 are the proportions of hemicellulose, cellulose, and lignin, respectively. The correlation coefficients are all larger than 0.99. It is noteworthy that the two assumptions used for eqs 3 and 4 are also applicable for eq 6. It can be seen in eq 6

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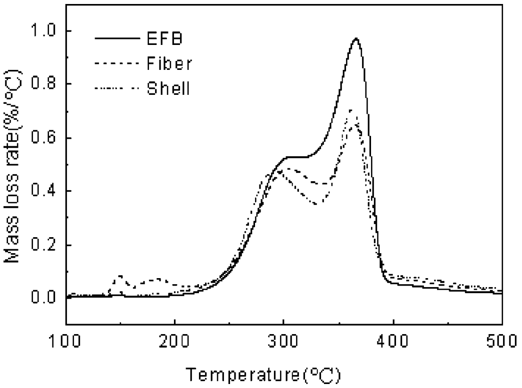

Figure 8. Pyrolysis curves of water-washed palm oil waste samples.

that the weight losses at 220−315 (w_1) and 315−400 °C (w_2) have a positive influence on the proportion of hemicellulose and cellulose in biomass, respectively, while that at >400 °C (w_3) plays a significant role in the proportion of lignin, together with part of the weight loss occurring at 315−400 °C (w_2).

In eq 6, the selection of temperature ranges (220−315, 315−400, and >400 °C) should play a critical role in measuring the weight loss of the contents (w_1, w_2, and w_3), which consequently determines the amounts of the three components in a given biomass. The initial and final temperatures are selected to be 220 °C and 400 °C, respectively; even a wider range of temperature should not influence the weight measurement much (see Figures 2−6). However, the selection of the cross point temperature (315 °C) is significant. The sensitivity of selecting different cross point temperatures (315 °C ± 10 °C) was carried out, and the variances of the calculated three components contents are within 0.015 wt %; therefore, they are negligible.

For comparison, the proportions of the three components (both calculated using eq 6 and known data of the synthesized samples) are plotted in Figure 7b. Solid symbols represent the known data and blank symbols indicate those from calculations. Again, the computed results are consistent with the experimental measurements. In comparison with those of hemicellulose and cellulose, the difference in the proportion of lignin between the experiment and calculation is larger.

However, the synthesized biomass samples of the three components are still different from the natural biomass. To validate the applicability of eq 6 in predicting the proportion of the three components in a given biomass, the pyrolysis of three palm oil wastes (representatives of local biomass), fiber, shell, and EFB, was carried out using TGA under the same operating conditions. To mitigate the influence of mineral matters, palm oil waste samples were pretreated by water washing.[29] The DTG curves of water-washed samples are plotted in Figure 8, indicating two peaks for all the three wastes. Assuming the palm oil wastes consist mainly of the 3 components (hemicellulose, cellulose, and lignin),[20] using the computational approach developed (eq 6), the proportions of the three components can be estimated. The thermal characteristics of waste pyrolysis at the three temperature ranges and the predicted proportions of the three components are indicated in Table 1. In general, the results are consistent with the content ranges of the three components in biomass.[3,4]

Meanwhile, the proportions of the three components in palm oil waste are determined via experimental analysis (refer to Section 2.4). The results are given in Table 2. If the part of measured extractives (Table 2) is combined with hemicellulose (the practice we used in the TGA test), the predicted hemicellulose contents for fiber and EFB (51% and 46%) in Table 1 are quite close to the experimental results (48% and 50%), while that of shell (46%) is slightly larger than the experimental value (32%). However, the amount of lignin predicted (Table 1) is much lower than that measured (Table 2) causing the predicted cellulose content (by difference) to be much higher than the measured value, particularly for EFB. This may be the result of (1) the inability to completely remove the minerals in a biomass with water washing, which causes a big difference between the synthesized biomass (mixture of the three components) and the natural sample, and (2) the inefficient or incomplete extractive procedure for the measurement of the three components (i.e., high residues are still left after several steps of chemical treatment leading to the high content of lignin in Table 2).

Table 1. Prediction of the Three Components of the Palm Oil Waste Sample (based on daf[a])

	weight loss content expl (wt %)			component proportions calcd (wt %)		
sample	220−315 °C	315−400 °C	>400 °C	hemicellulose	cellulose	lignin
EFB	25	48	17	46	54	0
fiber	27	35	28	51	38	11
shell	26	31	34	46	30	25

[a] daf = dry and free ash.

Table 2. Measured Contents of Hemicellulose, Cellulose, and Lignin in Palm Oil Waste (wt %, based on daf)

sample	extractive	hemicellulose	cellulose	lignin
EFB	7	43	26	24
fiber	11	37	19	33
shell	6	26	22	46

4. Conclusions

Hemicellulose, cellulose, and lignin, the three main components of a biomass, play individual roles in biomass pyrolysis. Similar to the previous studies, the experimental results in this work indicate that the whole process of biomass pyrolysis can be divided into the following 4 ranges: <220 °C, moisture evolution; 220−315 °C, predominantly hemicellulose decomposition; 315−400 °C, cellulose decomposition; >400 °C, lignin decomposition. Further analyses are carried out following the specified temperature ranges. Moreover, there is no significant interaction among the three components in pyrolysis.

Two sets of prediction equations were set up to relate the amounts of the three main components and the weight loss at specified temperature ranges. For the synthetic biomass samples, the results of the calculation are consistent with experimental measurements. The correlation coefficients are close to 1. For palm oil waste, the natural biomass samples, after water washing, the predicted hemicellulose content is relatively comparable to the experimental measurement. However, the predicted lignin content is much lower than measured value, causing the predicted cellulose content to be much higher. To improve the prediction accuracy, the influence of minerals should be taken into account in the model. Furthermore, a future validation of the developed prediction approach for a remarkably large number of biomass samples is necessary.

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