# Characteristics of hemicellulose, cellulose and lignin pyrolysis

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## Abstract

The pyrolysis characteristics of three main components (hemicellulose, cellulose and lignin) of biomass were investigated using, respectively, a thermogravimetric analyzer (TGA) with differential scanning calorimetry (DSC) detector and a pack bed. The releasing of main gas products from biomass pyrolysis in TGA was on-line measured using Fourier transform infrared (FTIR) spectroscopy. In thermal analysis, the pyrolysis of hemicellulose and cellulose occurred quickly, with the weight loss of hemicellulose mainly happened at 220–315 °C and that of cellulose at 315–400 °C. However, lignin was more difficult to decompose, as its weight loss happened in a wide temperature range (from 160 to 900 °C) and the generated solid residue was very high ($\sim$40 wt.%). From the viewpoint of energy consumption in the course of pyrolysis, cellulose behaved differently from hemicellulose and lignin; the pyrolysis of the former was endothermic while that of the latter was exothermic. The main gas products from pyrolyzing the three components were similar, including $CO_2$, CO, $CH_4$ and some organics. The releasing behaviors of $H_2$ and the total gas yield were measured using Micro-GC when pyrolyzing the three components in a packed bed. It was observed that hemicellulose had higher $CO_2$ yield, cellulose generated higher CO yield, and lignin owned higher $H_2$ and $CH_4$ yield. A better understanding to the gas products releasing from biomass pyrolysis could be achieved based on this in-depth investigation on three main biomass components.
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## 1. Introduction

With the depletion of fossil fuel and the concern of environmental protection, the utilization of biomass resources has attracted increasing worldwide interest. Pyrolysis, as one of the promising thermochemical conversion routes, plays a vital role in biomass conversion. However, pyrolysis is an extremely complex process; it generally goes through a series of reactions and can be influenced by many factors [1–4]. It is thus essential to study the fundamentals of biomass pyrolysis. Hemicellulose, cellulose and lignin are the three main components of biomass and they in general cover respectively 20–40, 40–60, and 10–25 wt.% for lignocellulosic biomass [5]. Previous studies showed that biomass pyrolysis can be divided into four individual stages: moisture evolution, hemicellulose decomposition, cellulose decomposition and lignin decomposition [6,7]. It was also suggested that the pyrolysis of any biomass can be considered as the superposition of the three main components [2,7–9]. Knowledge of the pyrolysis characteristics of the three main components is the basis and thus essentially important for a better understanding to biomass thermal chemical conversion.

So far, numerous studies based on the main components have been carried out, most of them were focused on developing kinetics models for predicting behavior of biomass pyrolysis [2,6,8,10]. Our previous study on the three components [11] focused on the prediction of biomass pyrolysis behavior in TGA from the fractions of the three components. The structure property of the three components

was found to influence greatly the pyrolysis characteristics [7,12]. Li et al. [13] using FTIR analyzed the formation characteristics of gas compounds from cellulose pyrolysis at various conditions, involving different heating rates, residence times, and gas flows. Ferdous, et al. [14] investigated the gas product property from lignin pyrolysis at changing temperatures and heating rates. Bassilakis et al. [15] studied the gas product releasing from D-glucose, chlorogenic acid and xylan pyrolysis using FTIR quantitatively. The organics mixtures were classified into methanol, formaldehyde, formic acid, acetaldehyde, acetic acid and others, but it was difficult to distinguish these components using FTIR. Evans and Milne [16] carried out the pyrolysis of wood and the main constituents (cellulose, xylan and lignin) using molecular-beam with mass spectrometry, the intermediates of the gas products were determined and a potential reaction pathway was suggested. Still, the characteristics of different gas products formation from pyrolyzing the three biomass components, the energy consumption occurring in the process, and their relationships with the chemical structure of biomass components were not discussed in-depth in the previous studies.

In the present study, the pyrolysis of hemicellulose, cellulose and lignin in TGA and packed bed, together with the energy consumption and gas product releasing behaviors were investigated in detail. The objective of this study is to gain a comprehensive understanding to the three components pyrolysis with focuses on the gas product releasing properties, thus facilitate to establish an universe model to simulate biomass pyrolysis based the three model compounds. It is favorable for the development of advanced biomass pyrolysis process.

## 2. Materials and experimental methods

### 2.1. Materials

The three main components (cellulose, hemicellulose, and lignin) were purchased from commercial chemical shop (Sigma-Aldrich Chemie GmbH). Cellulose is in powder fibrous form, and lignin is alkali lignin in brown powders. A commercial hemicellulose can hardly be purchased whereas xylan, although it might have different physical and chemical properties, has been widely used as a representative component of hemicellulose in pyrolysis processes [8,9,17]. Here, xylan, in yellow powder form, was processed from Birchwood, was also bought from Sigma-Aldrich Chemie GmbH, and was used as hemicellulose. Particle size of hemicellulose is averaged at ∼100 μm and those of cellulose and lignin are at ∼50 μm.

### 2.2. Experimental methods

The pyrolysis of biomass components was first carried out in a TGA (NETZSCH STA 409C, Germany). To mitigate the difference of heat and mass transfer, the sample weight was kept at ∼10 mg. The sample was heated up to 900 °C at a constant heating rate of 10 °C/min, and kept for 3 min. Purified nitrogen (99.9995%) at a flow rate of 120 ml/min was used as the carrier gas to provide an inert atmosphere for pyrolysis and to remove the gaseous and condensable products, thus minimizing any secondary vapor-phase interactions.

The gases released in the TGA were swept immediately to a gas cell, followed by the FTIR (BioRad Excalibur Series, Model FTS 3000) analysis using deuterated triglycine sulfate (DTGS) detector. The transfer line and gas cell were heated to an internal temperature of 230 °C, to avoid condensation or adsorption of semi-volatile products. Each IR spectrum was obtained in 5 s and the IR scanning range was from 4000 to 500 cm$^{-1}$.

As we know, the pyrolysis gas mainly contains $H_2$, $CO_2$, CO, $CH_4$, $C_2H_6$, $C_2H_4$, trace amounts of larger gaseous organics and water vapor [18]. However, $H_2$ has no IR absorption and cannot be detected using FTIR [15]. Instead, Micro-GC was used for determining quantitatively the $H_2$ yield from the pyrolysis of biomass components [19]. Also, the gas volume from biomass pyrolysis in TGA was limited due to the small sample loading (∼10 mg); therefore, another trial of biomass pyrolysis was carried out in a packed bed allowing ∼2 g of sample loading, with other operating parameters kept the same as those in TGA. The schematic of the packed bed reactor system was shown in our previous publication [20]. The gas products released from biomass pyrolysis in the packed bed were analyzed using dual Channel Micro-GC (Varian, CP-4900) with a thermal conductivity detector (TCD). To verify the result derived from FTIR, several other gas species were also checked by Micro-GC together with $H_2$. The used Micro-GC contains two channels and the operating conditions are listed as follows: Channel A with molecular sieve 5A column (MS-5A) was set at 95 °C for determination of $H_2$, CO and $CH_4$; Channel B with Porapak Q (PPQ) was set at 60 °C for checking the releasing property of $CO_2$, $C_2H_4$, and $C_2H_6$.

## 3. Results and discussion

### 3.1. Chemical structure of three components

The chemical structure of the three components was analyzed using FTIR through pelleting the sample with KBr powder, the method was described in detail in our previous publication [20]. The IR spectra of cellulose, hemicellulose and lignin are shown in Fig. 1. The typical functional groups and the IR signal with the possible compounds are listed in Table 1 for a reference [12,20,21]. It can be observed that the three components of biomass are most likely consisted of alkene, esters, aromatics, ketone and alcohol, with different oxygen-containing functional groups observed, e.g., OH (3400–3200 cm$^{-1}$), C=O (1765–1715 cm$^{-1}$), C–O–C (1270 cm$^{-1}$), and C–O–(H) (∼1050 cm$^{-1}$), etc. [22]. Still, they showed different IR structures. The highest IR absorbance of OH and C–O was found with cellulose while hemicellulose contained higher C=O compounds. Compared
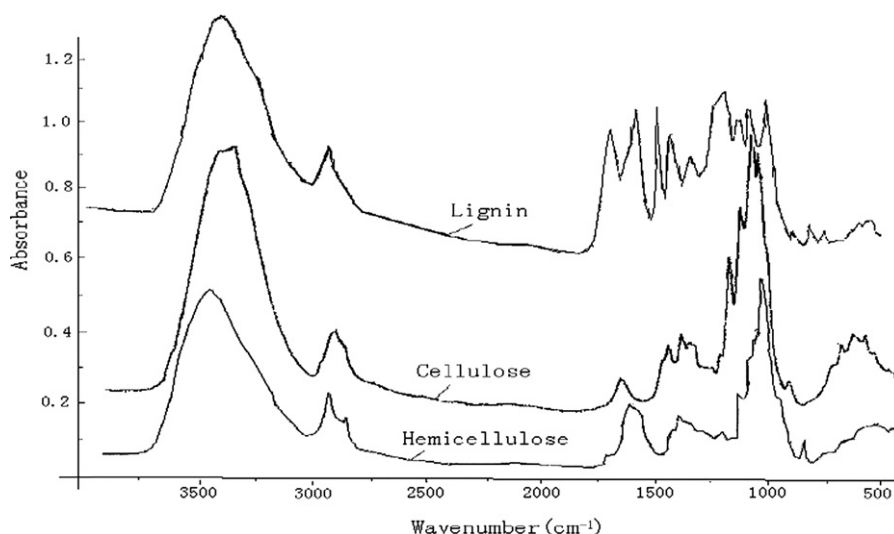
Fig. 1. FTIR spectra of the three typical components of biomass.

Table 1
The main functional groups of the three components

| Wave number (cm$^{-1}$)[a] | Functional groups | Compounds |
|---|---|---|
| 3600–3000 (s) | OH stretching | Acid, methanol |
| 2860–2970 (m) 1700–1730 (m), | C–H$_n$ stretching | Alkyl, aliphatic, aromatic |
| 1510–1560 (m) | C=O stretching | Ketone and carbonyl |
| 1632 (m) | C=C | Benzene stretching ring |
| 1613 (w), 1450 (w) | C=C stretching | Aromatic skeletal mode |
| 1470–1430 (s) | O–CH$_3$ | Methoxyl–O–CH$_3$ |
| 1440–1400 (s) | OH bending | Acid |
| 1402 (m) | CH bending | |
| 1232 (s) | C–O–C stretching | Aryl-alkyl ether linkage |
| 1215 (s) | C–O stretching | Phenol |
| 1170 (s), 1082 (s) | C–O–C stretching vibration | Pyranose ring skeletal |
| 1108 (m) | OH association | C–OH |
| 1060 (w) | C–O stretching and C–O deformation | C–OH (ethanol) |
| 700–900 (m) | C–H | Aromatic hydrogen |
| 700–400 (w) | C–C stretching | |

[a] s: strong, m: middle, w: weak.

with hemicellulose and cellulose, a big difference was found in the finger print region (1830–730 cm$^{-1}$) for lignin's IR spectra. A group of complex IR absorbance of lignin was found there, indicating that lignin might be rich of methoxyl–O–CH$_3$, C–O–C stretching and C=C stretching (aromatic ring) containing compounds.

### 3.2. Pyrolysis of three components in TGA/DSC-FTIR

#### 3.2.1. Thermal analysis of the three components

The pyrolysis characteristics, both TG (in wt.%) and DTG (in wt.%/°C) curves of the three components, are shown in Fig. 2. Great differences were found among the pyrolysis behaviors of the three components. Hemicellulose started its decomposition easily, with the weight loss mainly happened at 220–315 °C. It got the maximum mass loss rate (0.95 wt.%/°C) at 268 °C, and there was still ∼20% solid residue left even at 900 °C. Cellulose pyrolysis was focused at a higher temperature range (315–400 °C) with the maximum weight loss rate (2.84 wt.%/°C) attained at 355 °C. When temperature was higher than 400 °C, almost all cellulose was pyrolyzed with a very low solid residue (∼6.5 wt.%/°C) left. Among the three components, lignin was the most difficult one to decompose. Its decomposition happened slowly under the whole temperature range from ambient to 900 °C, but at a very low mass loss rate (<0.14 wt.%/°C). The solid residue left from lignin pyrolysis (∼45.7 wt.%) was the highest. The differences in the inherent structures and chemical nature of the three components possibly account for the different behaviors observed [5,9]. Hemicellulose is consisted of various saccharides (xylose, mannose, glucose, galactose, etc.), it
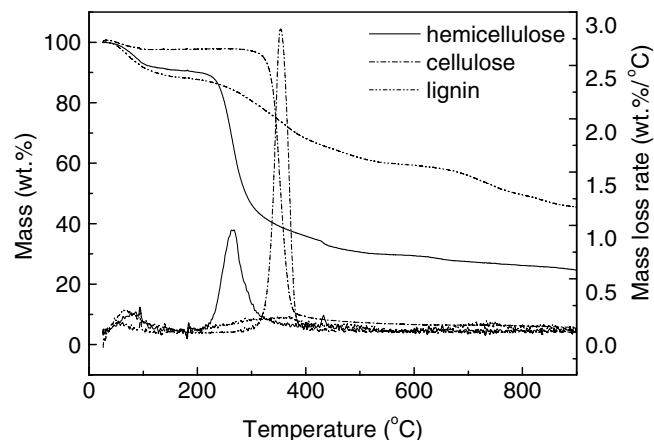


Fig. 2. Pyrolysis curves of hemicellulose, cellulose and lignin in TGA.

appears a random, amorphous structure, rich of branches, which are very easy to remove from the main stem and to degrade to volatiles evolving out (CO, $CO_2$, and some hydrocarbon, etc.) at low temperatures. The FTIR results for on-line gas monitoring (to present in the subsequent texts) will confirm it. Different to hemicellulose, cellulose is consisted of a long polymer of glucose without branches, its structure is in a good order and very strong, and the thermal stability of cellulose is high. Lignin is full of aromatic rings with various branches, the activity of the chemical bonds in lignin covered an extremely wide range, which led to the degradation of lignin occurring in a wide temperature range (100–900 °C).

### 3.2.2. Analysis of the enthalpy of three components pyrolysis

Besides the TG and DTG curves of biomass pyrolysis which were used to reflect the degradation of biomass, the DSC curves showing the energy consumption property in pyrolysis were also measured. The results are plotted in Fig. 3. When temperature was lower than 200 °C, the DSC curve of the three components pyrolysis showed a similar tendency, the reactions occurred at ~100 °C were all endothermic, mainly attributed to the removal of moisture when the sample was heated up. With temperature increasing further (>200 °C), the DSC profile of cellulose showed an obvious and big endothermic peak at ~355 °C, different from those of hemicellulose and lignin. The DSC values of hemicellulose and lignin were above zero between 150 and 500 °C with two peaks found at ~275 and 365 °C respectively, indicating that their pyrolysis reactions are exothermic. It might be attributed to the different reactions or mechanisms involved in pyrolyzing the three components. Ball et al. [23] pointed out that the charring process was highly exothermal whereas volatilization was endothermal. With the much higher solid residues generated from hemicellulose and lignin pyrolysis, the exothermal peaks observed in hemicellulose and lignin pyrolysis could be attributed to the charring, while the full decomposition of cellulose might be attributed to the quick devolatilization reactions, leading to very few solid residues left.
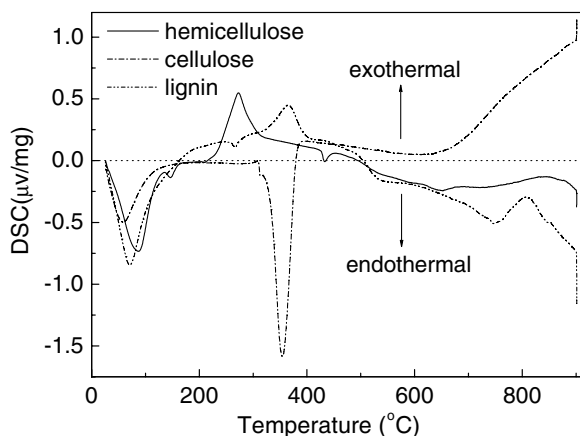
It seems that the DSC curves of the three components corresponded well with their DTG curves. For example, the DSC curves of hemicellulose and cellulose got the peaks at ~275 °C and 355 °C, respectively. They should be attributed to the primary pyrolysis of the two components as two DTG peaks (see Fig. 2) were also found at the almost same temperatures respectively for hemicellulose and cellulose. When temperature was higher than 500 °C, the DSC values of hemicellulose and lignin decreased to minus, it indicated the endothermic properties of the reactions related. In DSC curve of hemicellulose, no obvious change was displayed at temperatures higher than 500 °C, consistent to its DTG curves where no obvious reaction (pyrolysis) happened. Nevertheless, the DSC curve of lignin pyrolysis varied a lot with temperature increasing; a small endothermic peak of it was found near 750 °C. The secondary pyrolysis of lignin might contribute to it (see Fig. 2) [6,14]. However, the DSC curve of cellulose at high temperatures (>400 °C) showed an inverse trend; positive DSC values were observed indicating the exothermal properties of the related reactions in cellulose pyrolysis. From 500 to 700 °C, DSC curve of cellulose was stable but after that it increased greatly with temperature increasing further. It might be attributed to the cracking of some functional groups in cellulose residue. Although no obvious weight loss found from TG curves of cellulose pyrolysis in that temperature range, there still exist some reactions and the gas product releasing profiles (on-line monitored using FTIR) will confirm it later.

### 3.2.3. Releasing property of gas products from biomass pyrolysis

A typical stack plot of IR spectra from hemicellulose pyrolysis using TGA-FTIR is shown in Fig. 4. The IR spectra taken every 5 s from 150 to 900 °C in the experiment were plotted by placing one on top of the other to form the 3D spectra. It indicated the evolving of gas products during pyrolysis of hemicellulose, as a function of both wave number and temperature. From Fig. 4, it can be observed that the main gas products of biomass pyrolysis
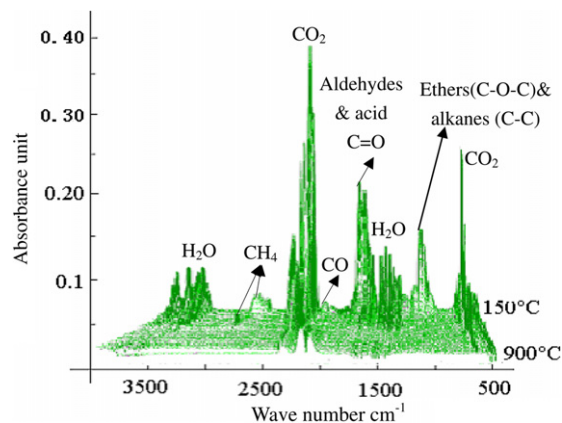


Fig. 3. DSC curves of hemicellulose, cellulose and lignin pyrolysis.



Fig. 4. Typical FTIR spectra of gas products from hemicellulose pyrolysis.

are: $CO_2$, $CH_4$, CO and some organics (a mixture of acids, aldehydes (C=O), alkanes (C–C), and ethers (C–O–C), etc.) with some $H_2O$. The releasing of gas products mainly focused at low temperatures (200–400 °C), which was corresponding well with the observation of biomass weight loss in Fig. 2, except for some $CO_2$ and CO evolving out at a higher temperature.

Since the methodology and operation in FTIR measurement followed exactly the same procedures, the change in IR peak heights will reflect the tendency of concentration variation of the gas species [10,15]. The specific wave numbers of the IR peak of the main gas species from biomass pyrolysis are listed as the following: $CO_2$: 2363 cm$^{-1}$, CO: 2167 cm$^{-1}$, $CH_4$: 3017 cm$^{-1}$, carbohydrate contained organic functional groups of C=O: 1730 cm$^{-1}$, carbohydrate contained organic functional groups C–O–C/C–C: 1167 cm$^{-1}$ (refer to Fig. 4). The releasing profiles of gas products (such as $CO_2$, $CH_4$, CO and organics functional bonds of C=O and C–O–C but excluding moisture $H_2O$) from the three components pyrolysis are plotted in Fig. 5, in IR absorbance height.

In Fig. 5, it was found that the releasing of $CO_2$ was mainly caused by the cracking and reforming of functional groups of carboxyl (C=O) and COOH. The $CO_2$ releasing profile from hemicellulose displayed three peaks (280 °C, 451 °C and 658 °C). The first peak was the highest, possibly attributed to the cracking and abscission of C–C and C–O bonds connected with the main branch of hemicellulose, thus leading to the high pyrolysis reactivity of hemicellulose. Lignin also got two releasing peaks of $CO_2$ (340 and

700 °C) with the second peak much higher than the first. However, the releasing of $CO_2$ from cellulose started at ~300 °C which was a bit delayed compared to that of hemicellulose and lignin, and only one small peak of $CO_2$ releasing (380 °C) from cellulose was observed. The small releasing of $CO_2$ from cellulose pyrolysis might be due to the lowest content of C=O group found using FTIR (refer to Fig. 1). It can be assumed that the releasing of $CO_2$ from biomass pyrolysis was mostly contributed by hemicellulose at low temperature (<500 °C) and by lignin at high temperature (>500 °C), whilst cellulose only contributed a small portion of it at low temperature.

With regards to CO, it was mainly released out with the cracking of carbonyl (C–O–C) and carboxyl (C=O). Similar with the case of $CO_2$ evolving, two peaks of CO releasing (280 and 500 °C) were shown for hemicellulose at lower temperature (<600 °C) while one big jump of it was found at high temperatures (>600 °C). The releasing of CO from cellulose was few with only a small peak observed at ~380 °C. Almost no CO was evolved out from lignin pyrolysis at lower temperature (<600 °C) whereas it increased greatly with temperature and got the highest value at 760 °C, most likely attributed to the secondary pyrolysis (thermal cracking of tar residue in the solid sample). Again, the contribution of cellulose pyrolysis to CO releasing was minor, and it was found that CO releasing was mostly caused by the pyrolysis of hemicellulose in the whole temperature range and that of lignin at high temperatures (>600 °C).

The releasing of $CH_4$ can be caused by the cracking of methoxyl–O–$CH_3$, and was mainly focused at low
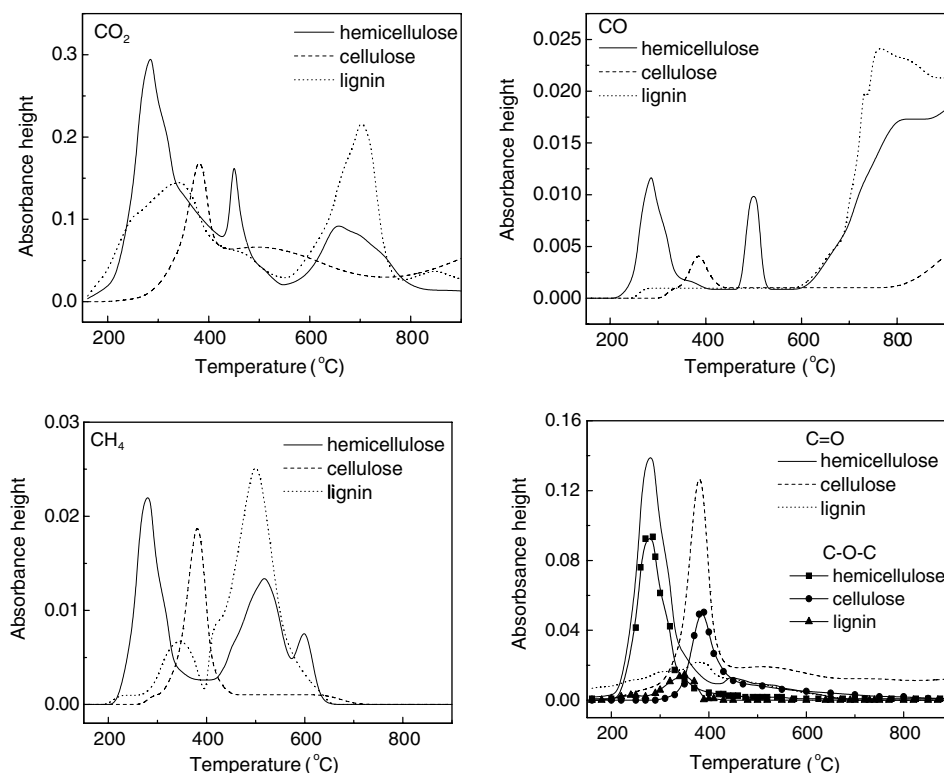


Fig. 5. FTIR profiles of gas product evolving from the three components pyrolysis.

temperatures (<600 °C). Hemicellulose, cellulose and lignin all contributed to the releasing of $CH_4$ from biomass pyrolysis, at respectively low, middle and high temperature ranges. Hemicellulose demonstrated two main releasing peaks (280 and 520 °C) of $CH_4$. The primary pyrolysis may give rise to the first releasing peak, while the secondary pyrolysis at a higher temperature might be the driving force of the second releasing peak of gas. Lignin showed the highest $CH_4$ releasing peak, possibly because of its highest $O–CH_3$ content (see Fig. 1).

The releasing of organic compounds was different from other gas products. It occurred mostly at low temperatures (for hemicellulose temperature was <400 °C, and for cellulose <450 °C) and mostly contributed by pyrolysis of hemicellulose and cellulose whilst that from lignin was negligible. Only one main peak of releasing organics with bonds of C=O and C–O–C was found and that from hemicellulose was higher than from cellulose.

From the FTIR profiles, it can be observed that the total amount of gas products from cellulose pyrolysis detected by FTIR was lower than that from hemicellulose. Furthermore, the solid residue of cellulose pyrolysis was also the lowest (6.5 wt.%) among the three components. Although the oil generated from biomass pyrolysis was not collected, their quantity was very small in our experiments thus not a big matter. Two things might explain the deviation in mass balance. The first is evolving of moisture from cellulose pyrolysis. As observed from the 3D plot of the FTIR profile (Fig. 4), there appeared a strong IR signal caused by absorption of $H_2O$ evolving from pyrolysis of cellulose than from other two components, attributed to possibly the higher OH content in cellulose. Secondly, there might also exist some gas products which are undetectable using FTIR, such as $H_2$. To clarify the mass balance issue, a further investigation was conducted using packed bed as a reactor and Micro-gas chromatograph was used to analyze the gas product released in the course of biomass pyrolysis.

## 3.3. Pyrolysis of the three components in packed bed

The gas evolving profiles from pyrolyzing the three components in a packed bed, monitored by Micro-GC, are plotted in Figs. 6–8. The released volatiles were cooled and condensed to liquid oil in an ice-water cooler, so the condensable volatiles (e.g. organic compounds containing C=O, C–C, C–O–C, etc.) were captured in the ice-water cooler. The releasing temperature of the main gas products from biomass pyrolysis in the packed bed was much higher than that in TGA (refer to Figs. 2, 5–7 and 8). It might be due to the larger sample size (2g) used in the packed bed [24]. The temperature difference inside the sample particles increased with a larger sample size. Simultaneously, the bed height increased, hence extended the residence time of volatiles in contacting with biomass particles, which might enhance the secondary reactions and lead to some differences of gas products releasing from packed bed and TGA. The incondensable gas products analyzed by
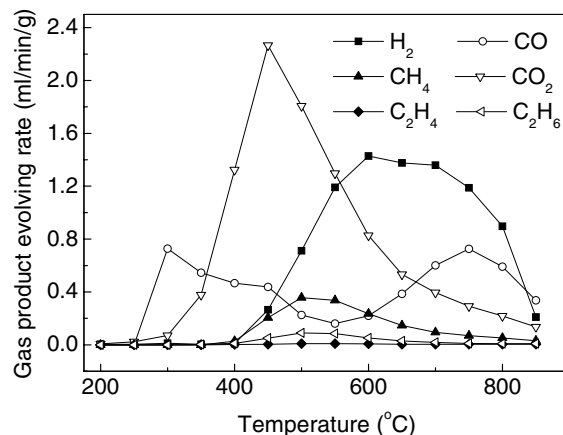


Fig. 6. Releasing profile of gas products from hemicellulose pyrolysis in packed bed.
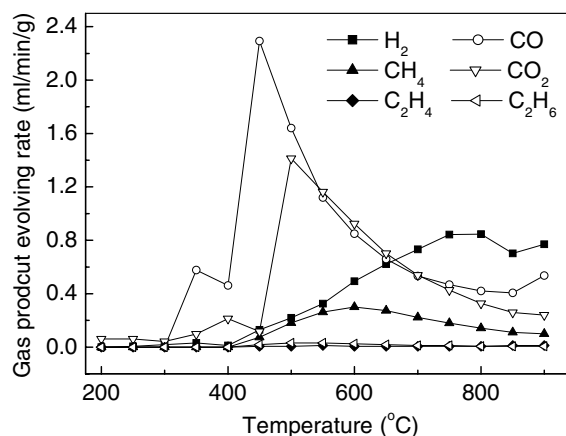


Fig. 7. Releasing profile of gas products from cellulose pyrolysis in packed bed.
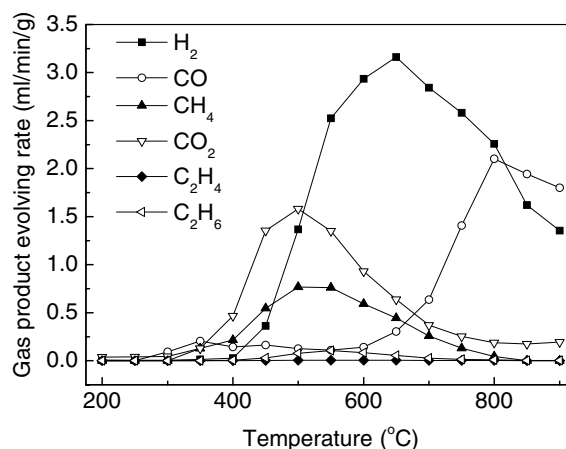


Fig. 8. Releasing profile of gas product from lignin pyrolysis in packed bed.

Micro-GC include $H_2$, CO, $CO_2$ and some light hydrocarbon ($CH_4$, $C_2H_4$ and $C_2H_6$) and the detailed method can be found in our previous publication [20].

Table 2
Yield of gas product from three components pyrolysis

| Sample | Gas product yield (milli mol/g-biomass ar.)[a] | | | | | |
|---|---|---|---|---|---|---|
| | $H_2$ | CO | $CH_4$ | $CO_2$ | $C_2H_4$ | $C_2H_6$ |
| Hemicellulose | 8.75 | 5.37 | 1.57 | 9.72 | 0.05 | 0.37 |
| Cellulose | 5.48 | 9.91 | 1.84 | 6.58 | 0.08 | 0.17 |
| Lignin | 20.84 | 8.46 | 3.98 | 7.81 | 0.03 | 0.42 |

[a] ar. as received basis.

Through the comparison of the three figures (Figs. 6–8), some similar points can be observed. $H_2$ was released out at a higher temperature (>400 °C) and the releasing of $H_2$ increased greatly with temperature increasing. For hemicellulose and lignin, the releasing of $H_2$ was significant and it got the maximum rate at ~600 °C. $CO_2$ was released out at 400–600 °C, and got the maximum releasing value at 450–500 °C. The releasing of $CH_4$ showed the similar pattern with that of $CO_2$. However, its releasing rate was much smaller and the maximum releasing rate of $CH_4$ was found at 500–600 °C. The releasing of $C_2H_4$ and $C_2H_6$ was generally very low. Compared with other gas species, CO demonstrated the different releasing property. For hemicellulose, CO got two separated peaks (300 and 750 °C), while for cellulose it showed a single peak (~450 °C). However, for lignin, CO releasing was started at 600 °C, and increased with temperature increasing, finally got the maximum value at 800 °C.

The yield of gas species from pyrolyzing the three main components is listed in Table 2. It was calculated by integrating the curve of gas product evolving rate in the whole temperature range (200–900 °C), thus it indicated the overall yield of each gas species from biomass pyrolysis. From the table, it can be observed that lignin owned the highest $H_2$ and $CH_4$ yield, it might be attributed to the higher content of aromatic ring and O–$CH_3$ functional groups in the origin lignin sample, as the $H_2$ from organics pyrolysis mainly came from the cracking and deformation of C=C (ar.) and C–H (ar.) while $CH_4$ was mainly brought by the cracking of methoxyl. Cellulose obtained the highest CO yield, due to the higher carbonyl content in it. Hemicellulose displayed the highest $CO_2$ yield, because of the higher carboxyl content.

The different contributions of biomass components to the gas products obtained from biomass pyrolysis in the packed bed was mostly consistent with those found from TGA, but a big difference was observed with CO releasing. In TGA (Fig. 5) only minor CO evolving was found from cellulose pyrolysis, whereas in the packed bed (Table 2) it seems that cellulose pyrolysis contributed the most to the overall CO releasing. The different reactor configurations and the sample sizes used in the two reactors might be the main reasons of the conflicted observation. Larger sample size and reactor volume in the packed bed extended the residence time of gas products, and promoted the secondary cracking of volatiles, hence improved the yield of CO from cellulose pyrolysis.

## 4. Conclusions

The pyrolysis characteristics of hemicellulose, cellulose and lignin were investigated using TGA-DSC and packed bed coupled respectively with FTIR and Micro-GC as on-line gas monitors. Great differences of the pyrolysis behavior among the three main components were drawn from the experimental results. Hemicellulose was easy to be degraded, and its pyrolysis was focused at 220–315 °C. The pyrolysis of cellulose was mainly happened at 315–400 °C, while that of lignin covered a whole temperature range (150–900 °C). At low temperatures (<500 °C), the pyrolysis of hemicellulose and lignin involved exothermic reactions while those of cellulose were endothermic. However, at high temperatures (>500 °C), the situation just changed inversely.

The behavior of gas products evolving from biomass pyrolysis in TGA, as detected on-line using FTIR, matched well with the degradation of biomass measured using TGA. $CO_2$ releasing was mainly caused by the primary pyrolysis, while secondary pyrolysis was the main source for releasing of CO and $CH_4$. Hemicellulose showed higher CO and $CO_2$ yield, while lignin displayed higher $CH_4$ releasing. Organics compounds (C=O, C–O–C, etc.) were mainly released out at low temperatures, i.e., 200–400 °C and 300–450 °C from hemicellulose and cellulose, respectively. Nevertheless, almost no organics compound was detected from lignin pyrolysis. The difference might be due to the inherent variance among the chemical structure of the three components, such as hemicellulose appeared more C=O contained organics compounds, while higher contents of OH and C–O was found with cellulose and more methoxyl–O–$CH_3$ with lignin.

In the packed bed, $CO_2$ and $CH_4$ mainly evolved out at 400–600 °C, $H_2$ evolved out at a higher temperature (>400 °C), and the yield of $H_2$ increased with pyrolysis temperature increasing. It was suggested that different chemical structures of biomass components attribute to different gas product releasing properties. Hemicellulose, with higher carboxyl content, accounted for a higher $CO_2$ yield. Cellulose displayed a higher CO yield, mainly attributed to the thermal cracking of carbonyl and carboxyl. With a higher presence of aromatic ring and methoxyl, the cracking and deformation of lignin released out much more $H_2$ and $CH_4$.

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