

Use of Extreme Vertices Method for Analysis of How Proportional Composition Affects Component Interactions and Product Distribution during Hydrothermal Treatment

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The interaction among three biomass components (hemicellulose, cellulose, and lignin) in an autoclave was studied based on the extreme vertices of a constrained region that had a significant effect on the distribution and characteristics of the products. The mathematical model of the three components was established according to the yield distribution. Based on the model, the biomass components and the hydrothermal characteristics of biomass were predicted. Subsequently, the contents of the main biomass components were analyzed, thus eliminating the complicated testing process and providing a convenient and reliable calculation tool for determining the three biomass components. The gaseous products showed that products from cellulose hydrolysis promoted hemicellulose hydrolysis and generated large amounts of CO₂. The lignin content, as well as the low cellulose and hemicellulose contents, inhibited the acids and ketones in light oil. In addition, the interaction among cellulose, hemicellulose, and lignin inhibited the production of acids in heavy oil and promoted phenolic synthesis. A series of hydrolysis product reactions such as polymerization and condensation were increased to produce a char at a high degree of aromatization by the interaction among the three components.

Keywords: *Hydrothermal treatment; Components interaction; Mixed biomass; Extreme vertices*

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INTRODUCTION

Bioenergy is a promising clean and renewable energy. Organic wastes, such as industrial wastewater and residues, urban living garbage, and agricultural and forest residues, are important for biomass energy. Converting biomass into energy is of great significance in solving energy and environmental problems. The energy density of biomass, whose main components are cellulose, hemicellulose, and lignin, is relatively low. Biomass has no liquid form and comes from a variety of sources, which inhibits bioenergy development and utilization (Sayigh 1999). Moreover, biomass has a low heating value, high moisture, and high transportation and storage costs. Combustion, pyrolysis, fermentation, and hydrothermal technologies have been developed for

bioenergy conversion (Raveendran *et al.* 1996; Vane 2005; Kruse *et al.* 2013; Mendiara *et al.* 2013). The biomass conversion and resource utilization fields have recently focused on hydrothermal technology (Toor *et al.* 2011; Coronella *et al.* 2014; Rostagno *et al.* 2014). This technology is not restricted by the moisture content of the raw materials and does not require biomass drying before the reaction. Hot compressed water, as an environment-friendly reaction medium, is characterized by miscibility with water, rapid reaction, and high efficiency. Through hydrothermal reactions, organic wastes can be converted into energy (Zhu *et al.* 2014; He *et al.* 2014; Singh *et al.* 2014). Therefore, hydrothermal technology increases biomass conversion while reducing conversion costs.

The biomass components are hemicellulose, cellulose, and lignin, which account for 38 to 50 wt%, 23 to 32 wt%, and 15 to 25 wt%, respectively, of moisture-free biomass (Rabemanolontsoa and Saka 2013). Given that these three components possess high molecular compounds with complex spatial structures, the hydrothermal conversion of biomass is a complicated physical and chemical process (Xiu and Shahbazi 2012). Many experiments and simulation studies on the hydrothermal conversion of biomass are based on one or two main components, focusing on the yield distribution and physicochemical properties of products (Liu and Wyman 2003; Karagöz *et al.* 2005; Bhaskar *et al.* 2008; Alriols *et al.* 2009).

Research on the physicochemical properties of hemicellulose, cellulose, and lignin are necessary to understand hydrothermal biomass characteristics. Research on the three biomass components mostly focus on establishing a kinetic model to predict the biomass pyrolysis process and study the three components using a thermo-gravimetric analyzer to predict this process (Giudicianni *et al.* 2013). However, the oxygen content, hydrogen-to-carbon ratio, and compound structures of cellulose, hemicellulose, and lignin are different, and these factors greatly affect biomass pyrolysis, product yield, and quality. With certain interactions, the three components cannot be completely separated without interference of biomass pyrolysis (Pasangulapati *et al.* 2012). The contents of the three biomass components differ in terms of biomass varieties, and the distribution of these components greatly influences the highly efficient utilization of biomass and technology selection (McKendry 2002; Yang *et al.* 2007).

However, few researchers have studied the influence of the interactions among the three components on the results of hydrothermal treatment. An extreme vertices design is used to cover the whole blending area with a few testing points (Snee and Marquardt 1974; Snee 1979). The contents of the three components are always constrained by the characteristics of the various biomass types (Piepel 1982). Therefore, the mixture of the three components is a mixture issue with the lower and upper limit constraints. This study proposes that the three components have obvious interactions and influences on the hydrothermal product distributions. Considering the different proportions of the three biomass components and the upper and lower limit constraints, that is, the constraint relationship among the three components, an extreme vertices design was adopted to synthesize biomass according to different mixing proportions. In addition, the distribution of hydrothermal product yields was comprehensively investigated. The yields of the hydrothermal biomass products was estimated from the known contents of the three components. In addition, the contents of the three components was calculated according to the hydrothermal product yields. Concurrently, the influence of the interaction among the three components on the characteristics of gas, light oil, heavy oil, and solid residue was analyzed.

EXPERIMENTAL

Samples

The model compounds of biomass used in the experiment (cellulose, hemicellulose, and alkali lignin) were purchased from Sigma (Shanghai, China). The microcrystalline cellulose was a white powder with an average particle size of 20 μm . The hemicellulose was a light yellow powder extracted from beech wood and was mainly composed of O-acetyl-4-O-methyl-glucuronoxylan. The alkali lignin was a brown powder soluble in water with a pH value of about 10.5 (3 wt%).

Experimental Method of biomass components mixtures

Cellulose, hemicellulose, and lignin were selected to form the biomass components mixtures according to different proportions. Cellulose, hemicellulose, and lignin contents in biomass have certain limitations (Kumar *et al.* 2009; Alvira *et al.* 2010). Generally, the cellulose content in biomass is within the range 20 to 80 wt%, the hemicellulose is 10 to 50 wt%, and the lignin is 10 to 40 wt%. Based on these characteristics, the mixing proportions of the three components were determined in accordance with the extreme vertices design method with the lower and upper limit constraints. The extreme vertices design contends that the optimal experimental design point comprises extreme vertices (McLean and Anderson 1966). The mixture experiment design satisfied the following constraint conditions:

$$\begin{cases} 0 \leq a_i \leq x_i \leq b_i \leq 1 \\ \sum_{i=1}^q x_i = 1 \end{cases} \quad i = 1, 2, \dots, q \quad (\text{i})$$

Those that met $\sum_{i=1}^q x_i = 1$ among the interaction points of the constraint plane $x_i = a_i$, $x_i = b_i$ ($i = 1, 2, \dots, q$) were regarded as extreme vertices. The extreme vertices design in the mixture experiment considered the number of vertices and the centers that form the planes, bodies, and edges of the polyhedron as the testing points. According to this design, regression coefficients were estimated through the least square method. The prediction equation could then be obtained, thus, the optimal factor combination would be provided.

The calculation of the vertices of the convex with the upper and lower limit constraints were as follows (Cornell 2011):

<1> The maximum range of the component was calculated by:

$$R = 1 - \sum_{i=1}^n \alpha_i$$

<2> The upper limit of the quasi component was calculated by:

$$b''_i = \min \left\{ \left(b'_i - \alpha_i \right) / R, 1 \right\} \quad (i = 1, 2, \dots, q)$$

<3> The vertices of the mixture convex with the upper and lower limit constraints were obtained through the following:

(a) $b''_i = 1, (0, \dots, 0, i, 0, \dots, 0)$ was set as the vertices.

(b) $b''_i < 1, b''_i + b''_j > 1 (i \neq j)$, thus, $(0, \dots, 0, b''_i, 0, \dots, 0, 1 - b''_i, 0, \dots, 0)$ was the vertex.

(c) $b_i'' + b_j'' \leq 1$ and $b_i'' + b_j'' + b_k'' > 1 (i \neq j \neq k)$,

thus $(0, \dots, 0, \overset{i}{b_i''}, 0, \dots, 0, 1 - \overset{j}{b_j''}, 0, \dots, 0, 1 - \overset{i}{b_i''} - \overset{j}{b_j''}, 0, \dots, 0)$ was the vertex.

$(m+1)b_i'' + b_j'' + \dots + b_m'' \leq 1$, and $b_i'' + b_j'' + \dots + b_m'' + b_s'' > 1 (i \neq j \neq \dots \neq m \neq s)$,

hence, $(0, \dots, 0, \overset{i}{b_i''}, 0, \dots, 0, \overset{j}{b_j''}, \dots, \overset{m}{b_m''}, 0, \dots, 1 - \overset{i}{b_i''} - \overset{j}{b_j''}, \dots, -\overset{s}{b_s''}, 0, \dots, 0)$.

<4> The natural variables would be reverted.

$$x_i = \alpha_i + RZ_i (i = 1, 2, \dots, q)$$

Cellulose, hemicellulose, and lignin were factors x_1 , x_2 , and x_3 , respectively. These factors met the following constraints: $0.2 \leq x_1 \leq 0.8$, $0.1 \leq x_2 \leq 0.4$ and $0.1 \leq x_3 \leq 0.5$, where $a_1 = 0.2$, $b_1 = 0.8$; $a_2 = 0.1$, $b_2 = 0.4$; $a_3 = 0.1$, and $b_3 = 0.5$. According to the above formula, the maximum range of the upper limits of the three biomass components could be calculated, and $R = 0.6$. The upper limits of the quasi components were:

$$b_1'' = \min \{(0.8 - 0.2) / R, 1\} = 1$$

$$b_2'' = \min \{(0.4 - 0.1) / R, 1\} = \frac{0.1}{0.2}$$

$$b_3'' = \min \{(0.5 - 0.1) / R, 1\} = \frac{0.2}{0.3}$$

Thus, the vertices of the mixture convex of the three components with the upper and lower limit constraints could be calculated by:

$$b_2'' \leq b_3'' \leq b_1''$$

$$b_1'' = 1, \quad (d) (1, 0, 0);$$

$$b_2'' < 1, \quad b_1'' + b_2'' > 1, \quad (e) \left(\frac{0.1}{0.2}, \frac{0.1}{0.2}, 0 \right);$$

$$b_3'' < 1, \quad b_1'' + b_3'' > 1, \quad (f) \left(\frac{0.1}{0.3}, 0, \frac{0.2}{0.3} \right);$$

$$b_2'' + b_3'' > 1, \quad (g) \left(0, \frac{0.1}{0.2}, \frac{0.1}{0.2} \right);$$

$$b_3'' + b_2'' > 1, \quad (h) \left(0, \frac{0.1}{0.3}, \frac{0.2}{0.3} \right).$$

The five vertices of the convex surface could be obtained according to $x_i = \alpha_i + 0.6Z_i (i = 1, 2, 3)$, namely, (i)(0.8:0.1:0.1), (j)(0.5:0.4:0.5), (k)(0.4:0.1:0.4), (l)(0.2:0.4:0.2), and (m)(0.2:0.3:0.2). Next, the center and constraint boundary surface of each edge could be obtained. Each x_3 of Vertex (i), (j) was 0.1, thus, the center coordinate of this edge was (0.65:0.25:0.65). Similarly, the average value of the coordinates of (i) (k), (j) (l), (l) (m), and (m) (k) was the center coordinates of the five edges (Table 1). Thus, the 11-point test plan was formed, as shown in Fig. 1 of the ternary phase diagram.

To provide a better comparative analysis with the mixing results of the three components, the sequence numbers of the tests, where single cellulose, hemicellulose, and lignin were found, were named as 12, 13, and 14. The coordinates of the 14 groups with different proportions are listed in Table 1.

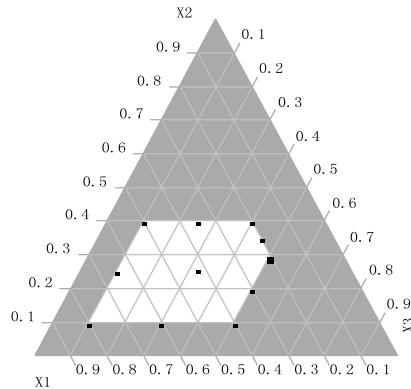


Fig. 1. Constrained factor space inside the ternary diagram

Table 1. Coordinates of the 14 Design Points for the Constrained Three Components Example

Sample	Cellulose	Hemicellulose	Lignin
Restriction on Proportion	[0.2, 0.8]	[0.1, 0.4]	[0.1, 0.5]
Factors Vertex	X1	X2	X3
1	0.8	0.1	0.1
2	0.5	0.4	0.1
3	0.4	0.1	0.5
4	0.2	0.4	0.4
5	0.2	0.3	0.5
Boundary Surface			
6	0.65	0.25	0.1
7	0.6	0.1	0.3
8	0.35	0.4	0.25
9	0.2	0.35	0.45
10	0.3	0.2	0.5
Center			
11	0.42	0.26	0.32
12	1	0	0
13	0	1	0
14	0	0	1

Experimental Process and Analysis Method

The cellulose, hemicellulose, and lignin of biomass components mixtures were prepared according to the proportions shown in Table 1. The total mass of the three components under different mass ratios was always 10 g for dry mixing. Subsequently, the components were mixed with 200 mL of water and placed in a reactor for hydrothermal treatment. The reaction device was a GSH-L autoclave reactor (Jia Yi Chemical Machinery Co., Ltd., Weihai, China). This reactor was made of stainless steel with a volume of 1 L. The design pressure and temperature of the reactor was 25 MPa

and 400 °C, respectively. The reactor was heated by an electric furnace. The temperature error measured through K-type thermocouple was ± 3 °C. All experiments were carried out under a nitrogen atmosphere. The reaction temperature was 300 °C, and the residence time was 30 min. When the reactor was fixed and sealed, nitrogen was introduced to the reactor to eliminate the air inside. Moreover, the exhaust valve of the reactor was closed. When the pressure gauge displayed 4 MPa, the charging valve was closed. The reactor was maintained for 10 min, and then the tightness of the reactor was detected. After meeting the tightness requirement, the exhaust valve was opened to allow the pressure in the reactor to be reduced to 2 MPa. The reaction temperature was subsequently set, and the magnetic stirring speed was 600 rpm for heating. After reaching the temperature and residence time, the reactor was cooled with water in the internal U-shape ring and the external fan. When the temperature of the reactor was reduced to 90 °C and the pressure fell to 2 MPa, the air valve was opened. The gas in the reactor was collected using an air bag. The experiments of several samples showed that the error of each result was within 3%. Thus, the experiments were repeated three times, and the results showed the average values. Figure 2 shows the typical temperature cycle for a 1-L autoclave reactor at 300 °C and with 30 min residence time.

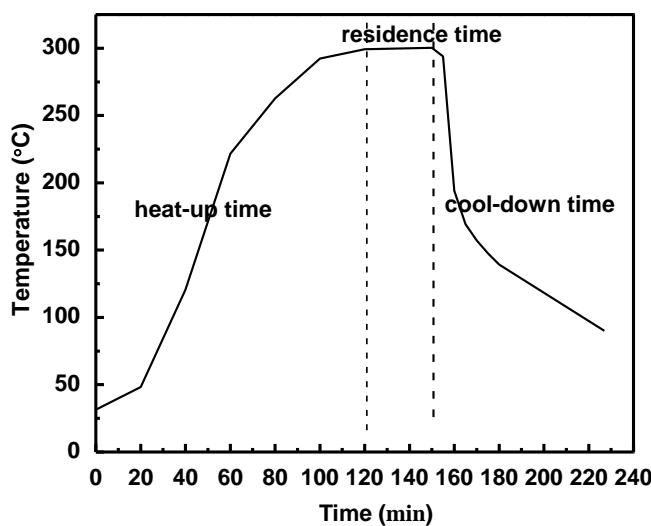


Fig. 2. Typical temperature cycle for a 1-L autoclave reactor at 300 °C and with 30 min residence time

The separation process of the products is shown in Fig. 3. After the solid-liquid separation of the reaction products, the aqueous phase and the solid product were obtained. Given that the aqueous phase contained acid, aldehyde, phenol, and other small molecule compounds, the aqueous phase was defined as light oil. The solid product contained numerous organic compounds. The solid product was extracted three times using 100 mL of acetone to obtain the black liquid. The black liquid was poured into 250-mL rotary evaporation bottles and heated in a 45 °C water bath. Subsequently, acetone and moisture were removed using an IKA RV10 rotary evaporation device (Staufen, Germany), and the remaining black oil in the bottle was heavy oil. The yield of the heavy oil was calculated through Eq. ii. The solid residue after extraction was dried at 105 °C to a constant weight and then sealed for preservation. The yield of this part of the solid residue was calculated through Eq. iii. Given that the gas yield from the reaction process was very low and the low molecular volatiles produced in the reaction process dissolved

in the liquid product, the total yield of gas + light oil (Eq. iv) could be obtained through subtraction, where:

$$\text{Heavy oil yield (wt\%)} = (\text{weight of Heavy oil}) / (\text{weight of raw material}) \times 100 \quad (\text{ii})$$

$$\text{Solid residue yield (wt\%)} = (\text{weight of Solid residue}) / (\text{weight of raw material}) \times 100 \quad (\text{iii})$$

$$\text{Light oil and gas yield (wt\%)} = 100 - \text{Heavy oil yield} - \text{Solid residue yield} \quad (\text{iv})$$

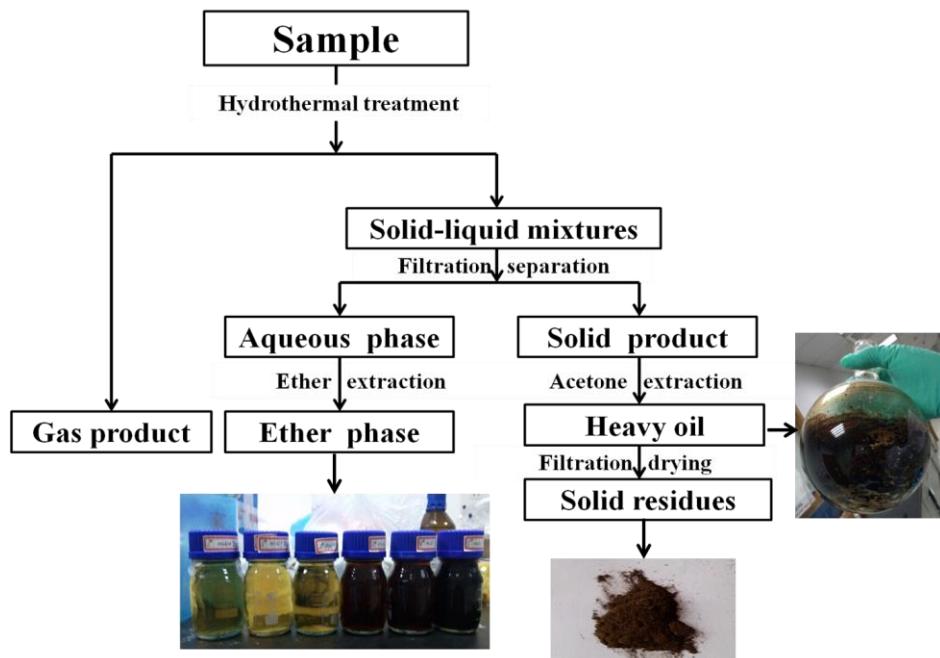


Fig. 3. Product separation after the hydrothermal treatment

The composition of the gas collected after the hydrothermal experiment was quantitatively analyzed using a 4-channel Micro-GC 3000A. The Micro-GC 3000A adopted a thermal conductivity detector with Ar and He as the carrier gases (one channel for Ar, while the remaining three for He). After being collected by a gas bag, the gas was carried into the chromatographic column through the carrier gas. Column A was the molecular sieve 5A with a column temperature of 110 °C and was used to detect H₂, O₂, N₂, CH₄, and CO; column B was Plot U with a temperature of 105 °C and was used to detect CO₂, C₂H₆, C₂H₄, and C₂H₂. Column C was alumina with a temperature of 140 °C and was used to detect C₃H₈ and C₃H₆. To perform a quantitative analysis of the gas, it is necessary to properly calibrate the instrument using a known calibration gas. The composition (v/v) of the calibrating gas was H₂ (9.83%), CO (20.7%), CH₄ (9.89%), CO₂ (20.1%), C₂H₂ (0.49%), C₂H₄ (0.5%), C₂H₆ (0.5%), and N₂ (37.99%). After the instrument stabilized, the gas was analyzed. The normalized average value was taken as the gas composition for analysis.

GC-MS (HP7890 series GC with an HP5975 MS detector; Agilent, Palo Alto, CA, USA) was used to analyze the liquid product composition in the hydrothermal process. Given the complex composition of heavy oil (containing acids, aldehydes, ketones, phenols, alcohols, and aromatic compounds), a DB-WAX polar column was

adopted for analysis. The mobile phase was helium. The temperature program started with a constant temperature of 45 °C, which was maintained for 5 min, and then the product was heated to 280 °C at a speed of 10 °C/min. Finally, a constant temperature of 280 °C was maintained for 10 min. The light oil composition was relatively simple. However, a large amount of moisture in the light oil made detecting the compounds difficult. Thus, di-ethyl ether was selected to extract these compounds. The aqueous phase was placed in a 500 mL separatory funnel, 100 mL of ether was added to extract a yellow liquid layer, the collected yellow liquid was added in a 250 mL rotary evaporation bottle, and ether and water were removed using a rotary evaporator. The rest of the products were then determined using an HP-5 weak polar capillary column. The temperature program was as follows: a constant temperature of 45 °C was maintained for 5 min, after which the product was heated to 250 °C at 5 °C/min. Finally, a constant temperature of 250 °C was maintained for 10 min. A sample volume of 0.5µL was injected. The NIST database was used to identify the peaks of compounds.

The organic elements of the raw materials were analyzed using a Series II CNHS/O 2400 element analyzer (PerkinElmer, Akron, OH, USA). The TGA-2000 instrument, produced by Spanish Las Navas, was used. Industrial analysis was conducted according to the thermogravimetric principle (Pazó *et al.* 2010). The samples were placed in pots. The pots were then sent to a low-temperature furnace through a mechanical transmission. Nitrogen was dried to a constant weight. Afterwards, the dried samples were sent to a high-temperature furnace pre-filled with nitrogen and heated for 7 min. Next, oxygen was piped into the furnace and ashed to a constant weight. The weight losses were evaluated *via* electronic balance to obtain the moisture contents, volatile matter, ash, and fixed carbon in the samples. Fourier transform infrared spectroscopy (FTIR) was conducted on a VERTEX-70 Series Fourier transform infrared spectrometer (Bruker, Karlsruhe, Germany) and was used to determine the surface functional groups of the char samples. First, the samples were ground into fine powder; 0.8 mg of the sample powder was mixed with KBr at a ratio of 1:100 and then oven-dried at 105 °C for 12 h. Next, the mixed powder was placed in a mold under a hydraulic pressure of 10 tons/cm² for 1 min. The pressure was removed, and the powder was turned into a transparent sheet. The transparent sheets of all the samples were made with the same conditions. The infrared testing parameters included a scanning range of 4,000 to 400 cm⁻¹ and a resolution of 4 cm⁻¹. To remove the influence of background information (such as moisture and CO₂), a pure KBr sheet was scanned before testing the samples.

RESULTS AND DISCUSSION

Characteristics of Raw Materials

The ultimate and elemental analyses of the three components are shown in Table 2. The highest volatile content was 95.5% in cellulose, and the lowest was 58.9% in lignin. In contrast, the highest fixed carbon content was 36.9% in lignin, and the lowest was 4.5% in cellulose. The highest heating value was 19.31% in lignin. The highest sulfur content was 3.1% in lignin. To understand the internal structure of the three components, FTIR analysis was performed on the three components (Fig. 4). The chemical components of the three components were alkyl, ether, aromatic, ketone, and alcohol (3,000 to 2,800 cm⁻¹ and 900 to 700 cm⁻¹) with different oxygen functional groups [OH (3,400 to 3,200 cm⁻¹), C = O (1,765 to 1,715 cm⁻¹), C—O—C (1,270 cm⁻¹), and

C–O–(H) (about 1,050 cm⁻¹]. Cellulose showed the following typical polysaccharide characteristics: OH (3,500 to 3,300 cm⁻¹); C–O (1,100; 1,060; and 1,035 cm⁻¹ pyranose alcohol base); the β-glucosidic bond (897 cm⁻¹); and C–H (aliphatic 2,930 to 2,850 cm⁻¹). The main hemicellulose structure contained the following: C–O–C (1,168 cm⁻¹); OH (3,412 cm⁻¹); O–Ac (2,250 cm⁻¹); –COOH (3,600 to 1,400 cm⁻¹); –H3CO (1,470 to 1,430 cm⁻¹); and –CH₂ (2,960 to 2,950 cm⁻¹, cyclopentane). The strong peak at 900 cm⁻¹ was a typical β-glucosidic bond in hemicellulose. Compared with cellulose and hemicellulose, lignin was mainly a special aromatic functional group (1,250 to 1,120 cm⁻¹) and diaryl ether bond (873 to 734 cm⁻¹), which corresponded to the large peak between 1,470 to 1,430 cm⁻¹ and 1,445 to 1,430 cm⁻¹ of the oxygen function. This finding illustrated that the branched structure of lignin contained a large amount of oxygen function. Both the C–O stretching vibration of phenol (1,215 cm⁻¹) and the C = C stretching vibration (1,513 cm⁻¹) corresponded to aromatic rings containing sub-functional groups, such as OH (phenolic ring), that were specific to lignin.

Table 2. Main Characteristics of Cellulose, Hemicellulose, and Lignin (wt%)

	Ultimate analysis (wt%, ad.)			Elemental analysis, (wt%, d.)					LHV (MJ/kg)
	V	FC	A	C	H	N	S	O ^d	
Cellulose	95.5	4.5	0.0	42.7	6.2	0.03	0.05	51.0	15.47
Hemicellulose	76.8	21.4	1.8	41.6	5.7	0.02	0.03	52.6	15.31
Lignin	58.9	36.9	4.2	48.3	4.9	0.1	3.1	43.6	19.31

^d Oxygen (O) content was determined by the difference
ad: on an air-dried basis; d: on a dry basis.

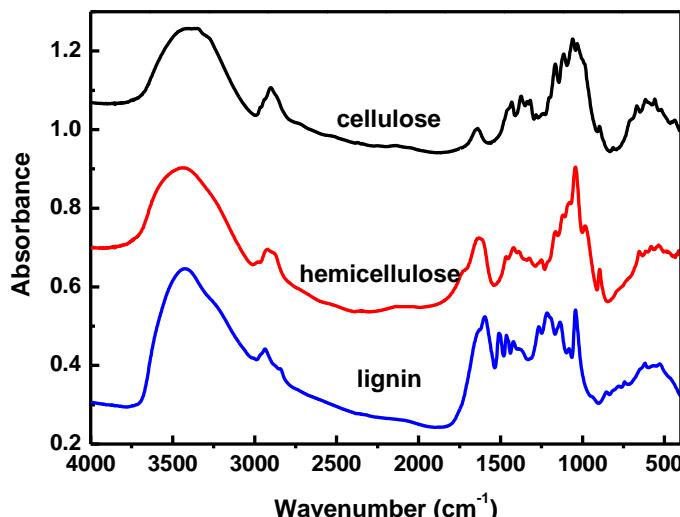


Fig. 4. FTIR spectra of cellulose, hemicellulose, and lignin

Yield Distribution of Products

Figure 5 shows the yield distribution of the products of the 14 samples. The yield of the heavy oil was highest and lowest when the mixing proportions of the three components were, respectively, 0.2:0.4:0.4 (4) at 40.10 wt% and 0.65:0.25:0.1 (6) at 28.20 wt%, respectively. When the mixing proportions were 0.3:0.2:0.5 (10) and 0.2:0.3:0.5 (5), the yield of the solid residue in the two proportions were virtually identical at 14.00 wt%. When the mixing proportion was 0.5:0.4:0.1 (2), the yield of the solid residue was lowest at 5.50 wt%. When lignin accounted for a low proportion but

hemicellulose and cellulose accounted for a high proportion in the mixture, the light oil and gas yields were high at about 65.00 wt%, where the proportions of the three components were 0.5:0.4:0.1 (2) and 0.65:0.25:0.1 (6). With the high cellulose proportion in the mixing experiment of the three components, the heavy oil and solid residue yields were low, and meanwhile those of light oil and gas were high, which indicated that cellulose was first hydrolyzed into sugar products through a hydrothermal conversion. As the hydrolysis reaction continued, the sugar products were decomposed into small molecule compounds, such as acids, aldehydes, and ketones. After reactions such as condensation and polymerization, only a small amount of these compounds produced heavy oil and solid residue. Most of the hydrolysis products of cellulose were converted into gas and light oil. When the lignin proportion was high, the yields of heavy oil and solid residue were high, and those of light oil and gas were low. These results indicated that high lignin content accelerated the production of heavy oil and solid residue but inhibited the production of light oil and gas products. Lignin usually existed as soluble lignin polymerized into phenolic char and insoluble lignin that generated isomerized aromatics char. Heavy oil was extracted from these two kinds of char in an organic acetone solvent, and some large molecules that were not fully reacted were solid residues. The hemicellulose slightly affected the product yield. When the hemicellulose proportion was the highest at 0.4, the heavy oil and solid residue yields were high when the proportions were 0.2:0.4:0.4 (4) and 0.35:0.4:0.25 (8), respectively. The heavy oil and solid residue yields were low when the proportion was 0.5:0.4:0.1 (2). This finding showed that the cellulose in Group 2 was high, whereas that of hemicellulose was low. When the proportion was 0.35:0.4:0.25 (8), the heavy oil and solid residue yields were high. The phenolic compounds produced through the hydrolysis of hemicellulose increased the concentration of light oil, and promoted the condensation and polymerization between this part of the products and the hydrolysis products of cellulose to form heavy oil.

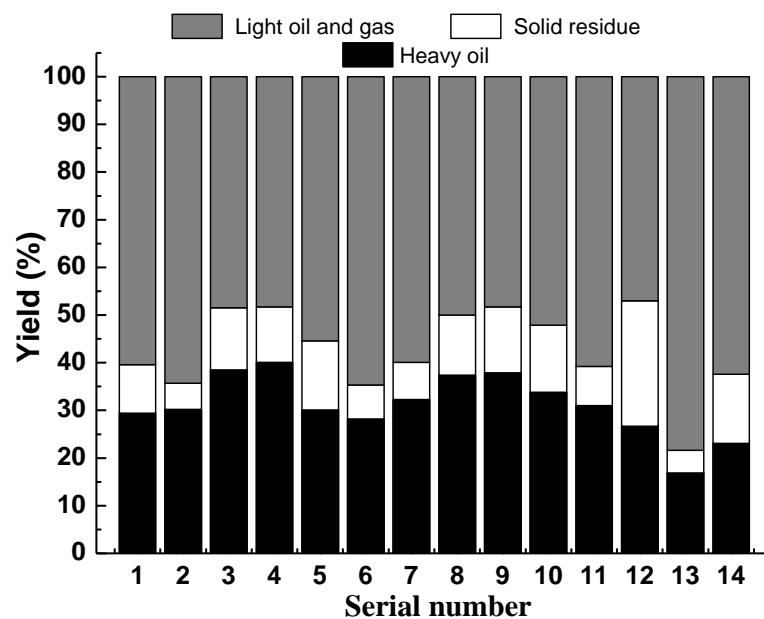


Fig. 5. Yield distribution of the products from different mixed ratios at 300 °C for 30 min

When the results of the mixing and single-component experiments were compared, it was observed that the yield of the heavy oil increased, whereas the yield of the solid residue decreased when cellulose, hemicellulose, and lignin were mixed in different proportions to form biomass. The yields of the light oil and gas were between those of cellulose and lignin. The yields of the heavy oil of cellulose and lignin were 26.70 and 23.10 wt%, respectively, and those of the heavy oil and the solid residue of hemicellulose were low at 16.90 and 4.70 wt%, respectively. The yields of the light oil and gas obtained from hemicellulose were significantly higher than those of cellulose and lignin. In sum, when the cellulose was high, the yield of heavy oil was also high. In addition, with single cellulose and by comparing the results with those of the mixing experiments, the yield of the heavy oil obviously reduced, which indicated a certain interaction among the three components, thus, generating heavy oil. Similarly, in the mixing experiment, the participation of lignin made the yield of the solid residue much lower than that of the single component.

Simulation on the Yield

Because the extreme vertices mixture design was different from a general regression design, the mathematical model required transformation, and then regression analysis was performed. The Scheffe polynomial model of was used (Cox 1971):

$$y = \sum_{i=1}^p \beta_i x_i + \sum_{i < j} \beta_{ij} x_i x_j \quad (\text{v})$$

$$y = \sum_{i=1}^p \beta_i x_i + \sum_{i < j} \beta_{ij} x_i x_j + \sum_{i < j < k} \beta_{ijk} x_i x_j x_k \quad (\text{vi})$$

$$y = \sum_{i=1}^p \beta_i x_i + \sum_{i_1 < i_2} \beta_{i_1 i_2} x_{i_1} x_{i_2} + \cdots + \sum_{i_1 < i_2 < \cdots < i_d} \beta_{i_1 i_2 \cdots i_d} x_{i_1} x_{i_2} \cdots x_{i_d} \quad (\text{vii})$$

This study proposed a regression equation relating heavy oil yield (y_1), solid residue yield (y_2), and light oil and gas yield (y_3), the x_i in the three components. The constraint conditions of the three components determined the mathematical model of the synthetic biomass design, namely, no constant or quadratic terms. This experiment had three factors that only considered the interaction between the monomial and any two factors. The regression model was a three-factor quadratic polynomial, as follows:

$$y = b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 \quad (\text{viii})$$

Multi-regression fitting was performed on the data in Fig. 5 to obtain the quadratic polynomial regression model of the response values of the heavy oil yield (y_1), solid residue yield (y_2), and light oil and gas yield (y_3) to the key factors that affected the yields, namely, cellulose (x_1), hemicellulose (x_2), and lignin (x_3):

$$y_1 = 78.16 - 44.30 \cdot x_1 + 78.07 \cdot x_2 - 40.84 \cdot x_3 - 225.3 \cdot x_1 \cdot x_2 + 36.34 \cdot x_1 \cdot x_3 - 188.51 \cdot x_2 \cdot x_3 \quad (\text{ix})$$

$$y_2 = 12.52 + 2 \cdot x_1 + 15.55 \cdot x_2 + 24.04 \cdot x_3 - 53.84 \cdot x_1 \cdot x_2 - 48.73 \cdot x_1 \cdot x_3 - 45.46 \cdot x_2 \cdot x_3 \quad (\text{x})$$

$$y_3 = -39.26 + 90.88 \cdot x_1 - 45.04 \cdot x_2 + 65.38 \cdot x_3 + 279.15 \cdot x_1 \cdot x_2 + 12.39 \cdot x_1 \cdot x_3 + 233.97 \cdot x_2 \cdot x_3 \quad (\text{xi})$$

Figure 6 shows the contour relationship between the three components and the yields of the hydrothermal products; this relationship was obtained according to the formula. According to Figure 6a, the heavy oil yield gradually increased with the increasing x_1 and reached the maximum value when cellulose was between 0.75 and 0.9. The contour slightly changed along the direction of x_2 , which indicated that x_2 had no obvious effect on the heavy oil yield. The heavy oil yield first increased and then decreased as x_3 increased; it reached the maximum value within the range of 0.1 to 0.3. Thus, x_1 and x_3 had obvious influence on the heavy oil yield. According to Fig. 6b, the solid residue yield gradually decreased as x_1 increased; as x_2 increased, the solid residue yield first decreased, and then increased. Increasing x_2 and x_3 had a noticeable influence, whereas x_1 only slightly influenced the yield change of the solid residue. According to Fig. 6c, x_1 and x_3 had great influence, whereas x_2 had a slight influence on the yield change of the light oil and gas.

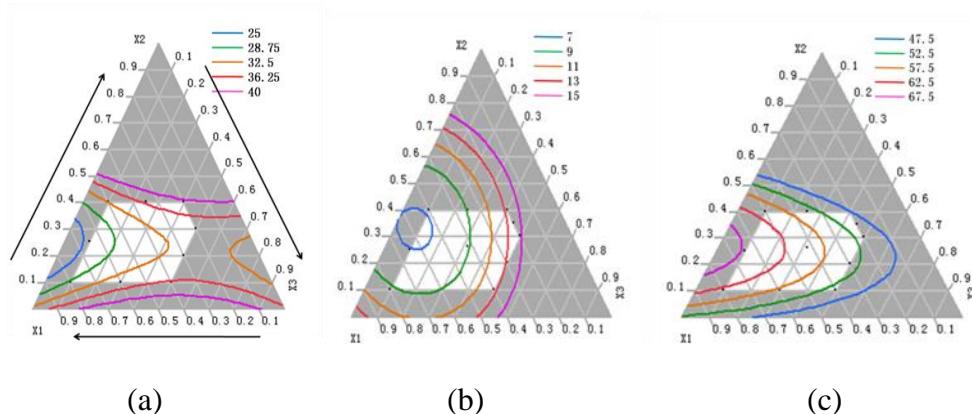


Fig. 6. Contour relation between the three components and the yields of hydrothermal products
(a) heavy oil, (b) solid residue, and (c) light oil and gas

Characteristics of the Products

Gaseous products

Figure 7 shows the gas composition of the three components with different mixing proportions. The interaction between cellulose and hemicellulose under different mixing proportions raised the CO_2 yield more than that of the single component. Correspondingly, the influence on CO , CH_4 , and C_nH_m was weak. When the cellulose content was high and the mixing proportions were 0.8:0.1:0.1 (1), 0.65:0.25:0.1 (6), and 0.6:0.1:0.3 (7), the production of CO_2 was mildly inhibited. When the cellulose was less than 0.6, CO_2 production was promoted. Based on the hydrothermal process of the single component, the gas composition and proportions of cellulose and hemicellulose were similar, mainly containing CO_2 and CO . The gas composition of lignin included CO_2 , CH_4 , and C_nH_m . The CO_2 yields produced by the cellulose and hemicellulose were higher than that produced by lignin. This result reflected the breaking of glycosidic bonds in cellulose and hemicellulose in the hydrothermal condition; this hydrolysis produced

oligosaccharide, which was further degraded into glucose. Glucose was dehydrated to produce 5-HMF, and 5-HMF underwent open-loop and dehydration reactions to generate furfural or acid. The thermal decomposition of acid generated CO₂. Light oil and heavy oil underwent secondary decomposition to generate CO, CH₄, and C_nH_m, which further showed that the interaction under these reaction conditions weakened the secondary decomposition of the products. However, the total gas yield was attributed to CO₂ produced *via* hemicellulose hydrolysis. Thus, the hydrolysis products of cellulose promoted the hydrolysis of hemicellulose.

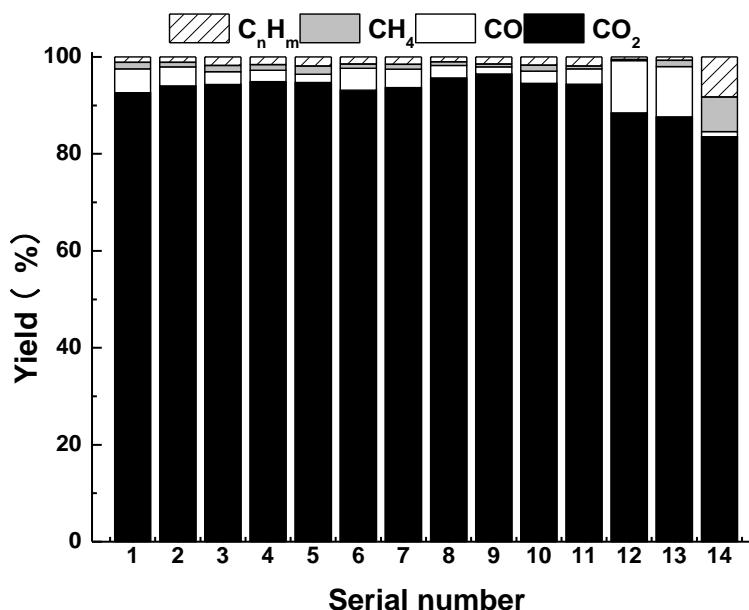


Fig. 7. Gas distribution from different mixed ratios at 300 °C for 30 min

Liquid product

The composition of light and heavy oils was determined *via* gas chromatography and mass spectrometry (GC/MS). Table 3 shows the analysis of light oil at 300 °C for 30 min; mixing the three components obviously affected the generation of small molecular oxygen compounds. The phenolic compounds in 0.2:0.4:0.4 (4) and 0.42:0.26:0.32 (11) were higher than that in the single lignin. The acids and ketones in compound 11 were low, whereas that of the ketones in compound 4 was very low. Under this mixing proportion, the light oil composition was single, which was beneficial to refining phenol chemicals. Thus, ketones were mainly generated through secondary decomposition of the hydrolysis products of cellulose and hemicellulose.

The high lignin content and the low cellulose and hemicellulose contents had inhibitory effects on acids and ketones. The acids in 0.4:0.1:0.5 (3) and compound 4 were 8.07% and 5.72%, respectively. The content was very low in the other mixing proportions, which indicated that high lignin content improved the hydrolysis of cellulose and hemicellulose to synthetic acids, but the interaction among the three components inhibited the generation of acids. In addition, the lignin proportion also affected the relative content of acids. The inhibition effect of the interaction on the acids gradually weakened when the lignin proportion was greater than 0.4. The acids in the light oil of hemicellulose were highest at 46.77%.

Table 3. GC/MS Analysis Results of Light Oil with Different Mixed Proportions at 300 °C for 30 min

Type	Compound	Run (area %)									
		1	3	4	6	8	11	12	13	14	
Ketone	2-Cyclopenten-1-one	0.47	2.62	-	1.48	1.24	-	0.97	1.98	0.04	
	2-Cyclopenten-1-one, 3-methyl-	0.99	5.43	-	0.19	5.94	-	3.6	2.31	0.58	
	2-Cyclopenten-1-one, 2,3-dimethyl-	1.65	-	-	4.95	6.76	-	3.11	-	1.59	
	2-Cyclopenten-1-one, 3,4-dimethyl-	0.38	7.9	-	0.17	-	-	0.44	-	0.43	
	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	3.32	-	-	1.34	-	-	0.33	4.17	-	
	2-Cyclopenten-1-one, 2-hydroxy-3,4-dimethyl-	0.81	5.4	-	2.37	2.14	-	0.39	-	-	
	Ethanone, 1-(2,4-dihydroxyphenyl)-	-	2.7	-	2.1	-	-	-	3.7	-	
	Phenol, 4-ethyl-2-methoxy-	2.67	-	1.29	2.13	2.61	1.26	2.95	-	-	
Phenolic	Phenol, 2-methyl-	0.98	-	0.54	0.84	1.45	0.54	1.86	-	1.6	
	Phenol, 2-methoxy-3-methyl-	-	-	0.62	0.49	0.99	0.62	0.91	-	-	
	Phenol, 2-methoxy-	3.03	30.57	16.27	7.14	20.55	16.27	6.41	-	3.24	
	Phenol, 4-ethoxy-	-	1.95	-	0.88	-	-	-	-	-	
	Phenol, 2,6-dimethoxy-	-	-	-	-	0.71	-	0.6	-	2.1	
	Phenol	3.64	-	-	1.94	1.52	2.9	1.6	-	1.5	
	Orcinol	2.17	0.18	-	-	0.89	-	-	-	4.03	
	Creosol	0.63	2.76	3.89	1.42	3.74	3.89	3.34	0.39	0.38	
	Hydroquinone	0.53	-	-	-	-	-	4.86	5.23	-	
	Catechol	7.71	5.81	36.32	5.83	4.78	34.32	6.68	0.39	11.03	
Acids	1,4-Benzenediol, 2-methyl-	2.94	2.82	-	4.87	2.01	-	1.28	1.76	2.02	
	1,2-Benzenediol, 3-methyl-	-	-	4.45	-	0.13	20.69	1.64	-	6.89	
	1,2-Benzenediol, 4-methyl-	3.05	-	16.24	3.53	2.37	-	3.38	8.22	10.66	
	1,3-Benzenediol, 4,5-dimethyl-	-	-	0.73	-	0.73	0.73	2.85	-	2.87	
	1,3-Benzenediol, 2-methyl-	-	-	-	-	1.73	-	2.27	-	-	
	Levulinic acid	-	-	5.72	-	-	-	-	46.77	-	
	Homovanillic acid	-	8.07	-	-	0.63	-	4.69	-	-	

Given that lignin only inhibited decarboxylation in the hydrothermal process, some CO₂ in the gaseous products may have formed from dehydrated cellulose and hemicellulose. The lignin hydrolysis products promoted the generation of acids and ketones in the hydrolysis products of cellulose and hemicellulose. Anhydrosugar, generated after the hydrothermal reaction of cellulose, underwent a secondary decomposition. The produced carboxyl and carbonyl molecules did not have the reaction of decarbonylation but further reacted to generate a furan structure. The acids and ketones

in the light oil in compound 3 increased, and those of CH₄ and CO in the gaseous products reduced simultaneously.

The light oil produced by the hydrothermal process of cellulose, hemicellulose, and lignin mainly contained levulinic acid, 2-cyclopenten-1-one, 2,3-dimethyl-2-cyclopenten-1-one, and other small molecule oxygen compounds (Table 3). It also contained 2-methoxy-phenol, catechol, 4-methyl-1, 2-benzenediol, and other phenolics, which corresponded to the typical products in light oil after the hydrothermal process of cellulose, hemicellulose, and lignin. The levulinic acid in the light oil of a single hemicellulose was the highest at 46.77%. The homovanillic acid in cellulose was about 4.69%. Given the low light oil content in lignin, the acids in this light oil were disregarded. The acids in 0.8:0.1:0.1 (1), 0.65:0.25:0.1 (6), 0.35:0.4:0.25 (8), and 0.42:0.26:0.32 (11) were low after mixing, but those in 0.4:0.1:0.5 (3) and 0.2:0.4:0.4 (4) were 8.07% and 5.72%, respectively, which suggested that the high lignin content in the mixing proportion could generate levulinic and homovanillic acids. For phenolics, single-component lignin and cellulose were more advantageous in generating phenolics, but the phenolics in hemicellulose were low. The influence of the mixing proportion on the different compounds in light oil was different. The yield of 2-methoxy-phenol was low when the cellulose content was high. The content in the single component was also low. When three components were mixed in the proportions of 0.4:0.1:0.5 (3), 0.2:0.4:0.4 (4), 0.35:0.4:0.25 (8), and 0.42:0.26:0.32 (11), the content was high, which indicated that cellulose had a certain inhibitory effect on 2-methoxy-phenol and could promote the preparation of special phenolic chemicals. Catechol, an important intermediate product in the hydrolysis process of lignin, was also affected by the three components. The yield of catechol in the single lignin condition was only 11.03%. When catechol was mixed with hemicellulose and cellulose in certain proportions, the yields in 0.2:0.4:0.4 (4) and 0.42:0.26:0.32 (11) increased to 36.32% and 36.32%, respectively. The 4-methyl-1, 2-benzenediol in the single lignin was about 10.66%, the content increased to 16.24% in compound 4 after mixing, indicating that mixing the three components favored generating single chemicals. The ketones in lignin were lowest at about 2.64%. After mixing, the ketones in light oil were very high in compound 3, which indicated that the mixing proportion of cellulose and hemicellulose influenced the generation of ketones. The 2,3-dimethyl-2-cyclopenten-1-one content in 0.35:0.4:0.25 (8) was 6.76%. The 3,4-dimethyl-2-cyclopenten-1-one content in compound 3 was 7.9%.

Table 4 shows the GC-MS analysis of heavy oil under different mixing proportions. Heavy oil had a complex composition that includes many different kinds of compounds. The interaction among the three components had less influence on the content of the compounds in heavy oil than that in light oil. The heavy oil from single cellulose and hemicellulose mainly contained phenols, ketones, and olefins, whereas that from lignin was mainly composed of phenolics and acids. The composition of heavy oil produced after mixing the three components was very complex. In addition to phenols, ketones, acids, and olefins, the composition also included aldehydes, benzenes, and thiophenes. The amount of 4-hydroxy-4-methyl-2-pentanone produced by single lignin was detected in heavy oil about 2.47%, but many kinds of ketones were detected in heavy oil after mixing the three components, and the content was higher. The ketones obtained by the 0.65:0.25:0.1 (6) were 10.32%, which indicated that high lignin content had a certain inhibitory effect on the generation of ketones. The 2,3-dimethyl-2-cyclopenten-1-one content in compound 6 was the highest at approximately 3.35%.

Table 4. GC/MS Analysis Results of the Heavy Oil with Different Mixed Ratios at 300 °C for 30 min

Type	Compound	Run (area %)								
		1	3	4	6	8	11	12	13	14
Ketone	Ethanone, 1-(3-thienyl)-	-	1.01	0.41	-	0.18	0.48	2.61	0.78	-
	Ethanone, 1-(2,3-dihydro-1H-inden-5-yl)-	0.79	-	0.36	-	-	-	0.09	-	-
	Ethanone, 1-(2-methyl-1-cyclopenten-1-yl)-	0.37	-	-	-	-	0.32	-	-	-
	2-Pentanone, 4-hydroxy-4-methyl-	2.35	1.97	-	2.22	1.96	-	1.19	2.3	2.47
	2-Cyclopenten-1-one	0.4	0.78	0.33	0.58	0.75	0.48	0.19	-	-
	2-Cyclopenten-1-one, 2-methyl-	2	2.66	1.49	2.2	1.43	1.72	0.31	-	-
	2-Cyclopenten-1-one, 2,3-dimethyl-	1.46	2.22	1.47	1.86	3.35	2.2	-	0.78	-
	2-Cyclopenten-1-one, 3,4,4-trimethyl-	0.27	0.87	1.32	-	-	0.25	0.17	-	-
	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	1.96	-	-	2.03	-	0.17	-	3.01	-
Phenolic	1H-Inden-1-one, 2,3-dihydro-	1.58	0.99	0.22	1.43	1.91	2.01	1.11	0.77	-
	Phenol, 2-methoxy-4-propyl-	-	5.21	2.79	-	3.03	2.87	-	-	-
	Phenol, 4-methoxy-3-methyl-	1.34	3.31	1.31	0.87	1.34	1.13	-	0.4	10.56
	Phenol, 2-methoxy-	1.37	8.39	4.6	2.36	3.94	3.41	-	0.58	16.01
	Phenol, 3-methyl-	2.12	1.16	1.07	2.25	1.86	1.08	0.7	0.69	3.24
	Phenol, 4-ethyl-2-methoxy-	1.38	6.34	3.77	2.14	3.6	2.99	-	0.28	5.26
	Phenol, 2,6-dimethoxy-	1.31	1.27	1.85	0.3	0.2	-	-	-	0.27
	Phenol, 2,3-dimethyl-trans-Isoeugenol	1.84	0.28	1.36	1.08	1.88	0.47	0.73	1.45	-
Acids	1,4-Benzenediol, 2-methyl-	-	1.6	1.14	-	-	1.55	-	-	-
	Homovanillic acid	0.63	0.55	0.22	0.91	0.66	0.58	-	-	-
Aldehyde	Benzaldehyde, 2-hydroxy-3-(2-propenyl)-	2.4	1.95	1.23	0.96	3.72	0.76	0.57	0.58	9.07
	4-Hydroxy-2-methoxybenaldehyde	0.97	0.42	0.33	5.39	-	0.79	-	-	-
	-	-	4.05	2.51	2.85	2.68	-	7.2	-	-
Akene	trans-1,2-Bis(methyldichlorosilyl)ethylene	-	2.33	2.48	-	-	-	-	-	-
	β-Neoclovene	-	1.1	1.06	0.45	1.58	0.57	2.65	-	-
	Retene	-	1.37	0.84	1.03	1.32	0.45	-	0.67	-
	Tricosane	5.58	-	0.59	-	1.65	-	-	7.26	-
Others	Benzo[b]thiophene, 3,6-dimethyl-	5.07	-	1.29	0.84	0.86	1.06	-	2.7	-
	Benzene, 1-propenyl-	0.55	1.82	0.56	1.5	1.12	3.02	-	0.53	-

The phenolics content in the heavy oil of cellulose and hemicellulose was low, but the content was as high as 37.81% in the heavy oil of lignin, where 4-methoxy-3-methyl-phenol and 2-methoxy-phenol were 10.56% and 16.01%, respectively. The phenolics in the heavy oil were greater than 20% after mixing the three components, and the phenolics were about 38.61% in the 0.2:0.4:0.4 (4). Compared with the other mixing proportions,

the 2-methoxy-4-propyl-phenol, 2-methoxy-phenol, and 4-ethyl-2-methoxy-phenol were the highest in the 0.4:0.1:0.5 (3) at 5.21%, 8.39%, and 6.34%, respectively. Compared with the results of the single component, the hydrolysis products of the cellulose and hemicellulose promoted the production of phenolics through the hydrolysis of lignin. The generation of acids in lignin was realized through the decomposition of phenolics and the hydrolysis of lignin. While the hydrolysis products of lignin were mainly phenolics, the acids in heavy oil was also high. The acid in the heavy oil of lignin was mainly homovanillic acid (about 9.07%). When lignin, hemicellulose, and cellulose were mixed with certain proportions, the acid in the heavy oil was reduced. After mixing, the homovanillic acid was at a maximum at only 2.4%, which indicated that the interaction among the three components inhibited the synthesis of acids in heavy oil, and this improved the heavy oil quality. In addition, a high content of tricosane (7.26%), was detected in the heavy oil of hemicellulose, and the cognate substance β -neoclovene (2.65%) was detected in the cellulose. No alkenes were found in the heavy oil of lignin. After mixing the three components, the olefins in 0.8:0.1:0.1 (1), 0.2:0.4:0.4 (4), and 0.35:0.4:0.25 (8) were 5.58%, 4.97%, and 4.55%, respectively, which indicated that the interaction among the three components affected the generation of olefins, aldehyde compounds, benzenes, and thiophenes.

Solid products

Infrared spectrum analysis was performed on compounds 1 through 14 (Fig. 8). At 300 °C and 30 min, the main functional groups of the solid residue were OH (3,400 to 3,200 cm⁻¹ alcohol), C–H (2,936 to 2,916 cm⁻¹ olefin), O = C = O (CO₂) (2,350 to 2,310 cm⁻¹), O–C–O (1,762 to 1,687 cm⁻¹ carbonate), C = O (1,700 cm⁻¹ acid, anhydride, and aldehyde), C–C (1,475 to 1,435 cm⁻¹ alkane, R-CH₃, R'-CH₂-R' or aromatic ring), C–O–(C) (1,275 cm⁻¹), C–O–(H) (1,050 cm⁻¹), and CH (865 to 810 cm⁻¹ olefin and aromatic ring) (Gao *et al.* 2012; Kang *et al.* 2012). Compared with Fig. 4, the absorption peaks of the oxygen functional groups in the solid residue of cellulose, hemicellulose, and lignin were reduced, and the IR absorption of hemicellulose was the weakest. This result indicated that the hydrolysis and pyrolysis of hemicellulose at 300 °C were complete, which was consistent with previous observations (Kang *et al.* 2012). Thus, the branched chain of hemicellulose was completely removed, while the absorption intensity of the chelating hydroxyl, methylene, and olefin double bond decreased. At this time, the pyranose ring was decomposed into an oligomer, and the products of the pyranose ring further underwent dehydrogenation, demethylation, molecular rearrangement, and aromatic cyclization. The solid residue of the cellulose maintained the original polysaccharide characteristic, but there were some differences in the peak strength. After the hydrothermal process, the solid residue contained aromatic compounds (1,595 cm⁻¹, C = O/C = C) and carboxyl functional groups (1,702 cm⁻¹). Cellulose dehydroxylation may generate hydroxyl and conjugated dienes before the glycosidic bonds break and the pyranoid rings open. After these events, numerous aliphatic hydrocarbons that contained rich pyranoid, double bond, and carbonyl functional groups underwent further dehydration, C–C and C–O bond ruptures, molecular rearrangement, and condensation and aromatic cyclization to generate cyclic ether/aryl alkyl ether, benzene, and other structures, which led to the high aromatization degree of the char produced by cellulose. The aromatization degree of the char produced by lignin was also very high. Sub-functional groups, such as the C = C stretching vibration (1,513 cm⁻¹) corresponding to the aromatic ring of OH (phenolic ring), were also observed. These results indicated that

the hydrothermal process caused the absorption intensity of the surface functional groups of the char produced by lignin to reduce, the aromatic ether and aliphatic ether bonds to break, the three-dimensional structure of lignin to collapse, and the dehydroxylation and dehydrogenation reactions to be intensified. Thus, numerous aromatic ring systems that contained a short branched chain olefin structure were generated.

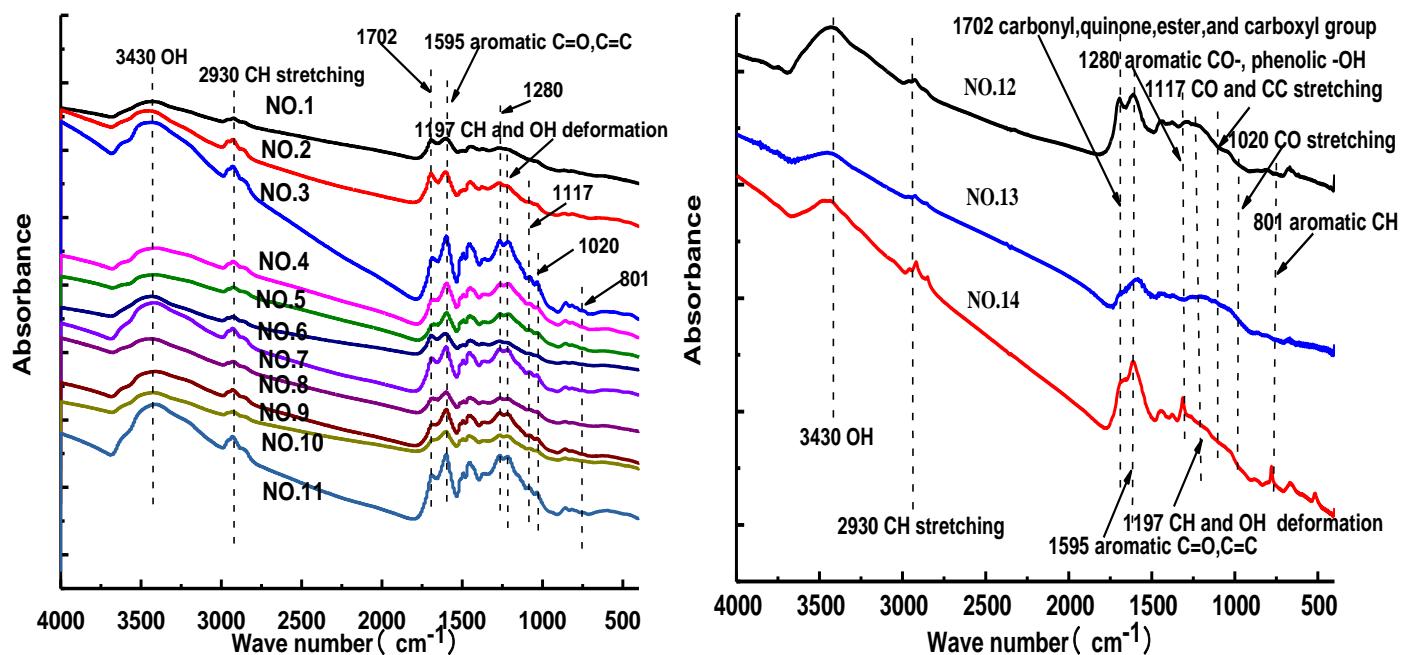


Fig. 8. FTIR spectra of different mixed ratios and single component at 300 °C for 30 min

The absorption peak intensity of the solid residue under 0.8:0.1:0.1 (1) was obviously weaker than the other mixed samples. Compared with the solid residue of single cellulose, the absorption peak was weak at both the hydroxyl and aromatic rings. According to the GC-MS results of light oil, the hydrolysis products of hemicellulose were mainly acids, whereas those of lignin were mainly phenolics, which indicated that acids and phenolics promoted the hydrolysis and pyrolysis of cellulose in the hydrothermal conversion process. While both acids and phenolics accelerated the dehydration reaction of cellulose, the condensation and aromatic cyclization were inhibited to generate cyclic ether/aryl alkyl ether, benzene ring, and other structures. Therefore, it led to the low aromatization degree of the char. In addition, the absorption peak intensity at 1,113, 1,060, and 1,163 cm^{-1} was sharply weakened, which indicated that some glycosidic bonds and pyranose rings of the cellulose molecules ruptured and decomposed, which could accelerate cellulose decomposition. When the mixing proportion was 0.4:0.1:0.5 (3), the intensity of the hydroxyl peak at 3,348 cm^{-1} , the guaiac cyclic aromatic nucleus at 1,280 cm^{-1} , the C = C stretching vibration of the benzene ring skeleton of the aromatic compounds at 1,595 cm^{-1} , and the alkyl ether bonds on the branched chain of aliphatic hydrocarbon of lignin (1,197 cm^{-1}) was significant, indicating that the hydrolysis products of the hemicellulose and cellulose functioned in removing the guaiacyl or oxygen-containing groups in lignin, which caused a higher aromatization degree in the samples. Thus, the liquid product under this proportion contained more guaiacol. Compared with the single solid residue of lignin, the absorption

peaks of the alkyl ether bond at 1,197 cm⁻¹ and the guaiacyl ring aromatic nuclear at 1,280 cm⁻¹ increased, which indicated that cellulose and hemicellulose promoted the aromatic cyclization of lignin, thus, increasing the aromatization degree of char. The hemicellulose in the mixed proportion slightly influenced the infrared absorption peak of the char. The absorption peaks under the compounds 1 through 11 were stronger than that of the single hemicellulose. Hemicellulose was hydrolyzed completely at 200 °C to 230 °C to generate gas, liquid products dissolved with plentiful CO₂, and small molecular oxygen compounds like sugars, acids, aldehydes, and phenols. These compounds had certain catalyst functions in the hydrolysis of cellulose and lignin, causing a series of new condensations and polymerizations that generated solid residue.

CONCLUSIONS

1. Hydrothermal conversion is a very complicated process involving a series of reactions that are affected by many factors. Different experimental conditions greatly influence the final products of hydrothermal treatment. Biomass samples assembled together by the proportional mixing of cellulose, hemicellulose, and lignin were determined by the extreme vertices method, indicating that the three components had obvious interactions and influences on the hydrolysis products. When cellulose, hemicellulose, and lignin were mixed in different proportions to form biomass, the heavy oil yield was increased, residue was reduced, and there were no obvious changes in light oil and gas yield. Based on the contents of the three components and the product distribution of the biomass components mixtures, the yields of the hydrothermal products of biomass were estimated. In addition, the contents of the three components was also estimated from the product yields.
2. Interactions between cellulose and hemicellulose under different mixing proportions increased the yield of CO₂, but these interactions had a negligible influence on the yields of CO, CH₄, and C_nH_m. The light oil and the contents of these components under the mixing proportions were greatly influenced by the interactions among the three components. The high lignin content and the low cellulose and hemicellulose contents had inhibitory effects on the acids, ketones, and refined the phenols.
3. Compared with light oil, interactions among the three components had negligible influence on the heavy oil. The composition of the heavy oil after mixing the three components was complex. In addition to phenols, ketones, acids, and olefins, heavy oil also contained aldehydes, benzenes, and thiophenes. The interaction among the cellulose, hemicellulose, and lignin inhibited production of acids in heavy oil, thus, improving the quality of the heavy oil. Moreover, the hydrolysis products of hemicellulose and cellulose could remove guaiacyl or oxygen-containing groups in lignin.
4. Compared with the single component solid residue, the aromatization degree of the solid residue somehow increased after mixing. The interactions among the three components had a certain influence on the change in the surface functional groups of hydrochar.

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