Comparative Studies of Products Obtained at Different Temperatures during Straw Liquefaction by Hot Compressed Water

X. Z. Yuan,* J. Y. Tong, G. M. Zeng, H. Li, and W. Xie

College of Environmental Science and Engineering, Hunan University, Changsha Hunan 410082, China

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Structure of bio-oil and residue obtained from the thermochemical liquefaction of straw by hot compressed water was investigated. The products were obtained by sampling during the experiment period at the temperature of 200, 220, 250, 300, and 310 °C. The products of liquefaction were separated into water-solution fraction, tetrahydrofuran solubles (bio-oil), and insolubles (residues). The raw straw and residues were analyzed by scanning electron microscopy (SEM), Fourier transform infrared (FTIR), and elemental analysis. The bio-oil and water-soluble products were analyzed by GC/MS and TOC, respectively. The results suggest that the main component including cellulose and hemicellulose of straw began to decompose at 200 °C, but the lignin decomposed at 250−300 °C. The main compounds of bio-oil were butylated hydroxytoluene and dibutyl phthalate; some high molecular compounds were produced by further repolymerization as the temperature increased. The results might be helpful to investigate the product characteristics at different temperatures during straw liquefaction and also establish pathways of the straw liquefaction, which can be utilized to improve the yield of goal products (bio-oil, phenols, and other useful chemicals).

Introduction

With the increasingly serious crisis of energy, biomass as a renewable resource has received more and more interest. The methods to utilize biomass are various, such as combustion,[1] pyrolysis,[2,3] gasification,[4] liquefaction,[5] and so on. Liquefaction is a cost-effective method with the aim of transforming the biomass to bio-oil and has been focused on for a long time due to its relatively mild reaction conditions without a drying process for wet stuff.

During liquefaction of lignocellulosic biomass, arrays of energy-related products including liquid, solid, and gaseous fuels, heat, chemicals, electricity and other materials were released.[6] The high quality and high yield bio-oil products were obtained under different experimental conditions during straw liquefaction.[7] Besides the bio-oil products, a range of valuable chemicals were also produced.[8,9] These compounds are mainly used as resins and antioxidants, and raw materials for the synthesis of other useful compounds. Especially, a two-step hydrothermal process to improve the production of acetic acid was discussed in Fang's research.[5]

The process of biomass liquefaction is very complex, biomass materials were broken up into fragments by hydrolysis first, and then degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation, and decarboxylation, and at last the residue was produced by repolymerization. No information on the research of straw liquefaction process, and only a few data on the reaction chemistry and phase behavior of lignin in high-temperature and supercritical water were reported in the literature.[10]

Researching the liquefaction process was necessary. It might be helpful to investigate the product characteristics at different temperatures during straw liquefaction and establish the pathway of the straw in hot compressed water, which can be utilized to improve the yield of goal products (bio-oil, phenols, and other useful chemicals) and provide the basis of pathways in controlling hydrothermal reaction to improve chemical production from carbohydrate biomass.

In this paper, the products of straw liquefaction were obtained by sampling during the experiment period at the temperatures of 200, 220, 250, 300, and 310 °C for 10 min. The products in different fractions were separated by an array of processes. By far, Fourier transform infrared (FTIR) is one of the best ways to detect the presence of typical groups in cellulose and lignin, and gas chromatography/mass spectrometry (GC/MS) is widely used in the research of the bio-oil component. To discover the effect of the heating period on the components of bio-oil, total organic carbon (TOC) value of the water-soluble fraction, and morphological structure, FTIR analysis and elementary analysis of raw straw and residue were researched. The research focused on comparing the component and the character of the water-

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* Corresponding author. Tel.:+86 731 8821413. Fax: +86 731 8823701. E-mail: yxz@hnu.cn.

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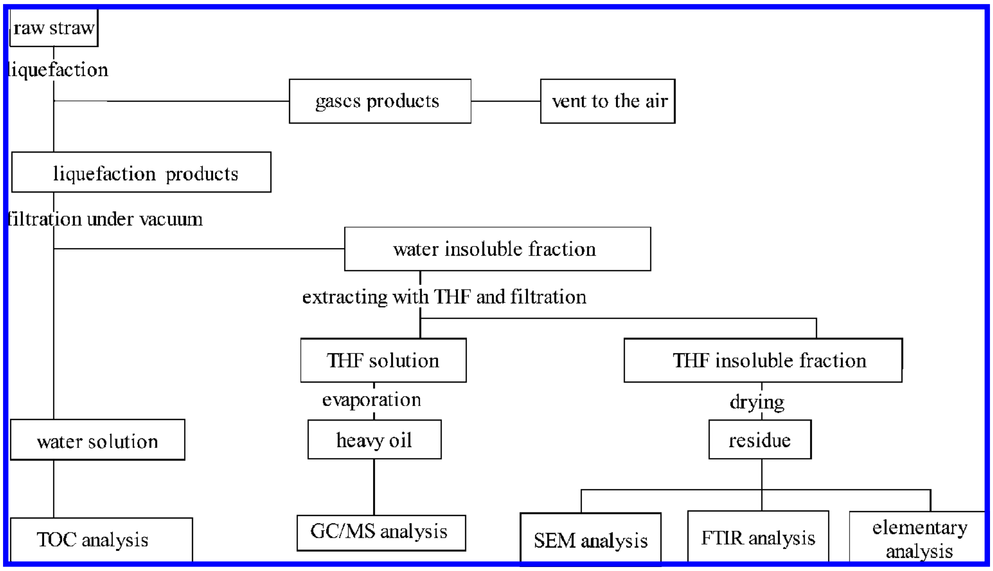

Figure 1. Flowchart of the operation and analysis on straw liquefaction products.

soluble fraction, bio-oil, and residue during the reaction period, but not on the maximum yields of products.

Experimental Section

Materials. Straw samples were obtained from the city of Changsha, Hunan province, located in central south China. The raw materials were primarily crushed by a high-speed rotary cutting mill and screened in a stack of sieves. The size fraction of 30−120 mesh was selected, and the samples were dried at 105 °C for 24 h.

Procedures for Straw Liquefaction. Batch experiments were carried out in a 1000 mL GSHA-1 stainless steel cylindrical autoclave. The autoclave was loaded with 20 g straw and 320 mL distilled water, and the straw was soaked for about 12 h. The autoclave was heated by the external electrical furnace; in the sampling run, the products were sampled when the temperature increased to 200, 220, 250, and 300 °C, respectively. In the typical hydrothermal liquefaction experiment, the autoclave was heated to 310 °C for 10 min. When the reaction finished, the electric furnace was switched off and the autoclave was cooled down to room temperature.

The products were separated as shown in Figure 1. The liquefaction products were filtered to separate the water-soluble fractions. The water-insoluble fraction was washed with tetrahydrofuran (THF), and the contents were separated by filtration under vacuum. The THF solution was evaporated in a rotary evaporator. Thus, in this paper, the term “bio-oil products” was defined to be the THF-soluble fraction. The THF-insoluble fraction was dried at 105 °C and called the solid residue.

Analysis. The element composition of raw straw and residues were analyzed by CHNOS Elemental Analyzer Vario EL III (Elementar Analysensysteme GmbH, Germany). The content of O was estimated by assuming that the straw and residue contain only the elements C, H, O, S, and N. The higher heating value (HHV) of bio-oil was calculated with the Dulong formula:

$$\text{HHV (MJ/kg)} = 0.3383Z_C + 1.422(Z_H - Z_O/8) \qquad (1)$$

where Z_C, Z_H, and Z_O are the weight percentages of carbon, hydrogen, and oxygen, respectively.

The morphological structures of raw straw and residues were analyzed by a scanning electron microscope (SEM; JEOL, model JSM-6700F).

The IR spectra of the raw straw and residues were made by a Perkin-Elmer FT-IR Spectrometer Spectrum 2000. Measurements were carried out on thin films between KBr plates.

Analysis of total organic carbon (TOC) content of water-solution fraction was carried out with a model Analytical 1010 TOC analyzer (O.I., USA).

GC/MS analyses of bio-oil products were carried out using a TRACE GC 2000, Palaris Q GC/MS spectrometer (Thermo-Finnigan, USA) with the carbon column DB-1 (30 m × 0.25 mm × 0.25 μm) and He as the carrier gas. The column temperature of GC was programmed from 130 to 230 °C with an increasing rate of 8 °C/min. The temperature of the injection chamber was 250 °C, and the temperature of transfer line was 230 °C. Compounds were identified by means of the NIST library of mass spectra.

Results and Discussion

Morphological Structure Changes of Straw during Liquefaction by Hot Compressed Water. The morphological structures of straw and residues generated during liquefaction were studied to gain insight into the role of the heating process on the liquefaction characteristics of residues. It is well-know that the morphology structure changes will be one of the important indices to evaluate the process of biomass thermochemical reaction.[11] The SEM photographs of raw straw and residues produced in the autoclave at different temperatures of 200, 220, 250, 300, and 310 °C for 10 min were illustrated in Figure 2A−F, respectively.

As can be seen in Figure 2A, the surface of the straw particle was typically a group of close-knit cells, and these solid cells were strongly bounded together but with apparent stripes, which might be seen inside the particle.

The particle shape was practically maintained with bubble surface at 200 °C. This is because in the soakage step before the reaction, the water molecule bulged when the temperature and pressure increased.

When the temperature continuously increased to 220 °C, the major morphological structure of straw was maintained but the natural slits of the material cracked deeper and deeper and the bubbles became bigger, which made the small molecule compounds release.

However, the cell structure showed distinct differences with raw straw, and the typical close-knit structure practically disappeared when the temperature increased to 250 °C. Specifically, the devolatilization of the straw was acute at this period, the particle began melting to a shapeless structure, and the bubble structure was destroyed; meanwhile, porous structures were formed and the high volatile products were released from

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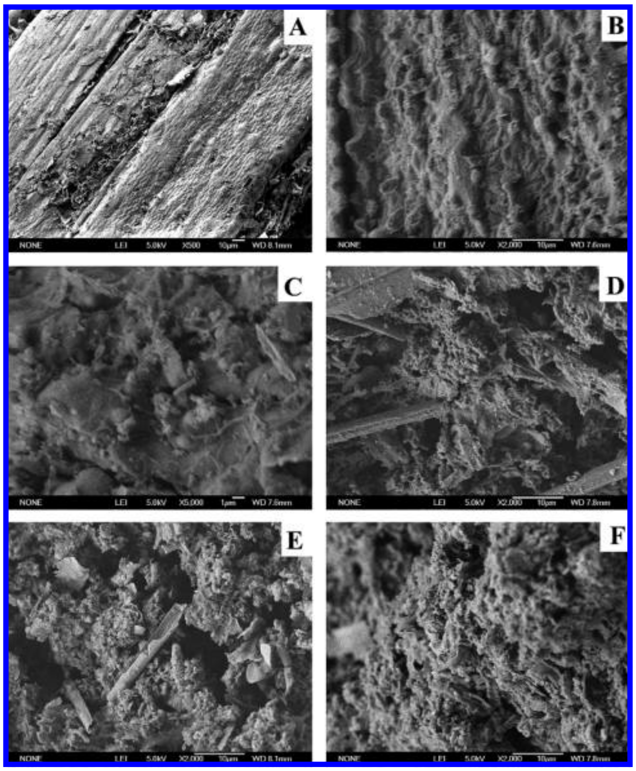

Figure 2. SEM images of raw straw (A) and liquefaction residue obtained at 200 (B), 220 (C), 250 (D), 300 (E), and 310 °C for 10 min (F).

the holes on the particle.[12,13] In addition, the lignin tissues, which were more difficult to liquefy,[14] might be represented by the obvious short branches in the shapeless structure.

Figure 2E showed a typical lacunose char particle; short branches almost disappeared at 300 °C, and the sizes of cavities in particles were larger and cell walls were thinner compared to the residues generated at relatively low temperature. At 310 °C for 10 min (Figure 2F), the particles were completely melted down and their structure was destroyed.

The changing morphological structure of the residues indicated that the most drastic reaction occurred between 220 and 300 °C. The raw straw structure was completely destroyed between 220 and 250 °C, and the typical char structure was almost formed between 250 and 300 °C.

FTIR Spectral Analysis of the Residues Obtained during Straw Liquefaction. In order to reveal the liquefaction process of the three major constituents of straw, FTIR analyses of the residues during straw liquefaction were carried out. FTIR spectra of the original straw and solid wastes obtained at the five reaction temperatures of 200, 220, 250, 300, and 310 °C for 10 min during the heating process were drawn in curves 1−6 in Figure 3.

Generally, lignin, cellulose, and semicellulose are the main constitutes of straw. As can be seen, the typical FTIR spectrum of the raw material in which the broad band of the CH, CH_2 stretching at 2919.53 cm^{-1} and the CH_2 shearing at 1429.40 cm^{-1} appeared were used for the elucidation of the cellulose and hemicellulose molecule. The wavenumbers of 1643.13, 1429.40, and 835.07 cm^{-1} respectively correspond to a benzene ring stretching, a CH_2 bending, and C—H in-plane bending, which indicate the presence of lignin.[15] Moreover various bands in the spectrum were identified as corresponding to OH (at wavenumber 3416.33 cm^{-1}), C≡C stretching (at wavenumber 2116.01 cm^{-1}), and aromatic CH (1510.83 cm^{-1}). The peak at 1252.96 cm^{-1} corresponds to C—O—C stretching in alkyl aromatics. The peak at 1051.82 cm^{-1} corresponds to C—O stretching. The peak at 880.96 cm^{-1} corresponds to ring CH_2 rocking. Aromatic compound group peaks can be seen between 900 and 650 cm^{-1}. C—H deformation peaks can be seen between 900 and 700 cm^{-1}.

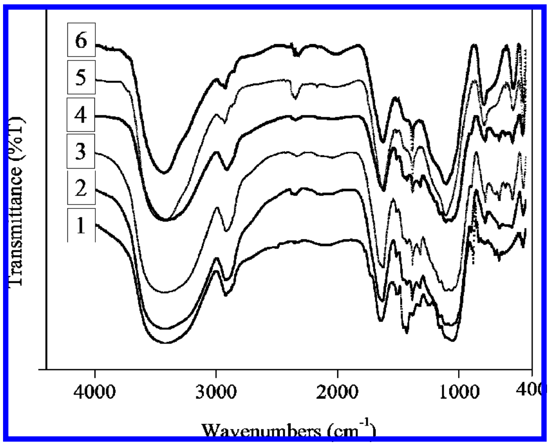

Figure 3. FTIR images of raw straw (1) and liquefaction residue obtained at 200 (2), 220 (3), 250 (4), 300 (5), and 310 °C for 10 min (6).

The residue formed during straw liquefaction consists of two parts: (a) the undecomposed part of the raw straw and (b) the repolymerized compounds in the water-soluble fraction and/or oil phase. The undecomposed part of the raw straw was gradually decreased during the heating period, so that by comparison of the representative peaks of cellulose, hemicellulose, and lignin, the liquefaction process of the three major constituents of straw will be revealed.

Compared with the FTIR spectrum of the raw straw and residue obtained at 200 °C, the absorbance peak of the OH stretching vibration (3416.33 cm^{-1}) drifts upward to high wavenumber (3429.49 cm^{-1}). At 220 °C, the bands (1514.61, 1428.36, 1062.62, and 901.56 cm^{-1}) showed that cellulose, hemicellulose, and lignin were still existent, but the intensity of these bands decreased, which implied some parts of the straw were already liquefied. The main different between 220 and 250 °C was that a new peak was appearance at the wavenumber 1106.41 cm^{-1} represented the C—O—C stretching vibration at 250 °C. During heating from 200−250 °C, the absorbance peak disappeared at wavenumber of 1060 and 900 cm^{-1}, and the CH_2 shearing and bending peak at number 1429 cm^{-1} still presented, but the intensity of the band decreased, as the cellulose and hemicellulose were decomposed primarily but the lignin was not liquefied yet. When the temperature continuously increased to 300 °C, the cellulose, hemicellulose, and lignin were almost totally liquefied, since the disappearance of absorption peaks at 1501, 1425, 1060, and 900 cm^{-1}. The absorbance curve of 310 °C for 10 min was almost the same as 300 °C, but the absorption peak at 2170.67 cm^{-1} (N=C=N stretching) disappeared, which showed the main reaction during this period did not occur in the solid part. Compared the FTIR spectra of the initial stuff (curve 1) and the final residue (curve 6), the

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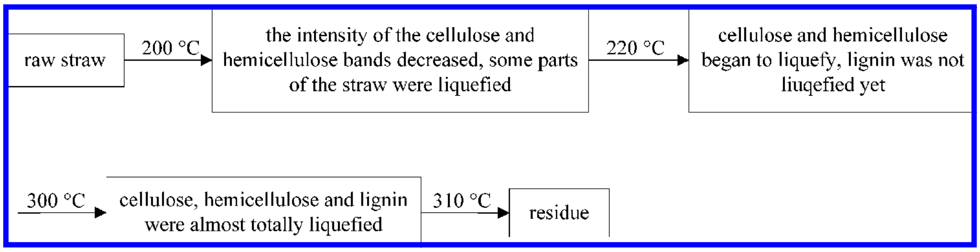

Figure 4. Flowchart of the decomposed process of cellulose, hemicellulose, and lignin during raw straw liquefaction.

Table 1. Identification of Compounds in Bio-oil by GC/MS Analysis Obtained at the Temperatures of 200, 220, 250, 300, and 310 °C for 10 min

			sample obtained at the temperature (area %)				
no.	RT, min	name of compounds	200	220	250	300	310
1	10.03	$C_{16}H_{28}O$ 7-methoxy-2,2,4,8-tetramethyltricyclo [5,3,1,0(4,11)]undecane			0.72		
2	11.04	$C_{15}H_{24}O$ butylated hydroxytoluene	52.56	61.25	54.15	62.59	73.34
3	12.85	$C_{15}H_{20}O_5$ anobic					0.41
4	14.03	$C_{15}H_{18}O_2$ 2,4,6-cyclohepttrien-1-one,2- hydroxy-5-(3-methyl-2-butenyl)-4 -(1-methylethenyl)				0.55	
5	14.58	$C_{20}H_{28}O_6$ phorbol			2.65	1.71	
6	15.12	$C_{16}H_{22}O$ 1,4-hexadien-3-one,5-methyl-[2,6,6-trimethyl-2,4-cuclohexadien-1-yl]					0.67
7	17.04	$C_{16}H_{22}O_4$ dibutyl phthalate	14.37	15.91	12.34	15.78	5.39
8	18.29	$C_{20}H_{30}O_4$ 1,2-benzenedicarboxylic acid, butyl 2-ethylhexyl ester	3.58	4.27	3.74	5.45	1.35
9	18.92	$C_{19}H_{24}O_2$ 5,19-Cyclo-5á-androst-6-ene-3,17-dione		1.39		1.04	0.68
10	20.24	$C_{19}H_{38}O_3$ octadecanoic acid,4-hydroxy-, methyl ester			1.18		
11	23.02	$C_{35}H_{70}$ 17-pentatriacontene			2.96		

composition of the straw is more complex. Thus, a simplified reaction scheme of the straw liquefaction is proposed as in Figure 4.

GC/MS Analysis of Bio-oil Obtained during Straw Liquefaction. The bio-oils were analyzed by GC/MS to study the effect of heating process on composition of bio-oils. Usually, the oil yield obtained at 200 °C was quite low, but the aim of this research was to investigate the composition of bio-oil, and the detection limit of GC/MS is relative low. The GC/MS analysis results of bio-oil obtained at 200, 220, 250, 300, and 310 °C with 10 min were shown in Table 1. The bio-oil, a complex mixture containing carbon, hydrogen, and oxygen, is composed of acids, alcohols, aldehydes, esters, ketones, lignin derived phenols, and extractible terpene with multifunctional groups. The main compounds in those six samples were dibutyl phthalate and butylated hydroxytoluene (BHT), which is usually used as food additive to prevent auto-oxidation. The BHT might be formed by the decomposition of lignin monomer (phenyl propane unit) with some side reactions during the hydrothermal treatment in the case of lignin. In the case of cellulose, it may be formed by decomposition of furans.[6] Combined with the information of FTIR mentioned above, the BHT and dibutyl phthalate were obtained from the cellulose decomposed at 200 °C. However, the formation of bio-oil started at 240−270 °C while cellulose was decomposed quickly.[16] This mainly attributed to two possible reasons as follows: One is the solvent used for dissolving the bio-oil was different, and the other is the liquefaction products in this research were obtained by sampling during the heating process.

The main compounds in bio-oil obtained at 200 °C were BHT, dibutyl phthalate, and 1,2-benzenedicarboxylic acid, butyl 2-ethylhexyl ester. When the temperature increased to 250 °C, the composition of the oil became more complex, many high molecular compounds were produced as well, such as phorbol, 4-hydroxy octadecanoic acid methyl ester, and 17-pentatriacontene. The contents of dibutyl phthalate and 1,2-benzenedicarboxylic acid, butyl 2-ethylhexyl ester decreased as well. When the reaction temperature increased to 300 °C, high molecular compounds were partly decomposed and the ratio of BHT became higher. The GC/MS result of the oil obtained at 300 °C was almost the same as that at 310 °C for 10 min. Some high molecular compounds were synthesized, such as 5,19-cyclo-5á-androst-6-ene-3,17-dione, caused by the further repolymerization of the oil product.

TOC Analysis of the Water Phase. The products in water-solution fraction were very important as well, because high additional value compounds were gained through further extraction of water solution in much biomass liquefaction research.[17−19] The organic composition of water solution was too difficult to measure, and the total organic level can be represented by TOC content, so that the water-solution fraction obtained at different temperatures during the heating period were measured by the TOC analyzer, and the analysis result was shown in Figure 5. Water-soluble products such as glucose, levoglucosan, and hydroxymethylfurfural (HMF) were mainly formed by hydrolysis of hemicellulose and cellulose. The decompositions of hemicellulose and cellulose were very slow at 200 °C; therefore, the TOC content was relatively low. While the temperature increased, the decomposition of straw became acute, especially in the hydrolysis reaction of the straw. The glycosidic linkages in straw were attacked, and water-soluble products were produced by the dehydration, decarboxylation, and decarbonylation reaction of the large molecules. Hence, the TOC increased dramatically during the heating period from 200 to 220 °C. The maximum value of TOC content is 2202.4 mg/L at 250 °C, but at 220−250 °C, the TOC increased inconspicuously, because some productions in the water-soluble fraction at low temper-

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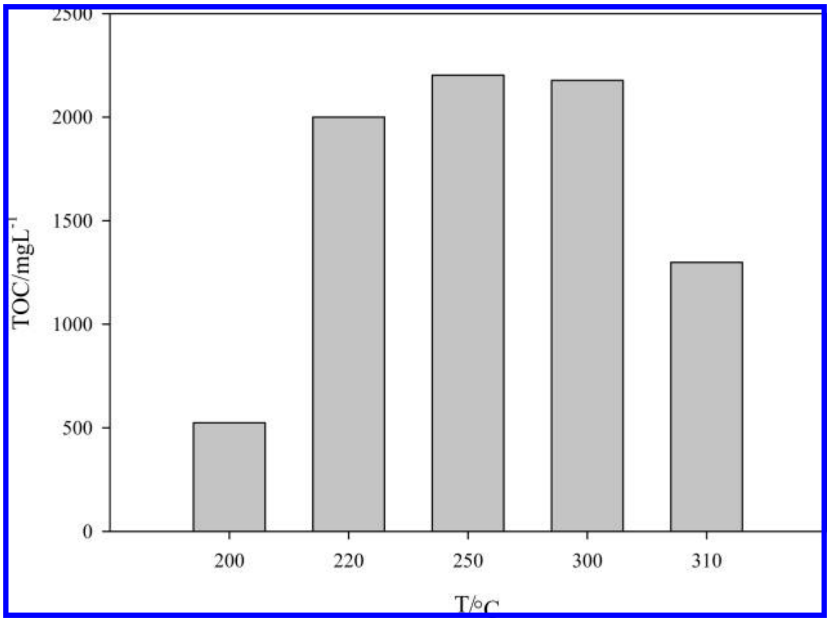

Figure 5. TOC value of the water-soluble phase obtained at straw liquefaction process.

ature were decomposed and some high molecule water-soluble hydrocarbons were produced through the repolymerization process, such as glucopyranose, benzenediol, and their derivatives.[20] The GC-MS results showed that the composition of the oil became more complex for many high molecular compounds were produced at 250 °C, because the repolymerization reaction occurred, and competition of hydrolysis and repolymerization was more drastic. The decline of TOC was not significant when the temperature increased to 300 °C, and the TOC dropped sharply when the temperature increased to 310 °C, which indicates that the repolymerization was predominated under relatively high temperature.

In summary, at the beginning of the liquefaction (room temperature−220 °C), the hydrolysis was dominant. The competition between hydrolysis and repolymerization was drastic at 220−300 °C, so that the effect of temperature on TOC was not evidence. With the temperature continuously increased, the reaction of repolymerization was more drastic compared with hydrolysis; the water-soluble products were decomposed and repolymerized into gases and oily products, so that the TOC content decreased sharply.

Elementary Analysis of Residues. The proximate analysis and elemental composition of straw and the residue obtained from liquefaction at different temperatures were presented in Table 2. The chemical compositions of straw are as follows: cellulose (41.33 wt %), hemicellulose (24.60 wt %), and lignin (9.22 wt %). Clearly, with the temperature increased, the ash content was increased and the volatile matter content was decreased. It can be seen that the carbon, hydrogen, and oxygen content in the residue obtained at 200 °C were almost the same as the original straw, but the nitrogen and sulfur content of the residue decreased sharply. This was also confirmed by FTIR spectrum, that the band at 1252.96 cm^{-1} (CH_2-S wagging) disappeared at 200 °C. The changes of the carbon content and oxygen content changed with temperature as it increased from 220 to 310 °C, and the maximum value of the carbon and oxygen content were obtained at 250 and 310 °C, respectively. The hydrogen content decreased linearly with the increasing temperature, the nitrogen content decreased with increasing temperature at first but increased subsequently when the temperature increased from 250 to 300 °C, and the effect of temperature on the sulfur content is not significant in the range of 220−300 °C. The empirical formula of the residue obtained at 310 °C for 10 min was established as $C_{396.74}H_{402.48}N_{12.23}O_{602.68}S$, which was calculated by the element compositions shown in Table 2 and the molecular weight. The ratios of sulfur and nitrogen were very small, and the H/C and O/C molar ratios were 1.01 and 1.52, separately. The HHVs of the residues, which was calculated by the Dulong formula, were listed in Table 2 and decreased sharply when the temperature increased from 250 to 310 °C. Although the HHV of the residue obtained at 310 °C for 10 min was quite low and it is not suited for combustion as a solid fuel, gas products could be obtained through further decomposing of the residue as the temperature increased[11] by hydrothermal conversion. On the basis of energy conservation, the energy loss from the raw straw to residue is translated into bio-oil.

Table 2. Proximate Analysis and Elemental Compositions of Raw Straw and Residue Obtained at the Temperatures of 200, 220, 250, 300, and 310 °C for 10 min

	sample					
	raw straw	200 °C	220 °C	250 °C	300 °C	310 °C
	proximate analysis (wt % dry basis)					
ash	6.883	6.960	7.339	9.62	11.967	24.3
volatile matter	89.90	89.03	88.41	87.45	87.05	74.52
fixed carbon	3.217	4.010	4.251	2.93	0.983	1.18
	elemental composition (wt % dry basis)					
C	36.81	37.93	36.04	38.04	32.45	31.69
H	5.025	5.307	5.025	4.698	2.865	2.679
O[a]	56.69	55.934	58.101	56.400	63.301	64.185
N	1.059	0.690	0.663	0.717	1.258	1.233
S	0.416	0.139	0.171	0.145	0.126	0.213
HHV (MJ/kg)	9.522	10.44	9.010	9.520	3.800	3.120

[a] Calculated by differences.

Conclusion

Straw liquefaction by hot compressed water without catalyst was carried out in the autoclave. The liquefaction process was

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investigated via comparing the components and the character of the water-soluble fraction, bio-oil, and residue obtained at different temperatures during the heating process.

In the low temperature region (room temperature−200 °C), the conversion rate of raw straw was slow, the changes of morphological structure was inconspicuous, and the TOC of the water solution was relatively low. During heating from 200 to 220 °C, the main reaction was the hydrolysis of cellulose and hemicellulose, so that the TOC increased sharply. However, the lignin decomposed at 250−300 °C, and the composition of the oil became more complex. The repolymerization reaction rate was much faster compared with the hydrolysis when the temperature increased from 250 to 300 °C; the bio-oil products were mainly produced in this period. When the temperature continuously increased to 310 °C, the repolymerization reaction was dominant and some high molecular compounds were synthesized.

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