

Chapter 2

Research Method

Abstract We know that the combustible solid waste (CSW) is a very complicated mixture of different components. Therefore, is there a way to simplify the research of CSW? The answer is yes. In this chapter, the classification of CSW based on thermochemical characteristics was first proposed. Based on the classification, nine kinds of basic components (hemicellulose, cellulose, lignin, pectin, starch, polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET)) were selected to simplify the study on thermochemical conversion of CSW. After that, the experimental systems in this study, including thermogravimetric analyzer (TGA), Macro-TGA, and horizontal fixed bed reactor, were introduced. TGA-Fourier transform infrared spectroscopy (FTIR) was used to obtain the intrinsic kinetics and gas products; Macro-TGA was used to obtain the gram level reaction kinetics with heat and mass transfer effect; and horizontal fixed bed reactor was used to obtain the product distribution, gas generation, and polycyclic aromatic hydrocarbons (PAHs) formation characteristics. Finally, the kinetic analysis method for slow pyrolysis and fast pyrolysis was introduced.

Keywords Combustible solid waste (CSW) · Basic component · Thermogravimetric analyzer (TGA) · Macro-TGA

2.1 Selection of Basic Components

2.1.1 *Classification of CSW*

According to physical composition, CSW can be classified into 6 categories, i.e., food residue, wood waste, paper, textiles, plastics, and rubber. However, there is a lack of CSW classification based on thermochemical characteristics. To further understand the thermochemical characteristics of CSW and explore the possibility of basic component selection, a series of CSW typical components were chosen for pre-experiments.

In pre-experiments, 26 kinds of CSW components were analyzed. The proximate analysis, ultimate analysis, and heating value measurement were tested in China Coal Research Institute (CCRI) and the Lab of Thermal Engineering, Tsinghua University. Proximate analyses were carried out based on GB/T 212 standard; C and N were analyzed based on GB/T 476 standard; N was analyzed based on GB/T 19,117; S was analyzed based on GB/T 214; and O was obtained from subtraction. Higher heating value (HHV) was measured based on GB/T 213. As shown in Table 2.1, the results of proximate analyses and heating values were based on the dry basis (drying at 105 °C) to eliminate the effect of moisture. The results of ultimate analyses were based on the dry ash-free basis.

The proximate and ultimate analyses of these components can be expressed in the ternary diagrams as shown in Fig. 2.1. As shown in Fig. 2.1a, 26 kinds of typical CSW could be classified into 5 groups according to proximate analyses. Group I includes PS, low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP), whose volatile matter content is nearly 100%, and the ash and fixed carbon content is close to zero, which has also been reported by other studies (Zheng et al. 2009; Li et al. 1999; Sorum et al. 2001). Group II includes PVC, absorbent cotton gauze, PET, tissue paper, terylene, cotton cloth, rice, and potato. Their ash content was low, and the volatile content was high. Newspaper and blank printing paper could be classified into one group, with the volatile content around 80% and the ash content close to 10%. Orange peel and tangerine peel could be classified into one group, with the ash amount lower than 3% and fixed carbon content approximately 20%. Other components, including some food residue components, wood waste, and rubber, could be classified into the last group, with the ash amount 7–19%, the volatile content 63–74%, and fixed carbon amount 15–26%. It could be concluded that the CSW component classification based on thermochemical characteristics was not the same with the physical classification.

The ternary figure of ultimate analyses is shown in Fig. 2.1b, where C and H are combined, and N, S, and Cl are combined (Vassilev et al. 2010). Twenty-six kinds of components could be classified into four groups. PVC itself was a group, with 56.96% chlorine content. LDPE, HDPE, PP, PS, and rubber could be classified into one group, with relatively high carbon content (>83%) and hydrogen content (>6%). PE and PP had similar elementary compositions, which has also been reported by others (Zheng et al. 2009; Li et al. 1999; Sorum et al. 2001). Terylene and PET could be classified into one group, with around 62% C, 4% H, 33% O, and a small amount of N and S (<0.3%). Actually, terylene and PET are different forms of the same chemical structure. Other components, including food residue, wood waste, paper, and textiles, could be classified into the last group, with 40–60% C + H, 40–60% O, less than 5% N + S + Cl. This group is biomass or natural polymers. The studies of Li et al. (1999) and Sorum et al. (2001) also showed that newspaper, paperboard, sawdust, and cotton cloth had similar elementary composition.

The classification of CSW components based on HHV is shown in Table 2.2. The HHVs of PP, HDPE, and LDPE were the highest (>40 MJ kg⁻¹); the HHVs of

Table 2.1 Proximate and ultimate analyses of CSW components

Group	Sample	Proximate analysis ^d (wt%)			Ultimate analysis ^{daf} (wt%)					HHV ^d (MJ kg ⁻¹)
		A	V	FC	C	H	O	N	S	
Food residue	Chinese cabbage	9.91	67.60	22.49	47.49	5.88	41.79	4.11	0.73	16.99
	Rice	0.40	84.42	15.18	45.97	6.35	45.74	1.69	0.25	18.14
	Potato	3.15	79.52	17.33	44.41	5.33	47.82	1.81	0.64	17.10
	Tangerine peel	2.91	76.49	20.60	48.74	5.92	43.83	1.43	0.08	18.47
	Banana peel	10.85	64.38	24.77	35.80	4.79	54.93	4.37	0.10	16.39
	Pakchoi	18.44	63.97	17.59	43.37	5.93	48.64	1.25	0.81	18.90
	Celery	14.58	65.36	20.06	38.46	6.16	54.52	0.21	0.65	13.57
	Orange peel	2.15	77.93	19.92	40.28	6.12	52.46	1.08	0.06	17.10
	Spinach	15.97	65.26	18.77	47.58	6.48	43.93	1.57	0.43	17.08
Wood waste	Poplar wood	7.54	73.85	18.61	51.36	5.89	41.00	1.52	0.22	18.50
	Poplar leaf	15.69	68.74	15.57	49.54	5.24	43.30	1.32	0.59	16.85
	Chinar leaf	9.23	69.74	21.03	52.95	4.88	40.51	1.01	0.65	19.12
	Gingko leaf	11.62	73.19	15.19	41.35	5.54	50.88	1.36	0.87	15.28
Paper	Blank printing paper	10.69	79.33	9.98	45.12	5.31	48.91	0.38	0.28	13.51
	Tissue paper	0.52	90.47	9.01	45.18	6.13	48.32	0.25	0.11	17.25
	Newspaper	8.07	79.54	12.39	48.01	5.71	45.86	0.33	0.09	17.16
Textiles	Cotton cloth	1.52	84.53	13.95	46.51	5.80	46.98	0.43	0.28	17.43
	Absorbent cotton gauze	0.14	94.85	5.01	46.74	5.69	47.23	0.27	0.08	16.82
	Terylene	0.49	88.60	10.91	62.16	4.14	33.12	0.29	0.28	20.86
Plastics	PS	0.04	99.57	0.39	86.06	6.27	1.93	5.73	0.00	38.93
	LDPE	0.00	99.98	0.02	85.98	11.20	2.61	0.21	0.00	46.48
	HDPE	0.18	99.57	0.25	85.35	12.70	1.90	0.05	0.14	46.36
	PVC	0.00	94.93	5.07	38.34	4.47	56.96 ^a	0.23	0.00	20.83
	PP	0.02	99.98	0.00	83.51	10.64	5.63	0.22	0.00	45.20
	PET	0.09	90.44	9.47	63.01	4.27	32.69	0.04	0.00	23.09
Rubber	Rubber	10.24	62.83	26.93	89.53	6.70	1.07	0.69	2.02	35.74

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Note: A ash; V volatile; FC fixed carbon; *d* dry basis; *daf* dry ash-free basis^aIt is chlorine here

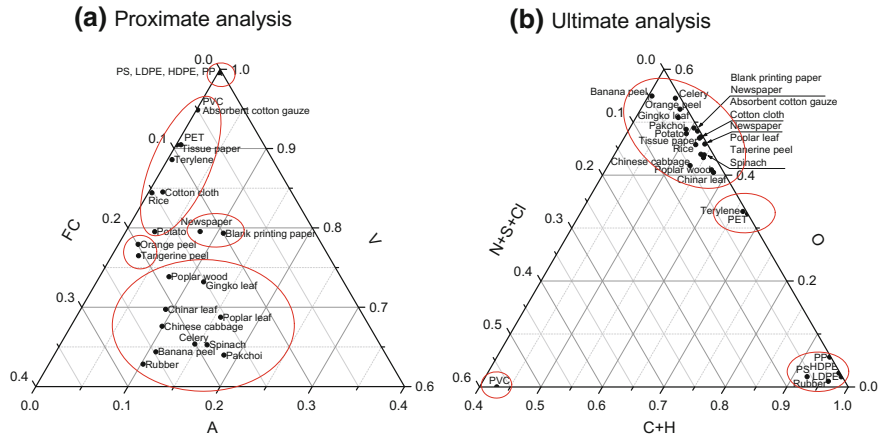


Fig. 2.1 Chemical composition of CSW components. Reprinted from Zhou et al. (2015b), Copyright 2015, with permission from Elsevier

Table 2.2 Classification of CSW components based on HHV

Heating value (MJ kg ⁻¹)	CSW components
>40	PP, HDPE, LDPE
30–40	Rubber, PS
20–30	PVC, terylene, PET
10–20	Blank printing paper, celery, banana peel, absorbent cotton gauze, poplar leaf, Chinese cabbage, spinach, potato, orange peel, newspaper, tissue paper, cotton cloth, rice, tangerine peel, poplar wood, pakchoi, chinar leaf, ginkgo leaf

rubber and PS were also very high (30–40 MJ kg⁻¹); the HHVs of PVC, terylene, and PET were between 20 and 25 MJ kg⁻¹; for other components, including food residue, wood waste, paper, and textiles, the heating values were 10–20 MJ kg⁻¹. It could be concluded that the classification based on HHV was similar to that based on ultimate analyses, as shown in Fig. 2.1b.

TGA experiments were carried out to understand the pyrolytic characteristics of CSW components. The heating zone was from room temperature to 1000 °C, with the heating rate 10 °C min⁻¹ and carrier gas N₂. According to TG characteristics, cluster analysis could be applied to CSW components. *N* sets of data were exported from the TG curves of two components, denoted by vector *X* and *Y*. The mass was relative mass, with the unit %.

$$X = (x_1, x_2, x_3, \dots, x_N), \quad Y = (y_1, y_2, y_3, \dots, y_N) \tag{2.1}$$

The distance between two TG curves was calculated by Euclidean distance, which was the most common distance metric, with the definition that the absolute distance of two vectors in multi-dimensional space (Janowitz 2010).

$$\text{dist}(X, Y) = \sqrt{\sum_{i=1}^N (x_i - y_i)^2} \quad (2.2)$$

During cluster analysis, data were selected every 10 °C between 100 and 1000 °C, which was large enough to reflect the TG characteristics. Group distance was utilized during the combination of groups. During the operation of cluster analysis step-by-step, the most similar components were clustered firstly, and the components with the most significant difference were clustered at last. Cluster analysis was carried out by SPSS. As shown in Fig. 2.2, 26 kinds of components could be classified into 11 groups.

As shown in Fig. 2.2, four kinds of wood waste components (chinar leaf, poplar leaf, poplar wood, and ginkgo leaf) could be classified into a group, whose derivative thermogravimetric (DTG) curves are shown in Fig. 2.3a. The main peaks of these four components are 320–350 °C, and there is a shoulder peak around 280 °C. Another peak is located around 700 °C, which is similar to the characteristics of spruce as reported by others (Sorum et al. 2001). The main compositions of wood waste are hemicellulose, cellulose, and lignin. The first peak (shoulder peak) was derived from the decomposition of hemicellulose (Yang et al. 2007); the main peak was derived from the decomposition of cellulose, which is also the main composition of wood waste (Skreiberg et al. 2011); the peak at 700 °C was derived from the decomposition of lignin (Zhou et al. 2013).

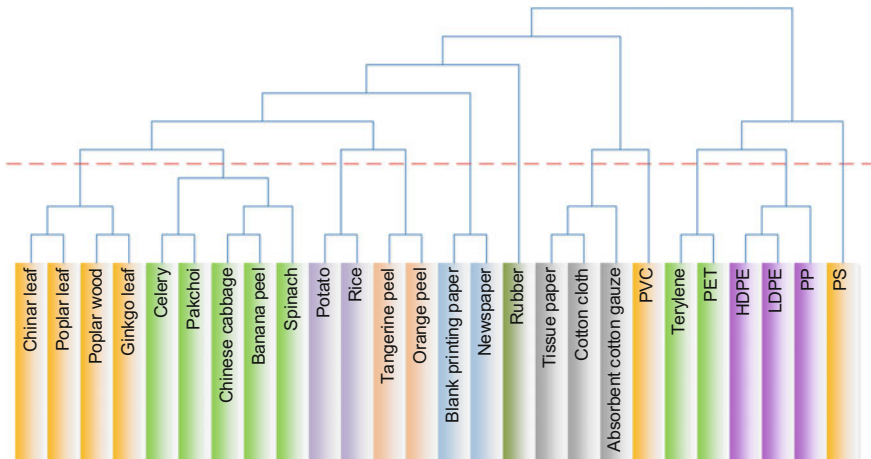


Fig. 2.2 Dendrogram of the cluster analysis of CSW components based on TG characteristics. Reprinted from Zhou et al. (2015b), Copyright 2015, with permission from Elsevier

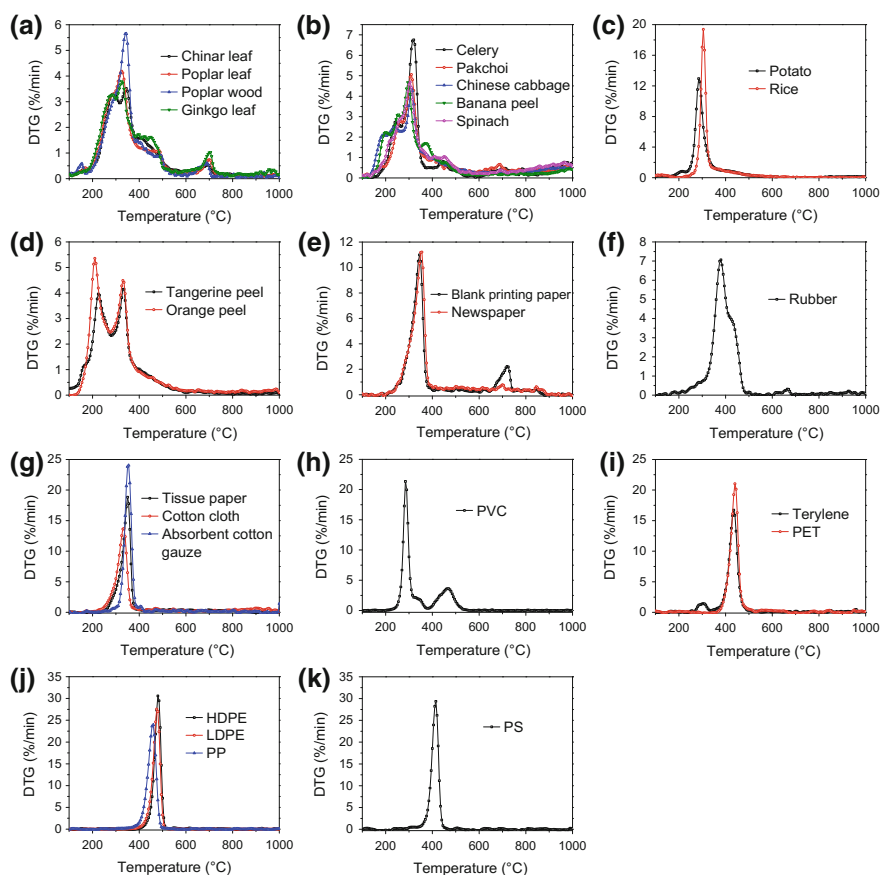


Fig. 2.3 DTG curves of different categories of CSW components based on thermogravimetric characteristics (Reprinted from Zhou et al. (2015a, b), Copyright 2015, with permission from Elsevier)

Five kinds of food residue components could be classified into a group, as shown in Fig. 2.2. The main peaks of this group were 290–320 °C, due to the decomposition of hemicellulose and cellulose; another one or two shoulder peaks at 200–260 °C were derived from the decomposition of hemicellulose (Zhou et al. 2013).

Potato and rice could be classified into a group, whose peaks were near 300 °C. Actually, the main composition of potato and rice is all starch (Dumitriu 2004). Two kinds of fruit peel, tangerine peel and orange peel, could be classified into a group, with two peaks, as shown in Fig. 2.3d. The first peak was at 210–230 °C, from the decomposition of pectin and hemicellulose (Fisher et al. 2002); the second peak was at 331–333 °C, from the decomposition of cellulose (Miranda et al. 2009; Lopez-Velazquez et al. 2013). Blank printing paper and newspaper could be classified into a group, with the main peak around 350 °C, from the decomposition

of cellulose, which is the main composition of paper (Soares et al. 1995; Wu et al. 2002, 2003). Chang et al. (1996) investigated the pyrolysis of uncoated printing paper and obtained similar results. However, blank printing paper had a mass loss peak at 721.7 °C, from the decomposition of additive CaCO_3 (Wu et al. 1997; Zhao et al. 2013). The pyrolysis of rubber was different from other components, with the main peak at 378.4 °C. Tissue paper, cotton cloth, and absorbent cotton gauze could be classified into a group, with a single peak at 333–353 °C, due to the decomposition of cellulose (Abidi et al. 2014; Yin et al. 2007).

PVC has a high content of chlorine, whose pyrolysis could be divided into two main stages. The first stage was dechlorination process, at 350–375 °C, with the peak at 286.3 °C. The second stage was the decomposition of C–H structure (Zhou et al. 2014), with the peak at 469.7 °C (Fig. 2.3h). Sorum et al. (2001) have reported similar results of PVC decomposition. Terylene and PET have the same structure, and thus, their TG characteristics were similar, with the main peak around 440 °C. It should be noted that terylene had a small peak at 304.9 °C, maybe due to impurity. The pyrolytic characteristics in TGA of HDPE, LDPE, and PP were similar, with only one peak at 455–485 °C. The pyrolytic characteristics of HDPE and LDPE were almost the same, which was consistent with the results of Sorum et al. (2001). The pyrolytic characteristics of PS were different from other plastics, with a single peak at 413.9 °C (Fig. 2.3k), lower than the peak temperatures of HDPE, LDPE, and PP.

According to the results in Fig. 2.1, Table 2.2, and Fig. 2.2, CSW can be classified according to proximate and ultimate analyses, heating value, and TG characteristics. Proximate analysis, ultimate analysis, and heating value provide a sketchy classification, while TG characteristics provide a detailed classification. Therefore, TG characteristics can be regarded as the “fingerprint” feature of CSW.

2.1.2 Selection of Basic Components

According to previous results, nine kinds of components are chosen as basic components, as shown in Fig. 2.4. Pectin, starch, hemicellulose, cellulose, and lignin are basic components for food residue category, and hemicellulose, cellulose, and lignin are basic components for wood waste and paper. Since PET and terylene are similar, and cotton cloth and biomass are similar, hemicellulose, cellulose, lignin, and PET are chosen as basic components for textiles. Since HDPE, LDPE, and PP have similar characteristics, PE, PS, PVC, and PET was chosen as basic components for plastic materials. Since the rubber content in CSW is very low (<1 wt%), as shown in Fig. 1.2, it was neglected when choosing basic components. These nine basic components could be divided into two groups. Hemicellulose, cellulose, lignin, starch, and pectin were biomass basic components. Therein, hemicellulose, cellulose, and lignin were the most important, which could be also called lignocellulosic basic component. PE, PS, PVC, and PET were plastic basic components.

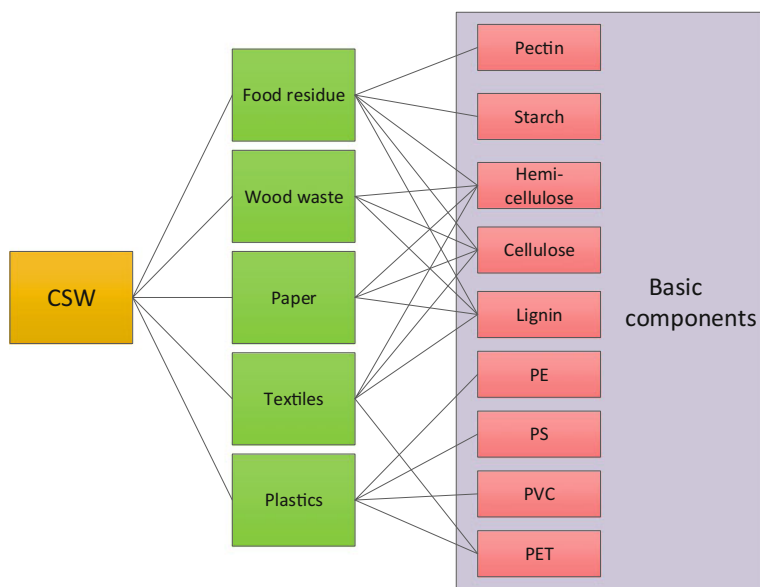


Fig. 2.4 Selection of basic components

During the selection of representatives of basic components, multiple samples were considered, as shown in Table 2.3. Considering sample stability, particle size, purity, availability, price, and authority, representatives were selected for each basic component, shown by bold and underline in Table 2.3. Since hemicellulose is a class of polysaccharides, xylan is usually selected as representative of hemicellulose for research (Couhert et al. 2009).

2.1.3 Basic Characteristics of Basic Components

The structural formulas of these nine basic components are shown in Fig. 2.5. Hemicellulose is a very complex polysaccharide, with various monomers. Cellulose and starch are natural polymers based on glucose monomer. Lignin has three main monomers, i.e., paracoumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Dorrestijn et al. 2000; Chatel and Rogers 2014). Pectin is a group of galacturonic acid, existing as the cell wall composition of the fruit, root, stem, and leaves of the plant. PE, PS, PVC, and PET are common plastics in CSW, whose structure is relatively simple.

The particle sizes of these nine basic components were less than 150 μm . Before the tests, samples were dried at 105 $^{\circ}\text{C}$ to remove the moisture. The proximate analyses, ultimate analyses, and heating values are shown in Table 2.4. In biomass components, lignin had the highest fixed carbon content (24.69%) and element

Table 2.3 Selection of representatives of basic components

Basic component	Real sample	Basic component	Real sample
Hemicellulose	Xylan (CSC)	Starch	Soluble starch (Jingqiu)
	<u>Xylan (Sigma)</u>		Starch from potato (Sigma)
Cellulose	Absorbent cotton		Starch from wheat (Sigma)
	Absorbent cotton gauze		<u>Starch from rice (Sigma)</u>
	Filter paper	PE	LDPE (Yangli)
	Microcrystalline cellulose (Jingqiu)		PE (Yanshan)
	Microcrystalline cellulose (RCL)		HDPE (Goodfellow)
	<u>Microcrystalline cellulose (Sigma)</u>		<u>HDPE (Yangli)</u>
Lignin	Sodium lignin sulfonate (Xingzhenghe)	PS	PS (Yanshan)
	Industrial lignin (Shanfeng)		PS (Goodfellow)
	Alkaline lignin (TCI)		<u>PS (Yangli)</u>
	Alkaline lignin (Kanto)	PVC	PVC (Yanshan)
	Sodium lignin sulfonate (TCI)		PVC (Yangli)
	<u>Dealkaline lignin (TCI)</u>		<u>PVC (Sigma)</u>
Pectin	<u>Pectin from citrus peel (Sigma)</u>	PET	<u>PET (Yangli)</u>

Note: CSC Corporation Service Company; *Sigma* Sigma-Aldrich Ltd.; *Jingqiu* Beijing Jingqiu Chemical Co., Ltd.; *RCL* Research Chemicals Ltd.; *Xingzhenghe* Shenyang Xingzhenghe Chemical Co., Ltd.; *Shanfeng* Changzhou Shanfeng Chemical Industry Co., Ltd.; *TCI* Tokyo Chemical Industry Co., Ltd.; *Kanto* Kanto Chemical Co., Ltd.; *Yangli* Shanghai Yangli Mechanical and Electrical Technology Co., Ltd.; *Yanshan* SINOPEC Beijing Yanshan Company; *Goodfellow* Goodfellow Cambridge Ltd.

carbon content (63.86%), and the lowest volatile content (46.10%) and O content (25.83%). Meanwhile, the sulfur content of lignin was very high, maybe due to the separation process. Cellulose had the highest volatile content (92.07%), the lowest fixed carbon content (4.63%), and almost no ash. The high volatile content of cellulose and high sulfur content of lignin have also been reported by others (Couhert et al. 2009; Yoon et al. 2012). Plastic basic components had very high volatile content, and PVC and PET had a certain amount of fixed carbon. PE had the highest H content (11.20%), and PVC had the highest Cl content (56.96%), which was consistent with the report of Li et al. (1999). PET had the highest O content (32.69%), as shown in Table 2.4.

Except for PE and PS, the dry basis HHV of the basic components varied between 15.44 and 23.09 MJ kg⁻¹. The HHV of PS was 38.93 MJ kg⁻¹, and the

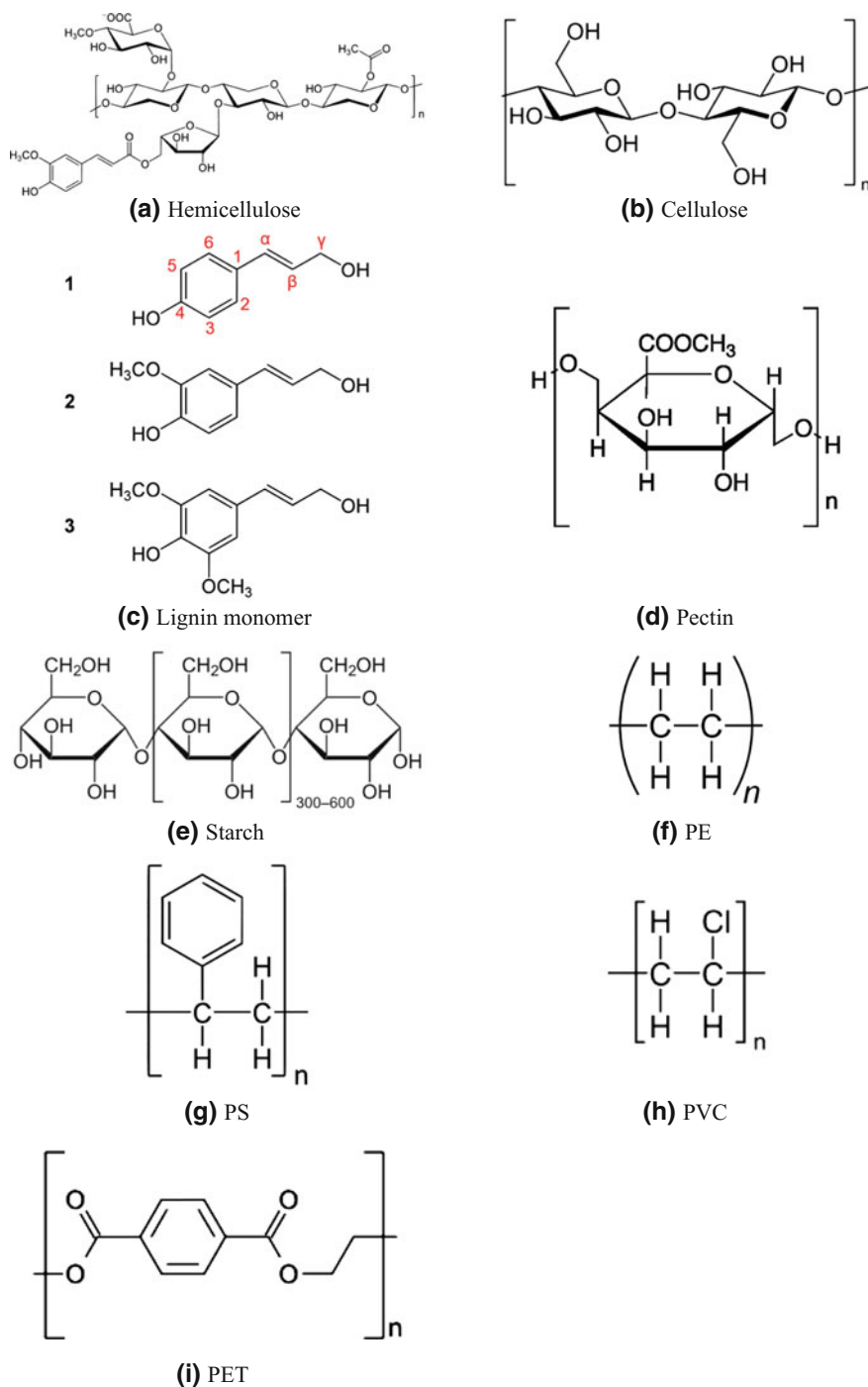


Fig. 2.5 Structural formula of basic components

Table 2.4 Proximate analyses, ultimate analyses, and heating values of basic components

Category	Basic component	Proximate analysis ^d (wt%)			Ultimate analysis ^{daf} (wt%)					HHV ^d (MJ kg ⁻¹)
		A	V	FC	C	H	O	N	S	
Biomass	Hemicellulose	2.11	78.57	19.33	39.18	6.32	54.50	0.00	0.01	17.47
	Cellulose	0.00	95.21	4.79	44.51	6.25	47.93	1.29	0.01	27.14
	Lignin	16.15	54.61	29.25	63.86	4.45	25.83	0.18	5.67	21.01
	Pectin	3.38	74.53	22.09	44.25	4.97	50.14	0.48	0.16	15.44
	Starch	0.14	95.20	4.66	43.83	5.21	50.56	0.20	0.19	17.31
Plastics	PE	0.00	99.98	0.02	85.98	11.20	2.61	0.21	0.00	46.48
	PS	0.04	99.57	0.39	86.06	6.27	1.93	5.73	0.00	38.93
	PVC	0.00	94.93	5.07	38.34	4.47	56.96 ^a	0.23	0.00	20.83
	PET	0.09	90.44	9.47	63.01	4.27	32.69	0.04	0.00	23.09

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Note: A Ash; V Volatile; FC fixed carbon; *d* dry basis; *daf* dry ash-free basis

^aIt is chlorine here

HHV of PE was as high as 46.48 MJ kg⁻¹, which was consistent with the report of Zheng et al. (2009).

To further understand the main functional groups of the basic components, solid FTIR was tested, as shown in Fig. 2.6. The main functional groups were shown in Table 2.5. The main functional groups of biomass were OH, CH₂, crystal water, CH₂ connected with oxygen or COOH, CH₃, alcohol, phenol, C–O in carboxylic

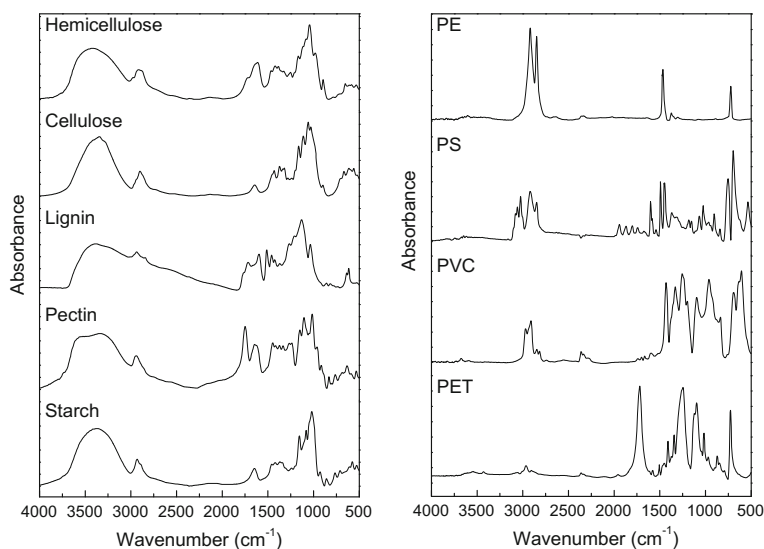
**Fig. 2.6** Solid FTIR spectra of nine basic components

Table 2.5 Main functional groups of basic components from FTIR

Functional group	Hemicellulose	Cellulose	Lignin	Pectin	Starch	PE	PS	PVC	PET
OH stretching	3435	3345	3393	3335	3374				
Symmetrical stretching of CH ₂ bonded with O									2967
CH ₂ -connected halogen-bonded C								2970	
CH ₂ asymmetrical stretching	2915	2900	2937	2939	2932	2919	2920	2910	2906
CH ₂ symmetrical stretching						2848	2848	2847	
Benzene ring							1942		1960
C=O stretching				1750					1717
Aromatic ester carbonyl stretching			1716						
C=C							1748	1700	
C=C stretching								1667	
Inorganic crystal water deviational vibration	1613	1645	1597	1645	1647				
CH ₂ =CHCl								1597	
Benzene ring C=C stretching			1514				1541 1492		1505
CH ₂ deviational vibration	1464	1458	1463	1447	1458	1467	1452		1455
CH ₂ connected with O or COOH	1424	1431	1426	1418	1418				1410
Deformation of CH ₂ -connected halogen-bonded C								1431	
CH ₃ symmetrical deviational vibration	1384	1372	1372	1375	1372	1374	1373		1372
C–OH plane bending	1326	1335 1318 1283		1334	1306				1343
Alkane CH ₂ twisting							1312		
Aryl ether			1266						
C–O stretching	1251	1236		1266	1240				
Stretching of C–O in alcohol, phenol, or carboxylic acid	1167	1164	1210	1238 1150	1156				1244

(continued)

Table 2.5 (continued)

Functional group	Hemicellulose	Cellulose	Lignin	Pectin	Starch	PE	PS	PVC	PET
Stretching of C–O in secondary alcohol		1113	1130	1104	1080				1121
C–C stretching						1081	1111	1097	1097
CH in-plane bending in aromatic ring							1068		1045
C–O stretching in primary alcohol	1044	1059	1035	1015	1020				1017
CH ₂ =CHCl								962	
Polycyclic ether	982	1032		962	929				970
β bond in cellulose	896	899			861				
CH out-of-plane in aromatic ring			856 817				840 755		872 846 793
Methyl benzoate									725
C–Cl stretching								689 605	
Out-of-plane bending of C–OH in alcohol	654	666	636	635					
Inorganic salts	531	615 559	614 526	533	608 576 528				

acid, C–O in primary alcohol, and inorganic salts. The functional groups of lignin also included carbonyl in aromatic ester, benzene ring, and aryl ether. The functional groups of PE were simple, mainly CH₂; PS also had benzene ring, C=C, and CH in aromatic ring besides CH₂; PVC also had CH₂-connected halogen-bonded carbon, CH₂=CHCl, and C–Cl; PET had CH₂ connected to oxygen, benzene ring, C=O, CH₂ connected to oxygen or COOH, C–OH, C–O, CH in aromatic ring, polycyclic ether, and methyl benzoate.

2.2 Experimental System

This research first carried out thermochemical conversion experiments in TGA-FTIR to explore mass loss and gas release characteristics of intrinsic chemical reactions. Furthermore, the mass loss kinetics were investigated in a self-designed Marco-TGA, while product distribution, gas products, and PAHs formation were investigated in another self-designed horizontal fixed bed reactor.

Fig. 2.7 Thermogravimetric analyzer-Fourier transform infrared spectroscopy



2.2.1 TGA-FTIR

The TGA-FTIR used in this study is shown in Fig. 2.7. The TGA is NETZSCH STA 409 C/3/F, with the carrier gas flow rate 100 ml min^{-1} , the heating rate $10 \text{ }^{\circ}\text{C min}^{-1}$, and the temperature range from room temperature to $1000 \text{ }^{\circ}\text{C}$. The particle sizes of these nine basic components were less than $150 \text{ }\mu\text{m}$. In TGA tests with these particle sizes, the influence of heat and mass transfer could be neglected (Bockhorn et al. 1999).

To verify the repeatability of TGA tests, lignin pyrolysis was chosen to run the repeated tests. As shown in Fig. 2.8, the repeatability of TG and DTG curves from three tests was quite good.

The gases from TGA will be blown into FTIR (Nicolet Nexus 670) by N_2 . The transfer line and FTIR gas cell were kept at $150 \text{ }^{\circ}\text{C}$. The range of FTIR spectrum was $4000\text{--}400 \text{ cm}^{-1}$, with the resolution 1 cm^{-1} . To obtain the gas amount per unit mass samples, the mass of samples in TGA was divided.

2.2.2 Macro-TGA

TGA is the most common method to investigate the kinetics of thermochemical reactions. In TGA experiments, the usual procedure is to load the sample first and then increase the furnace temperature. Therefore, the heating rate in TGA is usually less than $100 \text{ }^{\circ}\text{C min}^{-1}$ (Seo et al. 2011). Research has shown that heating rate had a significant influence on thermochemical kinetics (Biagini et al. 2008). In TGA, the heat and mass transfer is usually neglected, which is quite different from industrial reactors. In addition, the sample mass in TGA is usually milligram level, which is too low to investigate the interactions between samples. Based on the above reasons, a Macro-TGA which can realize gram level sample and online mass measurement of fast thermochemical reactions is designed to better investigate the component interactions of the thermochemical conversion process.

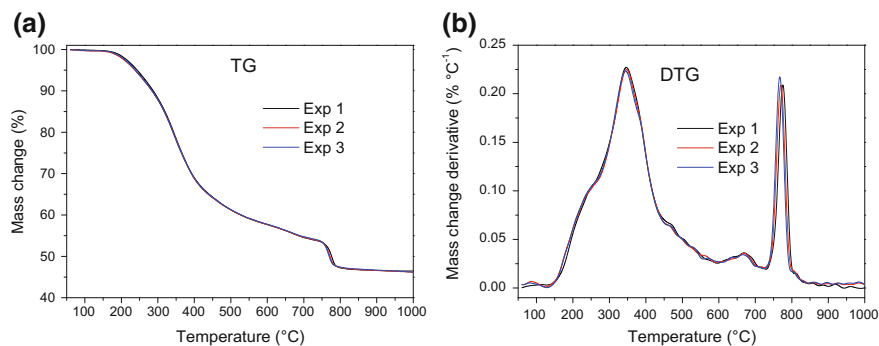


Fig. 2.8 Repeatability of TGA experiments

2.2.2.1 Experimental System

As shown in Figs. 2.9 and 2.10, the reaction system is composed of gas supply system, reaction system, and mass measurement system.

The gas was supplied into the reactor bottom from the high-pressure gas cylinder. The mass flow rate was controlled by a mass flow controller with the flow rate 1 L min^{-1} .

The reaction system was composed of furnace, quartz tube, and quartz crucible. The furnace was vertical, and the size is shown in Fig. 2.11. The heating element was HRE resistance wire, which was arranged annularly to obtain uniform temperature

Fig. 2.9 Schematic diagram of Macro-TGA system (Zhou et al. 2015a)—Reproduced by permission of The Royal Society of Chemistry

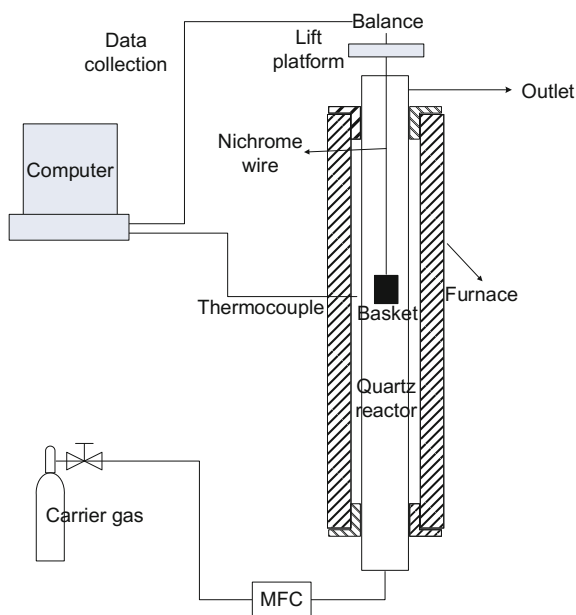


Fig. 2.10 Photo of Macro-TGA



distribution. The highest temperature of the furnace could reach 1200 °C. The inner diameter of the furnace was 80 mm. The heating zone was 800 mm long. The constant temperature zone was 350 mm long, with the temperature fluctuation less than 1 °C. The furnace had three temperature zones, and the rated power was 5 kW. The highest heating rate could reach 40 °C min⁻¹.

The furnace could be split to load reactor. The temperature could be monitored and controlled by a computer.

The inner diameter of the fixed bed quartz tube reactor was 60 mm, and the length was 1500 mm, with upper and lower ends extending furnace 250 mm. The ends of the quartz tube were sealed by 304 stainless steel multi-stage sealing quick release flanges.

The quartz crucible is shown in Fig. 2.12. It was cylinder-shaped, with the inner diameter 30 mm, height 30 mm, and weight 18 g. In each test, the sample mass was 1.50 ± 0.01 g.

Fig. 2.11 Geometry of Macro-TGA

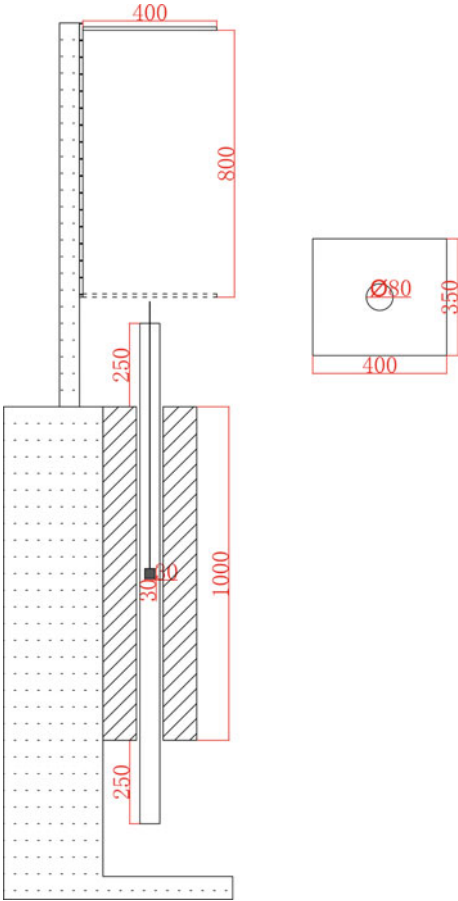
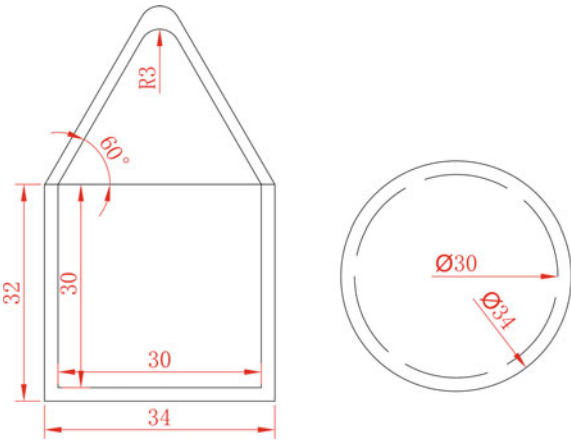


Fig. 2.12 Geometry of quartz crucible



As shown in Fig. 2.9, the online mass measurement was realized through a balance in the fixed bed reactor. The mass measurement system was composed of metal wire, balance, lift platform, and computer. As shown in Fig. 2.11, the crucible was hung below the balance by a metal wire. The top flange had a 5 mm hole in the center. The metal wire was 0.2 mm long, and made of Cr20Ni80 (20 wt% Cr and 80 wt% Ni). The metal wire was not brittle and not easy to break at high temperatures. The maximum permissible temperature was 1200 °C, with the linear expansion coefficient $1.8 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$ (Zou et al. 2009). From the definition of linear expansion coefficient $l_t = l_0(1 + \alpha\Delta t)$, when the furnace temperature increased from 20 to 1000 °C, imagining that temperature was linearly distributed along metal wire, i.e., the upper end was 20 °C and the lower end was 1000 °C, the extension of 1-m metal wire was

$$\Delta l = \int_0^1 \alpha \Delta t(l) dl = 8.82 \text{ mm} \quad (2.3)$$

As shown in Fig. 2.11, an electric lift platform was arranged above the furnace, with the track length 800 mm. The lift module was driven by motor and ball screw to reduce the vibration. The lowest position and highest position of the platform are shown in Fig. 2.11. The platform was 350 mm wide, 400 mm long, and dismountable. The maximum bearing capacity was more than 10 kg. Platform center had a $\varnothing$ 80 mm hole, homocentric with the furnace center.

The balance was Mettler Toledo ME 204E, with the maximum capacity 220 g, readability 0.1 mg, repeatability 0.1 mg, setting time 2 s, and sensitivity temperature drift 2.0 ppm $^{\circ}\text{C}^{-1}$. The balance base was 344 mm long and 210 mm wide. The height of the balance was 344 mm, and the net weight was 4.5 kg. During the experiments, the data of the balance could be collected by a computer at the sampling baud rate 9600 bps.

2.2.2.2 Experimental Procedure

Two kinds of experiments were carried out in Macro-TGA: slow pyrolysis and fast pyrolysis. The procedure of slow pyrolysis was as follows:

- (1) Open gas cylinder, adjust mass flow controller, and purge the reactor for 1 h;
- (2) Load the sample (~ 1.5 g) into the crucible and hang the crucible below the balance;
- (3) Set furnace temperature program and start to ramp;
- (4) When the furnace temperature was around 50 °C, start to collect data from balance and write down the furnace temperature;
- (5) When the temperature was stable at 1000 °C, stop collecting data from balance and save balance and temperature data.

The procedure of fast pyrolysis was as follows:

- (1) Open gas cylinder, adjust mass flow controller, and purge the reactor for 1 h;
- (2) When the furnace temperature was stable at setting temperature, collect data from balance;
- (3) Open the top flange, put crucible with sample in reactor and make sure it hung below the balance;
- (4) When the change of balance reading was less than 0.01 g min^{-1} , the reaction was thought ended. Stop collecting data from balance and save balance data.

2.2.2.3 Experimental System Debugging

To calibrate the temperature of fixed bed reactor, define the top of the furnace as 0 cm and the bottom of the furnace as 100 cm. The temperature was then calibrated every 10 cm from 4 to 100 cm by a thermocouple (precalibrated). As shown in Fig. 2.13, the tubular furnace had a more than 20-cm-long constant temperature zone at the furnace center with the deviation less than 5°C , which satisfied the demand of experiments.

To obtain the relationship of furnace display temperature and real temperature, the display temperature and real temperature at reactor center (50 cm) were fitted by a polynomial. The fitting function was $t_r = \sum_0^9 a_i t_f^i$, and the coefficients were shown in Table 2.6. The fitting results are shown in Fig. 2.14.

According to multiple tests, the sampling period of balance was 0.087365 s, and the sampling frequency was 11.45 Hz.

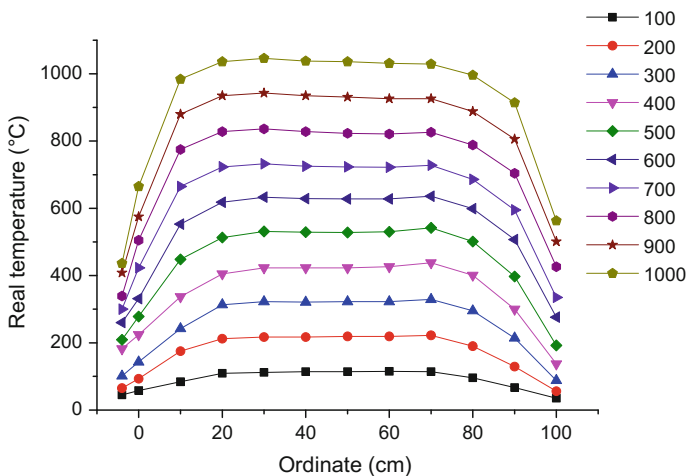
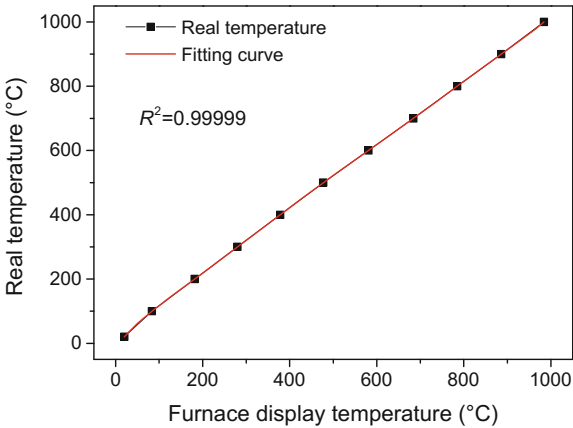


Fig. 2.13 Temperature calibration of Macro-TGA

Table 2.6 Fitting results of furnace display temperature and real temperature

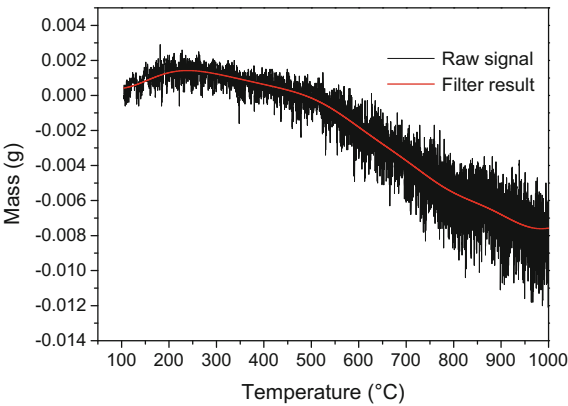
Coefficient	a_0	a_1	a_2	a_3	a_4
Value	-1.30×10	1.80	-8.36×10^{-3}	4.68×10^{-5}	-1.59×10^{-7}
Coefficient	a_5	a_6	a_7	a_8	a_9
Value	3.51×10^{-10}	-5.14×10^{-13}	4.79×10^{-16}	-2.55×10^{-19}	5.87×10^{-23}

Fig. 2.14 Calibration curve of furnace display temperature and real temperature



The change of temperature might affect the results of balance. The effects might come from the expansion of metal wire, the mass change of quartz crucible, or the temperature drift of balance itself. To obtain the influence of temperature on balance measurement, a blank test was performed. The blank test was heating the empty crucible at the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in N_2 (1 L min^{-1}). The result is shown in Fig. 2.15. The fluctuation of original signal could be filtered to obtain a smooth signal. According to many tests, the optimal cutoff frequency was 0.00689 Hz .

Fig. 2.15 Mass change of linear ramping blank experiment



When the start mass was zero at room temperature, the mass decreased to -0.008 g at 1000 °C. Considering the sample mass for each test was 1.5 g, the influence of temperature change was 0.53% . The blank result was subtracted for each test to obtain the real result.

To verify the repeatability of Macro-TGA, the repeated tests were performed for slow pyrolysis and fast pyrolysis of lignin. As shown in Fig. 2.16, the repeatability of Macro-TGA experiments was quite good.

2.2.2.4 Influence of Sample Mass and Particle Size

To investigate the influence of sample mass on pyrolysis, fast pyrolysis and slow pyrolysis of PVC were studied, as shown in Fig. 2.17. During the slow pyrolysis, the sample mass (0.5 – 4.5 g) did not affect mass loss process significantly. During the fast pyrolysis, the sample mass affected reaction process significantly. With the

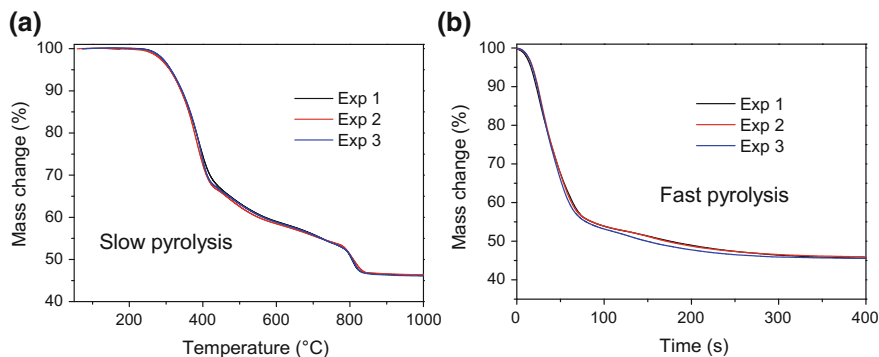


Fig. 2.16 Repeatability of Macro-TGA experiments (example of lignin)

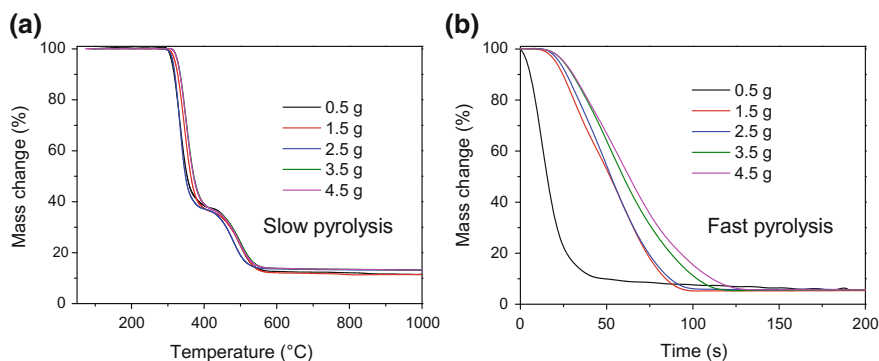


Fig. 2.17 Influence of sample mass on Macro-TGA experiments (example of PVC)

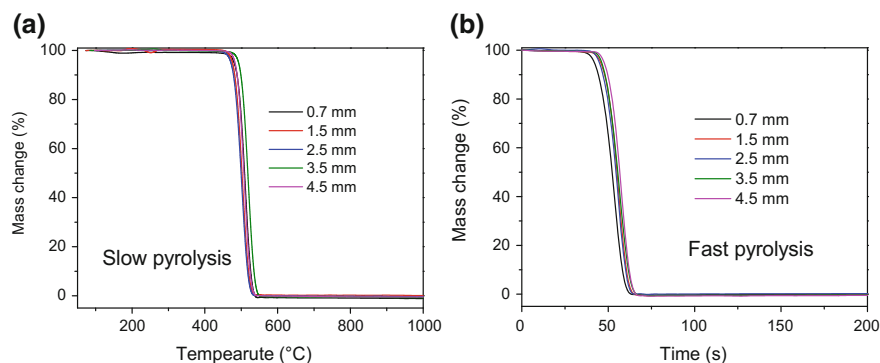


Fig. 2.18 Influence of sample particle size on Macro-TGA experiments (example of PE)

increase of sample mass, the mass loss process was slower and the reaction time was longer, due to the strong heat and mass transfer effect during fast pyrolysis. When the sample mass was 0.5 g, the curve smoothness was poor. Therefore, 1.5 g sample was adopted in the following experiments.

To investigate the influence of particle size on mass loss, the slow pyrolysis and fast pyrolysis of PE of different particle sizes (0.7–4.5 mm) were performed, as shown in Fig. 2.18. The influence of particle size on slow pyrolysis and fast pyrolysis was insignificant, which denoted that the heat and mass transfer effect caused by particle size was not obvious in Macro-TGA experiments.

2.2.3 Horizontal Fixed Bed Reactor (HFBR)

2.2.3.1 Experimental System

The horizontal fixed bed reaction system is shown in Figs. 2.19 and 2.20, including tubular furnace, tar collection system, and gas collection system. The steel reactor

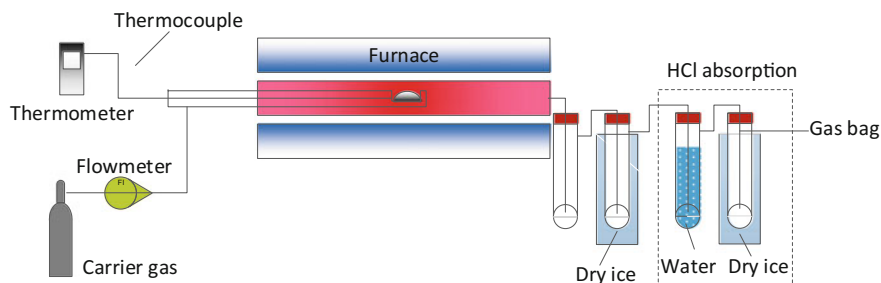


Fig. 2.19 Diagram of horizontal fixed bed reactor. Reprinted from Zhou et al. (2016), Copyright 2016, with permission from Elsevier



Fig. 2.20 Horizontal fixed bed reactor

was 40 cm long, with the diameter 1 cm. The carrier gas flow rate was 100 ml min^{-1} , and the residence time at 800°C was approximately 2.6 s. For fast pyrolysis reaction, the reactor was preheated to setting temperature. When the temperature was stabilized, sample boat with around 1 g sample was inserted into the reactor very fast. The average heating rate of fast pyrolysis was around $350^\circ\text{C min}^{-1}$, which was just a rough average evaluation of heating, since the heating rate for fast pyrolysis was not stable. For slow pyrolysis, the sample was put in the reactor first, and then the furnace was heated up to setting temperature at $10^\circ\text{C min}^{-1}$. The reactor was kept at the final temperature for another 30 min to make sure the reaction was completed.

The products first went through two condensers to collect tar. The first condenser was cooled by air, and the second condenser was cooled by dry ice. Preliminary experiments have shown that these two condensers were good enough to collect the tar. If HCl was produced from the reaction, HCl absorption bottle filled with water and a water collection bottle cooled by dry ice were added between tar collection system and gas collection system. Preliminary experiments have shown the HCl collection effect by water was the same with that by NaOH solution. The non-condensable gases were collected by a TedlarTM gas bag. Gas collection time was 20 min longer than reaction time to make sure the completed collection of gases. After the reaction, product mass balance (recovery rate) was calculated to verify the reliability of the experiment.

2.2.3.2 Gas Analysis

After the non-condensable gases were collected by a gas bag, they were analyzed by GC. H_2 , CO, and N_2 were analyzed by a Varian 3380 GC, with 60–80 mesh molecular sieve column and carrier gas Ar. CO_2 was analyzed by another Varian 3380 GC, with 80–100 mesh molecular sieve column and carrier gas Ar. C_1 – C_4 was analyzed by the third Varian 3380 GC, with flame ionization detector (FID), 80–100 mesh Hysep column, and carrier gas N_2 . According to the concentration of N_2 , together with the known N_2 flow rate and time, the amount of other gases could be calculated.

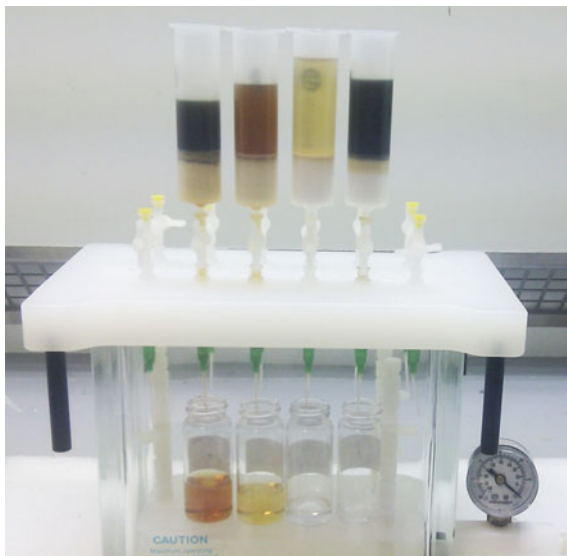
2.2.3.3 Analysis of PAHs

During each experiment, the mass of tar was calculated from the mass difference of condensers and connection tubes before and after the reaction. After that, different solvents were used to wash the condensers to get the aliphatics, aromatics, and oxygenates. Firstly, hexane was used to wash the condensers to collect all the aliphatics and part of aromatics and oxygenates. Secondly, ethyl acetate was used to wash the condensers to collect the rest of the aromatics and oxygenates. The collected tar samples are shown in Fig. 2.21. Thirdly, the water in the tar was removed by filtering through a column with anhydrous sodium sulfate. An EPH column packed with SiO_2 and Al_2O_3 was used to separate aliphatics, aromatics, and oxygenates in hexane. Firstly, the column was rinsed with pure hexane, and then, let tar solution go through the column and use more hexane to wash the column. Therefore, aliphatics would still be in hexane solution, and other compounds would



Fig. 2.21 Collected tar samples

Fig. 2.22 Separation process in EPH column



be captured by EPH column. Other compounds could be washed out by ethyl acetate. The vacuum filtration process was shown in Fig. 2.22.

Finally, PAHs in aromatic fractions were analyzed by a Varian CP-3800 GC coupled with Varian Saturn 2200 MS. The GC column was $30\text{ m} \times 0.25\text{ }\mu\text{m}$. Every time, $2\text{ }\mu\text{l}$ sample was injected. The injection inlet temperature was $290\text{ }^{\circ}\text{C}$. The column temperature program was as follows: stay at $50\text{ }^{\circ}\text{C}$ for 6 min; ramp to $210\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C min}^{-1}$ and stay for 1 min; ramp to $300\text{ }^{\circ}\text{C}$ at $8\text{ }^{\circ}\text{C min}^{-1}$. The total analysis time was 61 min. The transfer line temperature was $280\text{ }^{\circ}\text{C}$; the manifold temperature was $120\text{ }^{\circ}\text{C}$; and the ion trap temperature was $220\text{ }^{\circ}\text{C}$. The ion trap was initially switched off for 7 min to let the solvent flow in before data collection to protect the ion trap. During the measurement, 2-hydroxyacetophenone was used as internal standard (IS). GC/MS was calibrated by Sigma-Aldrich standard sample PAH Mix 3 to obtain quantitative results. During the measurement, ten kinds of 2–4 ring PAHs listed by USEPA with priority were detected, together with two naphthalene derivatives (1-methylnaphthalene and 2-methylnaphthalene). Since benzo [*a*]anthracene and chrysene could not be separated by GC, the concentrations of these two compounds were reported together.

Meanwhile, the molecular weight of tar was measured by size exclusion chromatography (SEC). In SEC test, compounds with high molecular weight came out first (Blanco et al. 2012). The instrument used in this study was Perkin Elmer Modular 225. Tar was first distilled to almost dry, then dissolved in tetrahydrofuran (THF), and kept the concentration around 0.2%. Polymer Laboratories $5\text{ }\mu\text{m}$ separation column was adopted in this study, and PS with molecular weight 800–860 000 g mol^{-1} , benzene, and PAHs were used for calibration. The detector was Perkin Elmer Series 200a refractive index detector.

2.3 Kinetic Analysis Method

The kinetics of pyrolysis means the mass loss properties for a pyrolytic reaction. Basic kinetic studies can help us to predict the pyrolytic behavior and then design better pyrolytic reactor (Cho et al. 2012; Zhang et al. 2014). Many studies have chosen DTG curves to investigate the kinetics, since DTG curves are more convenient for the kinetic calculation. In addition, DTG curves are more sensitive than TG curves, which means the tiny change in TG curves will be magnified in corresponding DTG curves (Caballero and Conesa 2005; Budrugaec 2002).

2.3.1 Kinetic Analysis Method of Slow Pyrolysis

The pyrolytic processes of many samples are complicated and cannot be denoted by a single kinetic reaction. In the paralleled reaction kinetic model, pyrolysis can be regarded as the superposition of a series of independent reactions (Manya et al. 2003).

$$\frac{dm}{d\tau} = \sum_{i=1}^n \frac{dm_i}{d\tau} \quad (2.4)$$

In Eq. (2.4), m denotes the sample conversion at time τ , with the unit %.

To obtain normalized results, α_i was used to denote the normalized conversion rate of Reaction i , i.e.,

$$\alpha_i = m_i / m_{i\infty} \quad (2.5)$$

In Eq. (2.5), $m_{i\infty}$ denotes the final conversion rate of Reaction i . Therefore, we know that $\alpha_{i\infty} = 100\%$.

Since DTG curves of slow pyrolysis may have multiple peaks, supposing that each peak (including shoulder peak) represents a reaction, peak analysis method could be used to divide the overall reaction into several single peak reactions. The reaction of each peak can be described by Gaussian peak, which is the most commonly used peak shape for peak analysis (Guo 2011).

The kinetics of each reaction can be expressed by (Coats and Redfern 1964)

$$\frac{d\alpha_i}{d\tau} = k_i(1 - \alpha_i)^{n_i} \quad (2.6)$$

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \quad (2.7)$$

Here, k_i denotes the reaction rate of Reaction i ; E_i denotes the apparent activation energy (kJ mol^{-1}); A_i denotes pre-exponential factor (min^{-1}); n_i is reaction order; R is universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$); T is absolute temperature (K).

In slow pyrolytic experiments, heating rate β is constant,

$$\beta = \frac{dT}{d\tau} \quad (2.8)$$

Therefore,

$$\frac{d\alpha_i}{dT} = \frac{A_i}{\beta} \exp\left(-\frac{E_i}{RT}\right) (1 - \alpha_i)^{n_i} \quad (2.9)$$

To calculate E_i , A_i , and n_i , least square method (LSM) was used.

$$S = \sum_{j=1}^N \left[\left(\frac{d\alpha}{dT} \right)_j^{\text{exp}} - \left(\frac{d\alpha}{dT} \right)_j^{\text{cal}} \right]^2 \quad (2.10)$$

In Eq. (2.10), N denotes points of data; $(d\alpha/dT)_{\text{exp}}$ denotes experimental value; $(d\alpha/dT)_{\text{cal}}$ denotes calculation value. Average deviation index (*ADI*) was used to evaluate the accuracy of the calculation results:

$$\text{ADI} = \frac{\sqrt{S/N}}{(d\alpha_i/dT)_{\text{max}}^{\text{exp}}} \times 100\% \quad (2.11)$$

In Eq. (2.11), $(d\alpha_i/dT)_{\text{max}}^{\text{exp}}$ denotes the maximum of experimental value.

2.3.2 Kinetic Analysis Method of Fast Pyrolysis

Since fast pyrolysis usually ends in a short time, many peaks in slow pyrolysis may be combined for fast pyrolysis, but peak analysis method could still be applied. For fast pyrolysis, Avrami-Erofeev Equation was widely used (Hancock and Sharp 1972; Go et al. 2008). Each peak can be described as

$$1 - \alpha_i = \exp(-k_i \tau^{n_i}) \quad (2.12)$$

In Eq. (2.12), k_i and n_i are determined by experiments, and τ denotes time. Taking the natural logarithm of Eq. (2.12),

$$\ln(1 - \alpha_i) = -k_i \tau^{n_i} \quad (2.13)$$

Therefore, LSM can still be used to obtain the optimal k_i and n_i .

The advantage of peak analysis-least square method (PA-LSM) is that DTG curves can be divided into paralleled reactions according to the peaks, which is more direct and has clear physical significance. LSM can help to find the optimal kinetic parameters more accurately, and avoid the errors from the assumption in integral method and differential method.

2.4 Summary

This chapter is the introduction of research methods, including three parts, selection of research objects, experimental apparatus, and kinetic analysis methods.

- (1) Based on the statistical analysis of CSW in China, nine basic components (hemicellulose, cellulose, lignin, pectin, starch, PE, PS, PVC, and PET) were selected. The characteristics of basic components were analyzed, including proximate analyses, ultimate analyses, heating values, and functional groups in solid FTIR.
- (2) Three experimental platforms were introduced: TGA, Macro-TGA, and horizontal fixed bed reactor. The latter two reactors were self-designed. Macro-TGA realized the online mass measurement of the thermochemical reaction of gram level sample, which could be applied to both fast reaction and slow reaction with good repeatability and reliability. PAHs from a horizontal fixed bed reactor were collected and analyzed. The PAHs in tar could be collected by a two-stage condenser system. In addition, aliphatics, aromatics, and oxygenates were separated for the better measurement of PAHs. The GC/MS was calibrated to obtain the quantitative results.
- (3) Based on parallel reaction model, peak analysis method was used to separate the paralleled reactions. Complex thermochemical reactions could be divided into several paralleled reactions, and then the kinetic parameters were determined by least square method.

This chapter introduced the selection method of basic components and fundamental characteristics (proximate analyses, ultimate analyses, heating values, and functional groups), experimental platforms (TGA, Macro-TGA, and horizontal fixed bed reactor), and kinetic analysis method (PA-LSM). This chapter is the foundation of the following research.

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