

Influence of mineral matter on pyrolysis of palm oil wastes

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Received 21 September 2005; received in revised form 15 June 2006; accepted 5 July 2006

Available online 7 August 2006

Abstract

The influence of mineral matter on pyrolysis of biomass (including pure biomass components, synthesized biomass, and natural biomass) was investigated using a thermogravimetric analyzer (TGA). First, the mineral matter, KCl, K₂CO₃, Na₂CO₃, CaMg(CO₃)₂, Fe₂O₃, and Al₂O₃, was mixed respectively with the three main biomass components (hemicellulose, cellulose, and lignin) at a weight ratio (C/W) of 0.1 and its pyrolysis characteristics were investigated. Most of these mineral additives, except for K₂CO₃, demonstrated negligible influence. Adding K₂CO₃ inhibited the pyrolysis of hemicellulose by lowering its mass loss rate by 0.3 wt%/°C, while it enhanced the pyrolysis of cellulose by shifting the pyrolysis to a lower temperature. With increased K₂CO₃ added, the weight loss of cellulose in the lower temperature zone (200–315 °C) increased greatly and the activation energies of hemicellulose and cellulose pyrolysis decreased notably from 204 to 42 kJ/mol. Second, studies on the synthetic biomass of hemicellulose, cellulose, lignin, and K₂CO₃ (as a representative of minerals) indicated that peaks of cellulose and hemicellulose pyrolysis became overlapped with addition of K₂CO₃ (at C/W = 0.05–0.1), due to the catalytic effect of K₂CO₃ lowering cellulose pyrolysis to a lower temperature. Finally, a local representative biomass—palm oil waste (in the forms of original material and material pretreated through water washing or K₂CO₃ addition)—was studied. Water washing shifted pyrolysis of palm oil waste to a higher temperature by 20 °C, while K₂CO₃ addition lowered the peak temperature of pyrolysis by ~50 °C. It was therefore concluded that the obvious catalytic effect of adding K₂CO₃ might be attributed to certain fundamental changes in terms of chemical structure of hemicellulose or decomposition steps of cellulose in the course of pyrolysis.

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Keywords: Biomass components; Thermogravimetric analysis; Pyrolysis; Mineral matter

1. Introduction

From the chemical point of view, biomass can be regarded as a mixture of three components (cellulose, hemicellulose, lignin) and trace amounts of mineral matter [1], and the pyrolytic behavior of biomass can be considered as a sum of the three compo-

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Table 1

XRF analysis of palm oil wastes ash (on dry ash basis wt%)

Sample	SiO ₂	K ₂ O	MgO	CaO	Al ₂ O ₃	P ₂ O ₅	Fe ₂ O ₃	SO ₃	Cl	Na ₂ O
Shell	58.8	10.9	5.0	2.1	6.1	5.7	6.7	2.4	0.2	1.7
Fiber	61.3	12.6	7.1	4.0	4.0	4.0	2.6	3.6	0.3	0.2
EFB	24.6	37.2	5.8	6.5	1.1	6.9	2.1	4.8	10.2	0.1

nents [2,3]. In our previous work [4–6], the pyrolysis of palm oil wastes and the three components was investigated thoroughly. It was found that the whole process of biomass pyrolysis can be divided into the following four ranges: <220 °C, moisture evolution; 220–315 °C, predominantly hemicellulose decomposition; 315–400 °C, cellulose decomposition; >400 °C, lignin decomposition. There is no significant interaction among the three components in pyrolysis. The behavior of natural biomass (palm oil wastes) was different from that of synthesized biomass based on the three main components; the activation energy of the former is much less than that of the latter, which might be attributed to the catalytic effect of mineral matter that occurs in the natural biomass [7,8]. Therefore, an investigation of the influence of mineral matter on biomass pyrolysis is beneficial.

In general, the concentrations of mineral matter range from less than 1% in softwoods to ~15% in herbaceous biomass and agriculture residues [9]. The main elemental constituents of biomass minerals are Al, Ca, Fe, K, Mg, Na, and Si, together with trace amounts of S, P, Cl, and Mn. They occur as oxides, silicates, carbonates, sulfates, chlorides, and phosphates in biomass [10]. Previous researches [7,11–15] have revealed the catalytic effect of mineral matter on biomass pyrolysis through various methods, such as demineralization (water washing or acid washing) and mineral addition in biomass. It was found that certain minerals (such as Ca, K, Na, Mg, and Fe) exert a significant catalytic effect, and even a small amount of them is sufficient to alter pyrolysis behavior to a large extent. So far, most of the previous studies have focused on the influence of mineral matter on product yields; few were found to understand the catalytic behavior of minerals in pyrolysis involving a natural biomass.

In this work, the pyrolysis of palm oil wastes was investigated with a focus on the influence of minerals, after a thorough study of the pyrolysis of three main components (hemicellulose, cellulose, and lignin) with addition of individual minerals (KCl, K₂CO₃, Na₂CO₃, CaMg(CO₃)₂, Fe₂O₃, Al₂O₃) at different levels. A further study of synthesized biomass based on the three main components and one representative of minerals—Na₂CO₃—was also taken into account. The information obtained allows identifying the min-

eral that plays a key role in catalyzing the biomass pyrolysis.

2. Materials and experimental methods

2.1. Materials

Three biomass components (cellulose, hemicellulose, and lignin), used as pure biomass samples, were purchased from Sigma–Aldrich Chemie GmbH. Three palm oil wastes, shell, fiber, and empty fruit bunches (EFB), were obtained from Malaysia. Detailed information on biomass samples can be found in our previous work [4,6]. The analysis of a palm oil waste ash component was carried out using X-ray fluorescence spectroscopy (XRF) and the results are listed in Table 1 on an oxides basis. The main inorganic elements in the three palm oil wastes are Si, K, Mg, Ca, Al, P, S, and Fe, in general, while EFB has extremely high chlorine content. There also exist some trace elements (not shown in Table 1), such as Zr, Ti, Mn, Zn, Cu, Rb, Sr, Br, Cr, and Tb, with concentrations less than 0.1% of the dry ash.

2.2. Biomass sample pretreatment methods

2.2.1. Demineralization (water washing)

To remove soluble mineral matter, palm oil wastes were washed using deionized (DI) water. One gram of biomass sample was immersed in 200 ml DI water while stirred for 20 h at room temperature. After being filtered and recleaned with 300 ml DI water, the sample was dried in ambient air to a constant weight [15].

2.2.2. Adding minerals

According to the ash analysis of palm oil wastes (see Table 1) and the literature [10,14,16], several mineral additives including KCl, K₂CO₃, Na₂CO₃, CaMg(CO₃)₂, Fe₂O₃, and Al₂O₃ were chosen in this study to directly dry-mix with the three components. The weight ratio of additive to biomass (C/W) is kept at 0.1. Silicon (Si), although it has the highest concentration in ash (for shell and fiber), was ignored, as negligible catalytic effect of Si was observed in biomass pyrolysis [3]. Synthesized biomass samples were also prepared by mixing the three components (cellulose,

hemicellulose, lignin) in desired proportions according to a {3, 4} simplex lattice [6]. Concentrations of K_2CO_3 , as one representative of additives, were varied at $C/W = 0, 0.01, 0.05, 0.1$, in mixing with the synthesized biomass.

2.3. Equipment and procedure

Pyrolysis of biomass samples was carried out using a thermogravimetric analyzer (TGA 2050, TA, USA). First, the sample was heated up to 150°C from the ambient temperature at $10^\circ\text{C}/\text{min}$ and kept isothermal for 5 min to remove moisture. Then it was continuously heated up to 900°C at $10^\circ\text{C}/\text{min}$ and kept for 3 min to complete the pyrolysis. Sample size was maintained at ~ 20 mg for every trial and the flow rate of carrier gas (N_2) was set at 120 ml/min. To make sure of the reproducibility and accuracy of analysis, duplicates of the sample were tested for each trial. The deviation is generally at 2–3%, among the experimental results available.

3. Results and discussion

3.1. Influence of minerals on pyrolysis of biomass components

The DTG curves (mass loss rate) of three biomass components with and without the addition of minerals (KCl, K_2CO_3 , Na_2CO_3 , $CaMg(CO_3)_2$, Fe_2O_3 , or Al_2O_3) are plotted in Figs. 1–3. From Fig. 1, it can be observed that dolomite, Al_2O_3 , KCl, and Fe_2O_3 did not display obvious effects on hemicellulose pyrolysis, except slightly lowering the peak value of mass loss rate. However, the addition of Na_2CO_3 and K_2CO_3 demonstrated significant influences. Adding Na_2CO_3 shifted the peak of mass loss rate to a higher temperature (from 260 to 280°C) and lowered the

peak value. With the addition of K_2CO_3 , the DTG curve showed two overlapping peaks, a shoulder peak at 240°C and the maximum peak at 280°C , but with a peak value lowered by $0.3 \text{ wt}\% / ^\circ\text{C}$. Furthermore, the DTG curve of K_2CO_3 alone (not shown here) indicates that it is quite stable at temperatures less than 800°C , with only a slight weight loss observed (4% of K_2CO_3 weight at temperatures $< 200^\circ\text{C}$) due to the removal of moisture. Therefore, the DTG peaks observed are attributed only to the decomposition of organic matter of biomass (hemicellulose in this case). All the added minerals are assumed to have negligible contribution to the weight loss occurring in the studied temperature range ($< 500^\circ\text{C}$).

The obvious influence of adding carbonates (Na_2CO_3 and K_2CO_3) on hemicellulose pyrolysis might be attributed to a different chemical decomposition mechanism, since pure physical addition (like other additives) will only have insignificant effects. Being enriched in branches of chain molecules, hemicellulose generally has a random, amorphous structure with little strength; it can be easily broken and converted to light gases at low temperature. It is as-

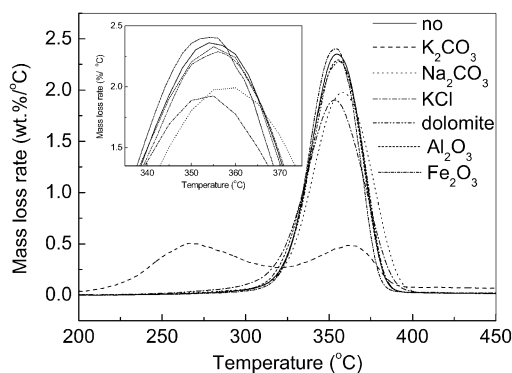


Fig. 2. DTG curves of cellulose pyrolysis with mineral additives ($C/W = 0.1$).

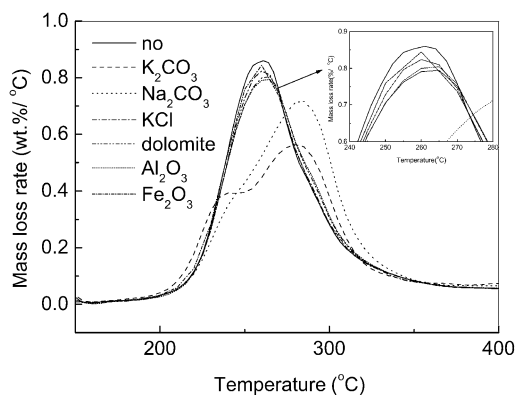


Fig. 1. DTG curves of hemicellulose pyrolysis with mineral additives ($C/W = 0.1$).

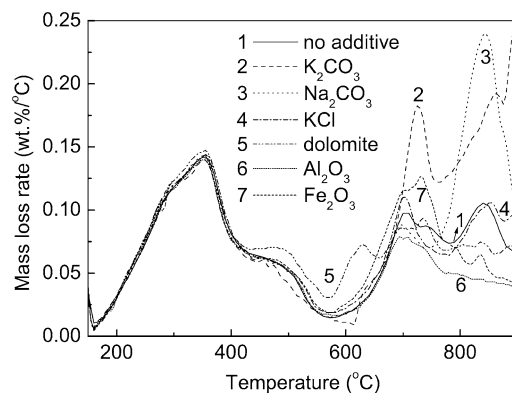


Fig. 3. DTG curves of lignin pyrolysis with mineral additives ($C/W = 0.1$).

Table 2

Char yields of biomass pyrolysis with and without additives (wt%)

Sample	Without	K ₂ CO ₃	KCl	Na ₂ CO ₃	Dolomite	Al ₂ O ₃	Fe ₂ O ₃
Hemicellulose	32.7	39.3	37.9	39.9	37.4	37.8	37.3
Cellulose	6.6	32.1	11.5	18.4	15.7	16.9	14.3
Lignin	37.3	23.7	41.5	33.9	42.2	48.7	43.0

sumed that the chemical and/or physical structure of hemicellulose changed with the addition of K₂CO₃ or Na₂CO₃. However, further investigation is needed to understand it.

In Fig. 2, the addition of dolomite, Al₂O₃, and Fe₂O₃ demonstrated negligible influence on pyrolysis of cellulose, similarly to the case of hemicellulose. Nevertheless, the addition of KCl and Na₂CO₃ decreased the peak value (mass loss rate) of cellulose pyrolysis from 2.3 to 1.8 wt%/°C. A big change happened with the addition of K₂CO₃: two small peaks were observed at 260 °C and 370 °C, respectively. At temperature <320 °C, the mass loss rate of cellulose with addition of K₂CO₃ is obviously higher than those in other cases (cellulose itself and together with other additives). Because of the stable presence of K₂CO₃, most of the weight loss occurring at the first peak (260 °C) in Fig. 2 should be attributed to the partial degradation of cellulose at lower temperatures with the help of K₂CO₃. When the temperature is higher than 320 °C, the mass loss rate of cellulose with addition of K₂CO₃ is much smaller than with other additives. Most likely, adding K₂CO₃ shifts the cellulose degradation to a lower temperature. Similar observation was found in the previous study of influence of NaCl and FeSO₄ on biomass pyrolysis [8].

The addition of K₂CO₃ caused different influence on pyrolysis of hemicellulose and cellulose, inhibiting the former with its peak shifted to a higher temperature and at a lower mass loss rate but enhancing the latter with its peak shifted to a lower temperature. Differently from hemicellulose, cellulose has a highly ordered crystalline structure without branches; its thermal stability and pyrolysis temperature are much higher than those of hemicellulose. Pyrolysis of cellulose generally proceeds in two steps: (1) convert to active cellulose with decreased crystallinity at lower temperature; (2) decomposition to gas, liquid oil, and solid charcoal at higher temperature [17, 18]. With the addition of K₂CO₃, cellulose pyrolysis mostly happened at lower temperatures, which might indicate the elimination of the first step due to the presence of K₂CO₃.

In Fig. 3, the addition of minerals did not show obvious influence on lignin pyrolysis at temperatures <450 °C. Their DTG curves are parallel to each other. However, with temperature increasing further, dolomite showed catalytic effects on lignin pyrolysis

at 450–700 °C and Fe₂O₃ enhanced biomass pyrolysis at 500–800 °C. The pyrolysis of lignin seems accelerated notably with addition of K₂CO₃ and Na₂CO₃ at temperatures higher than, respectively, 700 and 800 °C. However, it might also be attributed to the partial evaporation of the inorganic salt. As mentioned previously, the weight loss of natural biomass samples happens mostly at temperatures lower than 500 °C [4] and therefore the studied temperature range is selected at <500 °C for the following work. The influence of mineral matters on lignin pyrolysis is thus omitted.

The contents of char generated from pyrolysis of biomass with different additives were measured and the results are listed in Table 2 (mineral additions were subtracted). The residues from pyrolysis of hemicellulose and cellulose at 390 °C were recorded as their char yields, since no significant weight loss happened with temperature increasing further to 900 °C. For lignin the temperature was selected as 900 °C to complete pyrolysis. The addition of mineral matter highly increased the char yields from the pyrolysis of hemicellulose, cellulose, and lignin, except for the addition of K₂CO₃ and Na₂CO₃ to lignin. Similar observations were reported in a previous study with cellulose as biomass sample [7].

To investigate in depth the influence of K₂CO₃ on pyrolysis of cellulose and hemicellulose, adding K₂CO₃ into biomass at different ratios (C/W = 0, 0.01, 0.05, 0.1), was carried out. With the addition of only 1% K₂CO₃ (C/W = 0.01), the rate of hemicellulose pyrolysis is lowered greatly (from 0.86 to 0.70 wt%/°C) compared to the case of hemicellulose alone, and the peak was shifted from 261 to 283 °C. When the weight ratio (C/W) of K₂CO₃ increased from 0.01 to 0.1, the rate of hemicellulose decomposition decreased further, and the pattern of DTG curves changed gradually from one peak to two overlapped peaks (a shoulder peak comes out earlier than the main peak), indicating a possible change of pyrolysis mechanism. In the case of cellulose, when C/W is less than 0.05, the mass loss rate of cellulose in the low-temperature range (<315 °C) is very low (<0.1 wt%/°C). However, when the ratio increased to 0.1, the mass loss rate of cellulose in the low-temperature range (<315 °C) increased sharply to 0.59 wt%/°C with almost more than half of its weight loss happened at the lower temperature range.

Table 3

Kinetics properties of hemicellulose and cellulose pyrolysis with addition of K₂CO₃

	C/W (wt%)	Temperature range (°C)	Weight loss (wt%)	E_a (kJ/mol)	A (s ⁻¹)	R^*	E_m (kJ/mol)
Hemicellulose and K ₂ CO ₃	0	220–315	53.8	55.7	7.5E+01	0.99	55.7
	1	220–315	51.4	50.1	1.1E+01	0.99	50.1
	5	220–315	48.6	48.2	6.6E+00	0.99	48.2
	10	220–315	50.0	39.8	1.1E+00	0.99	39.8
Cellulose and K ₂ CO ₃	0	220–315	0	–	–	–	204.1
		315–390	86.7	204.1	4.9E+13	1	
	1	220–315	5.8	12.0	7.0E–05	0.96	139.1
		315–390	75.2	148.9	8.8E+08	0.99	
	5	220–315	13.2	20.7	1.6E–03	0.99	82.6
		315–390	54.9	103.1	1.3E+05	0.98	
	10	220–315	29.7	33.1	1.1E–01	0.99	42.7
		315–390	23.3	54.9	3.4E+02	0.92	

Note. R^* : correlation coefficient; –: nil.

The curve of mass loss rate showed two separated peaks with a cross point at ~315 °C.

The kinetic calculations were carried out, based on assuming a first-order reaction in the whole temperature range (220–390 °C) of hemicellulose and cellulose pyrolysis in the presence of K₂CO₃. The calculation equation is listed as

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = -(E_a/RT) + \ln(AR/\beta E_a), \quad (1)$$

where α is degree of conversion, β is heating rate, T is temperature, and E and A represent the activation energy and the preexponential factor, respectively. R is the general gas constant. E_m is the weight mean activation energy and was used to analyze the sample reactivity as a whole,

$$E_m = F_1 \times E_{a1} + F_2 \times E_{a2} + \cdots + F_n \times E_{an}, \quad (2)$$

where E_{a1} to E_{an} is the activation energy of every stage, and F_1 to F_n is the relative weight loss amount. The details of calculation were given in our previous report [4]. The calculation results are listed in Table 3. The weight loss content of hemicellulose at 220–315 °C has no significant change with the addition of K₂CO₃. For the case of cellulose, with the increase of K₂CO₃ addition from 0.01 to 0.1, an increase of weight loss occurring in the low-temperature range (220–315 °C) from 5.8 to 29.7% was observed, while in the high-temperature range (315–390 °C), it was decreased from 75.2 to 23.3%. The total weight loss from the two ranges also decreased, compared to the case of cellulose alone (86.7%); i.e., the residues of cellulose pyrolysis increased with the increasing addition of K₂CO₃. This is consistent with our previous observation in Table 2. In terms of the kinetic parameters, the activation energy (E_a) of hemicellulose decreases with the increasing addition of K₂CO₃.

For cellulose, E_a of the higher temperature range decreased greatly, but at lower temperatures the activation energy of cellulose increased slightly (from 12 to 33 kJ/mol). The overall activation energies (E_m) of cellulose pyrolysis with the addition of K₂CO₃ at three ratios are much smaller than that of cellulose alone; this also interprets the previous observation that thermal decomposition of natural lignocellulosic biomass is faster than that of pure cellulose and hemicellulose, and E_a is much smaller than that of pure cellulose and hemicellulose [4], which can be attributed potentially to the catalytic effect of mineral matter occurring in natural biomass [4,8]. Meanwhile, decreasing E_a partially confirmed our previous assumption that the chemical structure of biomass changed due to the addition of K₂CO₃.

3.2. Pyrolysis of synthetic biomass samples

The synthetic biomass samples were prepared by dry mixing the three components with weight ratios of hemicellulose, cellulose, and lignin (X:C:L) at 1:1:2, 1:2:1, and 2:1:1 [6], respectively. The ratio (C/W) of K₂CO₃ addition is 0.1. The pyrolysis curves of the synthetic biomass samples with and without the presence of K₂CO₃ are plotted in Fig. 4. It can be observed that without K₂CO₃, the DTG curves of the synthesized biomass (indicated by solid symbols) showed two separated peaks, one caused mainly by hemicellulose decomposition (220–315 °C) and another caused by cellulose degradation (315–390 °C) (see Figs. 1 and 2). However, with the presence of K₂CO₃, the DTG curves of the synthesized biomass (indicated by blank symbols) changed significantly. The second peak was diminished and the first peak was enlarged greatly. Most likely, the pyrolysis of cellulose was moved to a lower temperature under the catalytic effect of K₂CO₃, and combined together

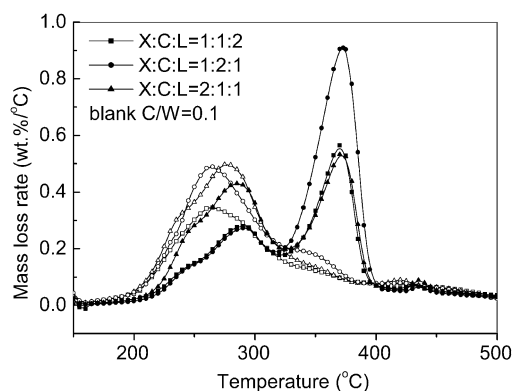


Fig. 4. DTG curves of synthetic biomass sample with/without K_2CO_3 ($C/W = 0.1$).

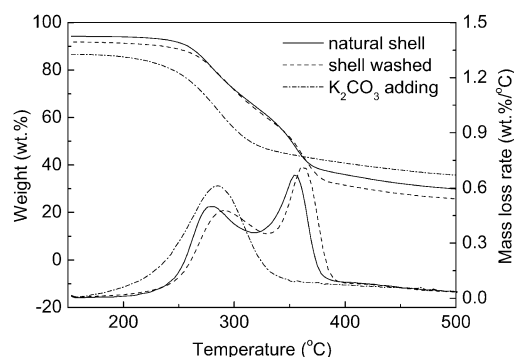


Fig. 5. Influence of pretreatment technologies on shell pyrolysis.

with hemicellulose pyrolysis. This result testified the previous assumption that the peak of cellulose pyrolysis overlapped with that of hemicellulose, with catalyst addition [8].

3.3. Influence of minerals on pyrolysis of palm oil wastes

Three palm oil wastes were pretreated in two ways: water washing and adding K_2CO_3 ($C/W = 0.1$). The typical pyrolysis curves of pretreated and original shell are plotted in Fig. 5. From the TGA curve, it can be observed that the amount of residues (i.e., solid charcoal) decreased with washing, but significantly increased with addition of K_2CO_3 , similarly to the cases of hemicellulose and cellulose, where adding minerals increased the char yield in general (Table 2). From DTG curves, water washing shifted the peak of pyrolysis of all three wastes to a higher temperature by 10–50 °C. For EFB and fiber, similar results were displayed. The DTG curve of washed EFB changed from one peak of the original to two overlapped peaks. This might be attributed to the shifting of cellulose decomposition back to a

higher temperature due to the removal of minerals by washing and, therefore, the pyrolysis of cellulose and hemicellulose was separated partially [8]. On the other hand, with addition of K_2CO_3 , the peak temperature of palm oil wastes pyrolysis (DTG curves) was lowered by 10–50 °C and the mass loss rate at lower temperatures was increased, compared to the original. With the presence of K_2CO_3 , only one peak was observed for shell pyrolysis, while for fiber, the two peaks of the original fiber became overlapped and the shape of EFB remains similar to its original as one peak is observed.

It was well known that biomass pyrolysis can be represented as a simple superposition of the behavior of its three components [2,3]. The two peaks of DTG curves observed in biomass pyrolysis are usually caused by separated decompositions of hemicellulose (200–315 °C) and cellulose (315–400 °C) [6]. With the addition of K_2CO_3 , pyrolysis of cellulose could be shifted to a lower temperature region, thus overlapped with hemicellulose pyrolysis. In contrast, with washing of the original biomass sample (such as EFB), the pyrolysis curve changed from one peak of the original to two overlapping peaks, attributed to the shifting of cellulose decomposition back to a higher temperature due to the removal of minerals by washing, and therefore, the pyrolysis of cellulose and hemicellulose was separated partially without the presence of certain minerals. Therefore, the catalytic effect of minerals is most likely attributable to shifting the pyrolysis of cellulose in biomass to a lower temperature.

4. Conclusions

The influence of mineral matter on biomass pyrolysis was investigated systematically. It was found that the dry addition of KCl , Na_2CO_3 , $CaMg(CO_3)_2$, Fe_2O_3 , or Al_2O_3 did not exert a significant influence on thermal degradation of pure components (cellulose, hemicellulose and lignin). The addition of K_2CO_3 inhibited the pyrolysis of hemicellulose but enhanced that of cellulose greatly by shifting its peak to a lower temperature. Consequently, for the synthetic biomass sample containing hemicellulose and cellulose, their DTG peaks of pyrolysis were overlapped in the presence of 0.1 K_2CO_3 . Pretreatment (water washing and K_2CO_3 addition) exerted a marked influence on pyrolysis of palm oil wastes, in terms of both pyrolysis temperature and gas product distributions. Washing might account for the shifting of cellulose decomposition back to a higher temperature due to the removal of minerals, while adding K_2CO_3 lowered the pyrolysis temperature of cellulose and overlapped with that of hemicellulose; thus

only one peak was observed for the pyrolysis of three palm oil wastes with addition of K_2CO_3 . It is reasonably assumed that the important influence of adding K_2CO_3 on biomass pyrolysis is attributable to certain fundamental changes in terms of chemical structure of hemicellulose or decomposition steps of cellulose, as pure physical addition (like other additives) will have only insignificant effects. The activation energies of cellulose and hemicellulose pyrolysis decreased with the addition of K_2CO_3 , which partially confirmed this assumption.

References

- [1] P. McKendry, *Bioresour. Technol.* 83 (2002) 37–46.
- [2] T.R. Rao, A. Sharma, *Energy* 23 (1998) 973–978.
- [3] K. Raveendran, A. Ganesh, K.C. Khilar, *Fuel* 75 (1996) 987–998.
- [4] H.P. Yang, R. Yan, T. Chin, D.T. Liang, H.P. Chen, C.G. Zheng, *Energy Fuels* 18 (2004) 1814–1821.
- [5] R. Yan, H.P. Yang, T. Chin, D.T. Liang, H.P. Chen, C.G. Zheng, *Combust. Flame* 142 (2005) 24–32.
- [6] H.P. Yang, R. Yan, H.P. Chen, C.G. Zheng, D.H. Lee, D.T. Liang, *Energy Fuels* 20 (2006) 388–393.
- [7] P.T. Williams, P.A. Horne, *Renewable Energy* 4 (1994) 1–13.
- [8] G. Varhegyi, J.J.M. Antal, E. Jakab, P. Szabo, *J. Anal. Appl. Pyrol.* 42 (1997) 73–87.
- [9] S. Yaman, *Energy Conversion Manage.* 45 (2004) 651–671.
- [10] M. Zevenhoven-Onderwater, R. Backman, B.-J. Skrifvars, M. Hupa, *Fuel* 80 (2001) 1489–1502.
- [11] G. Löffler, V.J. Wargadalam, F. Winter, *Fuel* 81 (2002) 711–717.
- [12] F.A. Agblevor, S. Besler, *Energy Fuels* 10 (1996) 293–298.
- [13] C.D. Blasi, C. Branca, G.D. Errico, *Thermochim. Acta* 364 (2000) 133–142.
- [14] K. Raveendran, A.K. Ganesh, C. Khilar, *Fuel* 74 (1995) 1812–1822.
- [15] P. Szabo, G. Varhegyi, F. Till, O. Faix, *J. Anal. Appl. Pyrol.* 36 (1996) 179–190.
- [16] D. Sutton, B. Kelleher, J.R.H. Ross, *Fuel Process. Technol.* 73 (2001) 155–173.
- [17] J.P. Diebold, A. Unified, *Biomass Bioenergy* 7 (1994) 69–74.
- [18] A.W. Bradbury, Y. Sakai, F. Shafizadeh, *J. Appl. Polym. Sci.* 23 (1979) 3271–3280.