Original Article

Product yields and characteristics of rice husk, rice straw and corncob during fast pyrolysis in a drop-tube/fixed-bed reactor

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Abstract

Fast pyrolysis of rice husk, rice straw and corncob were investigated in a newly constructed drop-tube/fixed-bed reactor, which enables pyrolysis experiments under conditions closely simulating those occurring in commercial gasifiers such as fluidised-bed gasifiers. Biomass samples were pyrolysed with a fast heating rate (i.e. > 1,000°C s^{-1}), up to 850°C and holding times ranging from 1 to 10,800 seconds. Within 1 second after the biomass was injected into the reactor, considerable weight loss occurred instantaneously, leaving only a small amount of char, i.e. ~10-30 %. For all three samples, the weight loss continued throughout the range of holding times used but at an extremely slow rate, i.e. 1.3 % hr^{-1}. The weight loss rates observed for the three biomass samples were affected by the proportion of the biomass chemical components as well as the metal species contents. Corncob, which had the lowest lignin content but highest cellulose content, had the highest pyrolysis weight loss rate. On the other hand, rice husk containing a relatively high lignin content, had the lowest pyrolysis rate. The metal species (Na, K, Ca and Mg) were found to increase devolatilisation yield depending on their contents in biomass. The influence of the metal species was the most pronounced for rice straw, having the highest total metal species content. As the pyrolysis progressed, each biomass exhibited different char characteristics. Scanning electron microscopy (SEM) pictures clearly showed the individual changes in geometry for all biomass-derived chars as well as their decrease in combustion reactivities. The gas formation profiles for all three biomass samples showed almost the same trend, with CO contributed by cellulose decomposition as the major gas product.

Keywords: fast pyrolysis, biomass, drop-tube/fixed-bed reactor, char, metal species

1. Introduction

Due to environmental concerns over excessive fossil fuel usage, biomass has increasingly become of interest as a promising renewable energy source to mitigate global warming (Rosillo-Calle *et al.*, 2000). In Thailand, well-recognized as one of the first rank exporters of agricultural and food products, biomass, including abundant by-products from agricultural process industries as well as residues from post harvest such as bagasse, corncob, coconut shell, etc., is largely available for use as alternative energy source (Utistham *et al.*, 2007). Particularly, three agricultural residues including rice husk, rice straw and corncob are statistically shown to have high resource potential in Thailand. Another study by Thailand Research Fund (2007) reported similar results in terms of annual production; the estimated maximum production of rice husk, rice straw and corncob were 6.2, 32.2 and 1.8 million tonnes per year, respectively. However, the potential of un-utilised rice husk and corncob at the national level was reported to be rather low due to extensive utilisation for both energy and non-energy purposes. On the other hand, as much as 12.9 million tonnes per year of rice straw remain un-utilized. Despite these findings, it is believed that rice husk and corncob still have potential at the local level for small-scale or decentralized systems.

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Various thermo-chemical processes have been developed and implemented worldwide. While direct combustion of biomass has widely been used for household and industrial purposes, biomass gasification is becoming an attractive conversion technology. The product gas from gasification can be used for various purposes, including fuel for direct combustion to produce heat, for use in gas engines or gas turbines, and to produce electricity. The product gas with high quality can be used as an intermediate for other value-added chemical syntheses such as synthetic diesel (via Fischer-Tropsch process), etc (Rosillo-Calle *et al.*, 2000). However, to date, only the production of heat in large scale applications and the production of electricity for small scale applications are seen in real practice, although biomass gasification has been studied for decades. Therefore, developments for more effective and reduced cost technologies (compared to fossil fuel technologies) as well as for advanced technologies like biomass-to-liquid (BTL) are still a challenge.

Similar to other thermal conversion processes, the initial step of gasification is pyrolysis, during which the volatiles are released leaving the solid char. In the presence of reactive agents, the volatiles and char are further reacted and converted into the final products. Not only the weight losses due to pyrolysis can reach as high as 70 % of the total weight loss of solid fuels during the entire gasification process, operational conditions during the pyrolysis step in which char is formed also have significant effects on the char characteristics and hence the reaction rate of char in the subsequent gasification step. Since the gasification rate of char is much slower compared to the pyrolysis rate, it determines the overall gasification rate. Therefore, studying the influence of pyrolysis parameters on the char yield as well as the reactivity and morphology of the recovered chars is necessary to explain the reaction behaviour and to predict the fate of char undergoing the gasification step.

Several investigations on biomass pyrolysis have been carried out using various apparatuses. Fixed-bed reactors and thermogravimetric analyzers (TGA) have been widely used (Caballero *et al.*, 1997; Cao *et al.*, 2004; Gani and Naruse, 2007; Pütün *et al.*, 2005; Sánchez *et al.*, 2004; Tsai *et al.*, 2007), especially for kinetic studies. However, these reactor configurations limit the attainable heating rates to a relatively slow range, i.e. less than $100^{\circ}C$ min^{-1}, which is far from the conditions in commercial reactors (Carpenter and Skorupska, 1993). Moreover, interactions between the volatiles and chars or entrainment of volatiles in the vicinity of the heated coal/char enhance secondary cracking reactions and consequently reduce the yield of volatiles, especially tar, significantly (Carpenter and Skorupska, 1993; Hayashi and Miura, 2004). The use of drop-tube or free fall reactors could overcome the heating rate limitation. In these reactors, cold particles are rapidly heated as they drop into the hot atmosphere inside the reactor, and the heating rate of particles is determined based on the terminal velocity of particles, which is comparable to or even higher than the gas

velocity (Carpenter and Skorupska, 1993). However, the time-temperature history cannot be defined accurately due to the interdependency of heating rate, peak temperature and holding time. Although wire-mesh reactors enable well-defined time-temperature profiles under high heating rate conditions as well as minimising secondary cracking reactions, the analysis of product gas composition is impossible due to the very diluted gas phase. The drop-tube/fixed-bed reactors, which integrate the desirable features of the drop-tube reactor and the fixed-bed reactor, allow rapid heating as well as an exact determination of the temperature and particle residence time (Hayashi *et al.*, 2002; Kumabe *et al.*, 2007).

In this study, a drop-tube/fixed-bed reactor was constructed for investigation of the behaviour of three selected agricultural residues available in Thailand, rice husk, rice straw and corncob, under fast pyrolysis conditions simulating those occurring in commercial fluidised bed gasifiers. The effects of pyrolysis temperature and holding time on the weight losses and characteristics of char and gases were investigated. The relative combustion reactivities of the char were determined using a thermogravimetric analyser and the char morphology examined using a scanning electron microscope, while the gas composition was analysed using a mass spectrometer.

2. Experimental

2.1 Biomass samples and sample preparation

The biomass samples used for this study were rice husk, rice straw and corncob. These were ground and sieved to a diameter less than 75 µm. After that, the samples were dried in a vacuum oven at $70^{\circ}C$ for 24 hours before the experiments. The proximate and ultimate analysis results are given in Table 1 and chemical components, including cellulose, hemicellulose, lignin and extractive matters, in Table 2. All three types of biomass have similarly high volatile matter contents and low fixed carbon contents, but their ash contents are different. Rice husk has the highest ash content, i.e. almost 20 %; while corncob contains almost no ash. Although there is no significant difference in the volatile matter contents and elemental contents among the three biomass samples, the variation of their chemical components can be clearly observed. To investigate the effect of the chemical components present in the biomass, a commercial microcrystalline cellulose powder [Sigma Aldrich] and organic-solved lignin [20-100 µm, Sigma Aldrich] were used in the study as the model components.

Although there have been a number of studies of the role of inherent metal species in the primary reactions during a rapid pyrolysis of brown coals and lignites (Kershaw *et al.*, 2000; Li *et al.*, 2000; Hayashi *et al.*, 2000), none have been carried out on biomass pyrolysis. Therefore, possible catalytic effect of the metal species on biomass pyrolysis behaviour was also investigated with a focus on the four

Table 1. Proximate and ultimate analysis of rice husk, rice straw and corncob

	Rice husk	Rice straw	Corncob
Proximate Analysis (% dry basis)			
Volatile Matter	72.8	74.7	78.7
Fixed Carbon	9.3	15.2	16.2
Ash	17.9	10.1	0.9
Ultimate Analysis (% dry-ash-free basis)			
C	48.9	45.2	45.5
H	6.2	6.5	6.2
N	0.8	0.8	1.3
O (by difference)	44.1	47.5	47.0

Table 2. Chemical components of rice husk, rice straw and corncob

Biomass	Hemicellulose	Cellulose	Lignin	Extractive matter	Reference
Rice husk	28.6	28.6	24.4	18.4	Di Blasi *et al.* (1999)
Rice straw	35.7	32.0	22.3	10.0	Xiao *et al.* (2001)
Corncob	31.0	50.5	15.0	3.5	Demirbas (2004)

Table 3. Content of ash and metal species in untreated and acid treated rice husk, rice straw and corncob

	Rice husk	Rice straw	Corncob
Untreated biomass			
Ash content	17.9	10.1	0.9
Metal ion content ($mg_{ion}\ g_{sample}^{-1}$)			
Na	0.21	1.01	0.76
Mg	0.58	1.84	0.05
K	5.37	16.79	7.26
Ca	1.67	4.48	1.04
Acid treated biomass			
Ash content	18.1	8.9	0.0
Metal ion content ($mg_{ion}\ g_{sample}^{-1}$)			
Na	0.03	0.07	0.08
Mg	0.00	0.01	0.00
K	0.09	0.03	0.02
Ca	0.29	0.00	0.00

major metal species typically found in biomass, including Na, Mg, K and Ca. These alkali metal species were analysed by means of the inductively coupled plasma-mass spectrometer (ICP-MS) technique. The biomass sample was treated with 0.1 M HCl aqueous solution to extract the ion-exchangeable metal species from the biomass, while maintaining the sample structure. Details of the preparation of acid treated samples have been presented elsewhere (Vamvuka *et al.*, 2006). The acid washed samples were also subjected to ICP-MS for analysis of metal species. The contents of ash and metal species in the treated and untreated biomass are given in Table 3.

2.2 Drop-tube/fixed-bed reactor

A drop-tube/fixed-bed reactor was constructed in this study based on the configuration developed by Hayashi *et al.* (2002). This type of reactor combines the desirable features of the drop-tube reactor and the fixed-bed reactor to allow rapid heating rate conditions as well as an exact determination of the temperature and particle residence time. The heating rate was estimated to be higher than $1,000^{\circ}C\ s^{-1}$. The schematic diagram of the reactor is shown in Figure 1. The reactor consists of an inner quartz tube with the inside diameter of ½ inches and an outer quartz tube with the inside diameter of ¾ inches. The lower end of the inner tube was fitted with a perforated plate on which quartz wool was placed. Prior to an experiment, 40-50 mg of the sample was filled in the tubular sample holder positioned at the top end of the inner tube, which was pressurised with nitrogen to about 0.5 MPa above the atmospheric pressure. The reactor was purged with nitrogen at 400 ml min^{-1} and the reactor temperature was raised by an external heater to the desired temperature. Approximately 30 minutes holding time at the temperature was maintained to ensure uniform gas atmosphere and temperature inside the reactor, after which the sample was injected into the inner tube by an instantaneous release of the pressure in the sample holder. The volatiles and product gases formed were immediately swept from the inner tube by the continued nitrogen flow, while the char particles were left on the quartz wool to undergo further reactions. After a desired holding time after sample injection (in a range from 1 to 10,800 seconds), the reaction was
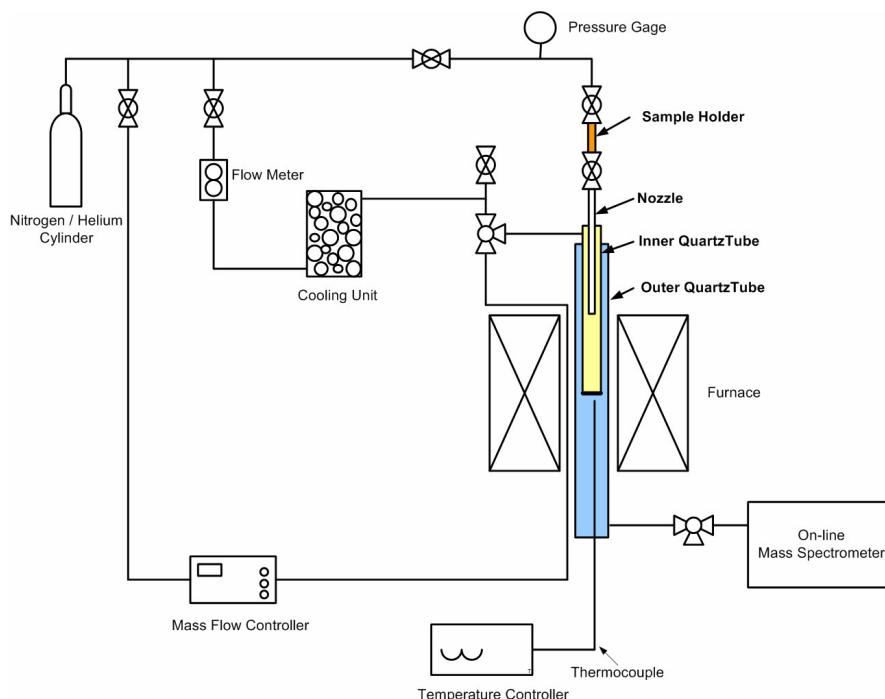
Figure 1. Schematic diagram of the drop-tube/fixed-bed reactor setup for pyrolysis experiments

quenched by cutting the external heat supply and the system was cooled down by the flow of cold nitrogen blowing down the inner tube. The residual char particles were collected for further analyses. The total weight loss was determined by the difference between the weight of quartz wool with sample before and after the pyrolysis experiment. A series of blank runs (i.e. quartz wool without sample) were conducted under the range of conditions studied. No weight change of quartz wool was observed. The total weight losses were found to be within 1% experimental error.

2.3 Analytical methods

Pyrolysis chars and gases were further analysed using the following analytical methods in order to obtain the information on pyrolysis product characteristics which benefits the subsequent utilisation.

2.3.1 On-line mass spectrometer (MS)

The compositions of the obtained product gases were analysed by on-line mass spectrometer (Pfeiffer vacuum, Omistar), MS. The MS was connected to the exit of the drop-tube/fixed bed reactor by a 1-meter transfer line, which was heated to 200°C to prevent the condensation of product gases. The m/z of 2, 15, 28, and 44 representing H_2, CH_4, CO and CO_2, respectively, were continuously monitored and the gas concentrations obtained by standard gas calibration.

2.3.2 Isothermal thermogravimetric analyser (TGA)

The relative combustion reactivities of the pyrolysis-

derived chars were measured in a standard thermogravimetric analyzer [Pyris 1 TGA, Perkin Elmer] under an isothermal condition in air at 500°C. The test temperature was chosen to ensure that the combustion would take place under the kinetic and not the mass transfer control regime (Messenböck *et al.*, 1999). Prior to the test, the pyrolysis char collected from the drop tube/fixed bed reactor after the experiment was dried in the vacuum oven at 70°C for 24 hours. For the measurement of the relative combustion reactivity, around 5 mg of the char samples were loaded onto the TGA sample pan. The sample was initially heated up under the flow of nitrogen (99.999 % purity) at 50 ml min^{-1} to 110°C to remove the remaining moisture and then to 500°C at a constant heating rate of 10°C min^{-1}. As soon as the desired temperature was reached, the flow of nitrogen was switched to air (Air Zero). The temperature was kept constant until the sample completely became ash. The combustion reactivity was calculated by taking the first derivative of the obtained weight profile normalized to the initial weight of sample, as shown in Equation 1. The maximum relative combustion reactivity, R_{max}, was taken as the indicator for char reactivities in this study.

$$R_{max} = -\frac{1}{W_0}\left(\frac{dW}{dt}\right)\bigg|_{max} \tag{1}$$

where t is the reaction time, W_0 is the initial weight of sample and W is the instantaneous weight of sample.

2.3.3 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) [JEOL, JSM-6400] was used to examine the morphology of samples

including both raw biomass and char particles derived from the pyrolysis experiments. The sample powder was sprinkled as a thin layer on an adhesive tape placed on the brass sample holder. Excess amount of the sample was removed by blowing with the air spray. The adhered sample was then coated with gold powder using the sputtering device [JEOL, JFC-1100E Ion] and then transferred into the JEOL sample chamber for the analysis. The accelerating voltage was set at 15-40 kV and 2,000 time magnification was selected.

2.3.4 Sorption Analyzer

The specific surface areas of the biomass samples as well as the biomass-derived char samples from the pyrolysis experiments were measured to examine the pore structures, which reflect the char active sites and its reactivity. The specific surface area was measured by a sorption analyzer (BELSORP-mini with BELPREP-flow, BEL JAPAN, INC) at -196°C. N_2 was used as the adsorption gas. Prior to the measurement, around 0.1 g of the char sample was pretreated by drying under nitrogen atmosphere for around 5 hours to remove the remaining moisture. The specific surface area of the sample was then calculated using the standard BET method (Yang, 2003).

3. Results and Discussions

3.1. Effects of temperature and holding time on the pyrolysis weight loss

Fast pyrolysis experiments of rice husk, rice straw and corncob were carried out in the drop-tube/fixed-bed reactor to investigate the effects of temperatures and holding times on the pyrolysis weight loss.

Although pyrolysis temperatures above 700°C were interesting for the investigation of the weight loss behaviour under the circumstances in biomass fluidized bed gasifiers, a temperature range of 200-850°C was used in order to sufficiently demonstrate the weight loss behaviour of the entire pyrolysis step. One minute holding time was used to ensure a uniform temperature. As shown in Figure 2, significant weight losses were observed for all three biomass samples studied at temperatures between 200 and 400°C, after which the weight loss rate was much slower. This is typical for lignocellulosic materials for which the devolatilisation rate depends strongly on the reaction temperature and the rapid release of volatiles starts at temperatures as low as 200°C (Gani and Naruse, 2007). This is likely due to the impact of the decomposition of cellulose, which decomposes quickly at 200-400°C (Gani and Naruse, 2007; Uzun *et al.*, 2007). The decomposition of lignin, which is slower but spans over the entire range of temperatures (Orfão *et al.*, 1999; Vamvuka *et al.*, 2003), is thought to be responsible for the additional small increase in the weight loss at high temperatures. At 850°C, which was the maximum pyrolysis temperature used in this set of experiments, the weight loss due to pyro-
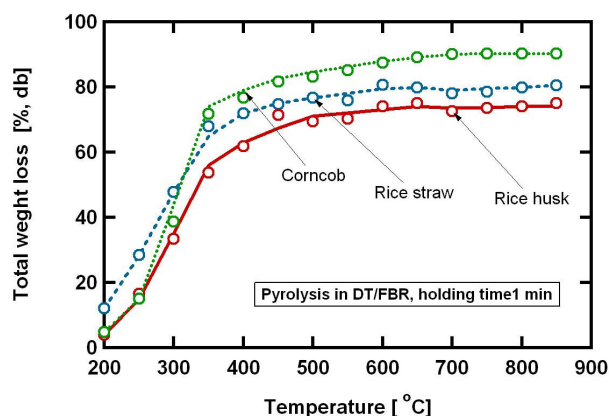

Figure 2. Total weight losses from pyrolysis of rice husk, rice straw and corncob at 200-850°C with 1 min holding time in the drop-tube/fixed-bed reactor

lysis accounted for 70-90% of the total weight loss. This generally implies that, in the commercial gasification processes, as soon as biomass particles are exposed to the high temperature inside the reactor, they are rapidly heated up and the majority of the volatiles are immediately released leaving a small amount of char.

It is noticed that, at the same temperature, the weight loss of rice straw was always higher than that of rice husk over the entire temperature range, while corncob exhibited a slight difference. Below 300°C, the weight loss of corncob was found to be the lowest; however, the devolatilisation rate of corncob accelerated at temperatures above 350°C giving a higher weight loss than for rice straw and rice husk. This rapid increase in the weight loss of corncob is likely attributed to the decomposition of its considerable cellulose content, i.e. almost double that of rice husk and rice straw. Previous studies (Gani and Naruse, 2007; Worasuwannarak *et al.*, 2007) have similarly found that the maximum decomposition rate of cellulose was at 350-400°C.

It can also be observed from Figure 2 that, at temperatures above 700°C, the weight losses apparently reached their maxima under the specified heating rate and holding time. However, additional weight loss obtained at sufficiently long holding times can be expected, especially at high heating rate and high temperatures. The effect of holding time was then investigated at 700-850°C, which are within the range of temperatures encountered in commercial biomass fluidised bed gasifiers. The results are shown in Figure 3 for the weight losses of rice husk, rice straw and corncob at the holding times ranging from 1 to 10,800 seconds. In all cases, the major weight loss occurred immediately after the sample was injected into the reactor, i.e. within the first second, leaving a small amount of char. At 850°C with 1 second holding time, the weight losses were 71.8%, 77.5% and 89.3% for rice husk, rice straw and corncob, respectively.

For all three samples, corncob pyrolysed at a faster rate than rice husk and rice straw. The pyrolysis weight loss continued throughout the range of holding times used but at
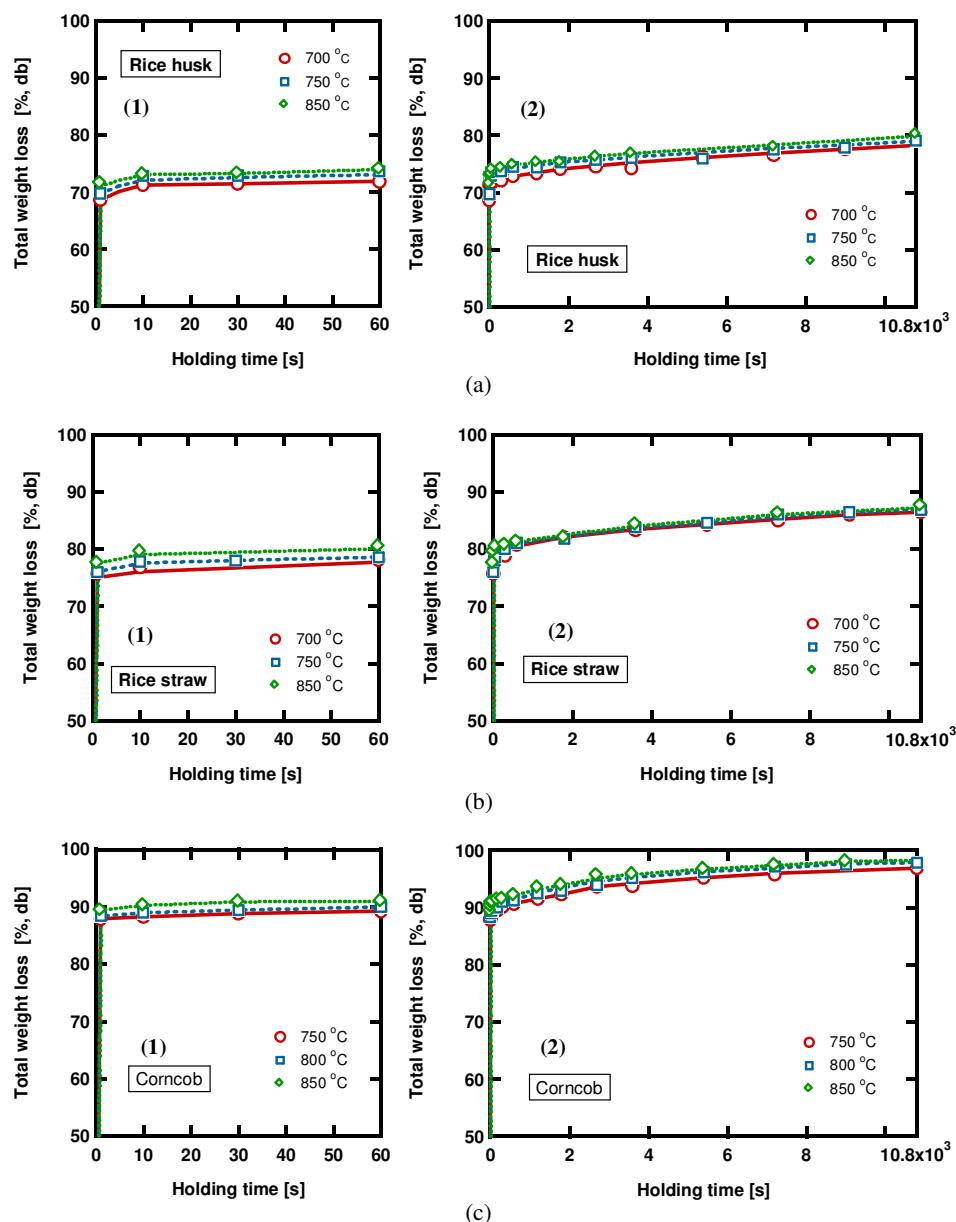
Figure 3. Total weight loss from pyrolysis at 700-850°C with 1 to 10,800 s holding time in the drop-tube/fixed-bed reactor of
         (a) rice husk, (b) rice straw and (c) corncob

an extremely slow rate, i.e. 1.3% hr^{-1}. This behaviour was similar to pyrolysis under helium atmosphere in standard TGA tests for both biomass and Thai lignite (the results are not shown), in which the yields reached the ash level after an extremely long holding time at the high temperatures. However, within the range of holding times in the same order of magnitude as the typical particle residence times inside the fluidised bed reactors, i.e. 1-2 minutes, the weight loss is considered unchanged.

3.2 The effect of chemical components on the pyrolysis weight loss

The analysis of the chemical components given in

Table 2 shows that the total cellulose content was more than the lignin content for all three biomass samples. Corncob had the highest total cellulose content (31% hemicellulose and 50% cellulose), while rice husk had an almost equal proportion of hemicellulose, cellulose and lignin.

The relationship between the chemical components and the pyrolysis weight losses of the three biomass samples was investigated at 850°C as a function of holding time (i.e. 1-10,800 seconds). The experiments were also carried out on cellulose and lignin chemicals under otherwise similar conditions. The pyrolysis weight losses are presented in Figure 4. Since the cellulose and lignin chemicals were the model compounds, which may not exactly represent the natural cellulose and lignin in biomass, such as the amount of ash,
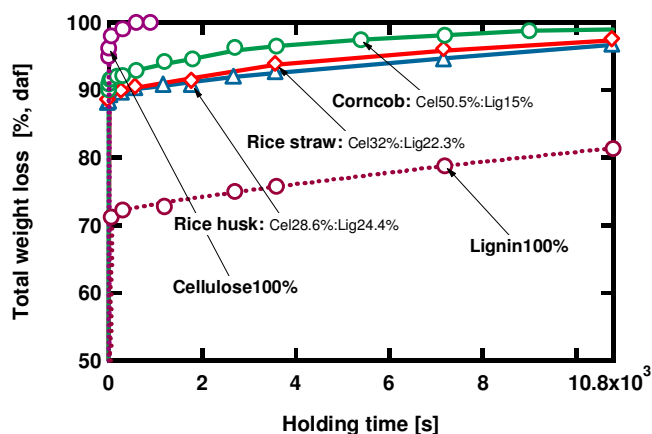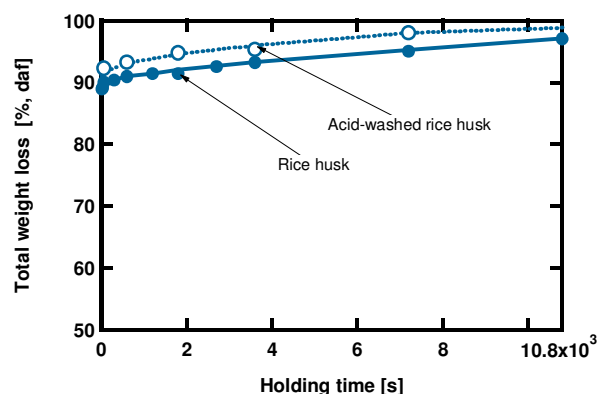
Figure 4. Total weight losses from pyrolysis of rice husk, rice straw, corncob, cellulose and lignin at 850°C with 1 to 10,800 s holding time in the drop-tube/fixed-bed reactor

the results are expressed on a dry-ash-free basis. Cellulose decomposed much faster than lignin, with almost all the possible weight loss of cellulose occurring within the first second after the sample injection. Lignin decomposition during the heat-up period was also considerable; however, a significant further weight loss, i.e. ~30 %, continued as the holding time proceeded but at a much slower rate. Generally, it is more difficult for lignin to decompose than cellulose. Lignin consists of more aromatic groups, which have higher chemical bond energies than the polysaccharide structures of cellulose consisting mostly of a series of glucose molecules (Sharma *et al*., 2004; Yang *et al*. 2007). The profiles of biomass decomposition were found to lie between those of cellulose and lignin, but closer to the former. This may be due to the higher proportion of cellulose than lignin in these biomass samples. The profile of corncob, which had the highest cellulose content, was the closest to the profile of cellulose; while rice husk having the lowest cellulose content and the highest lignin content exhibited the opposite. This clearly confirms that the proportion of chemical components in biomass is one of the important parameters to evaluate the pyrolysis behaviour.

3.3 The effect of metal species on the pyrolysis weight loss

Among the three biomass samples studied, rice straw had the highest contents of all four metal species of interest. These metal species in rice straw, especially the abundant potassium, tend to cause more fouling problems during combustion than the other two samples.

As described in the experimental section, biomass samples were treated by acid washing, which was shown to have no effect on either the quantity of ash present in biomass or the biomass structural properties. As shown in Table 3, the ash contents of treated and untreated samples were almost identical. The functional group analysis by FT-IR (the results are not shown) also confirmed that acid washing removed the metal species of concern (Na, Mg, Ca and K) from the

(a)
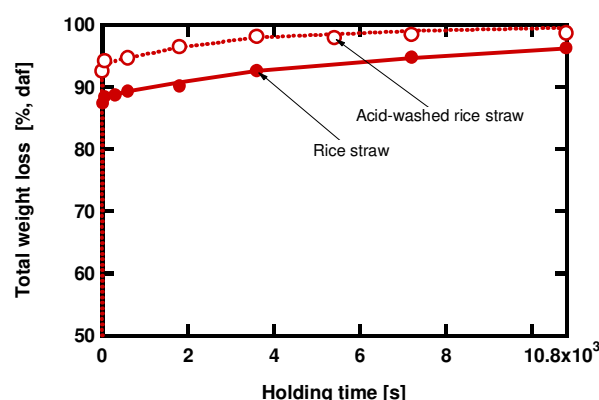
(b)
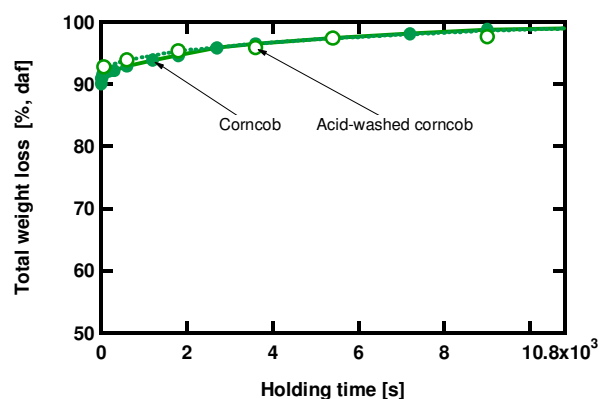
(c)

Figure 5. Total weight losses from pyrolysis of acid treated and untreated biomass at 850°C with 1 to 10,800 s holding time in the drop-tube/fixed-bed reactor: (a) rice husk, (b) rice straw and (c) corncob

samples, while the other structural properties of biomass remained unaltered. All the metal species were also the acid soluble species, which are likely to evolve from the biomass and interact with tar during pyrolysis.

The total weight losses from pyrolysis at 850°C of acid treated and untreated biomass are presented as a function of holding time on the dry-ash-free basis in Figure 5. Similar to the pyrolysis of untreated biomass, a significant

Rice husk   Rice husk char (1 second hold)   Rice husk char (10,800 second hold)

Rice straw   Rice straw char (1 second hold)   Rice straw char (10,800 second hold)

Corncob   Corncob char (1 second hold)   Corncob char (10,800 second hold)
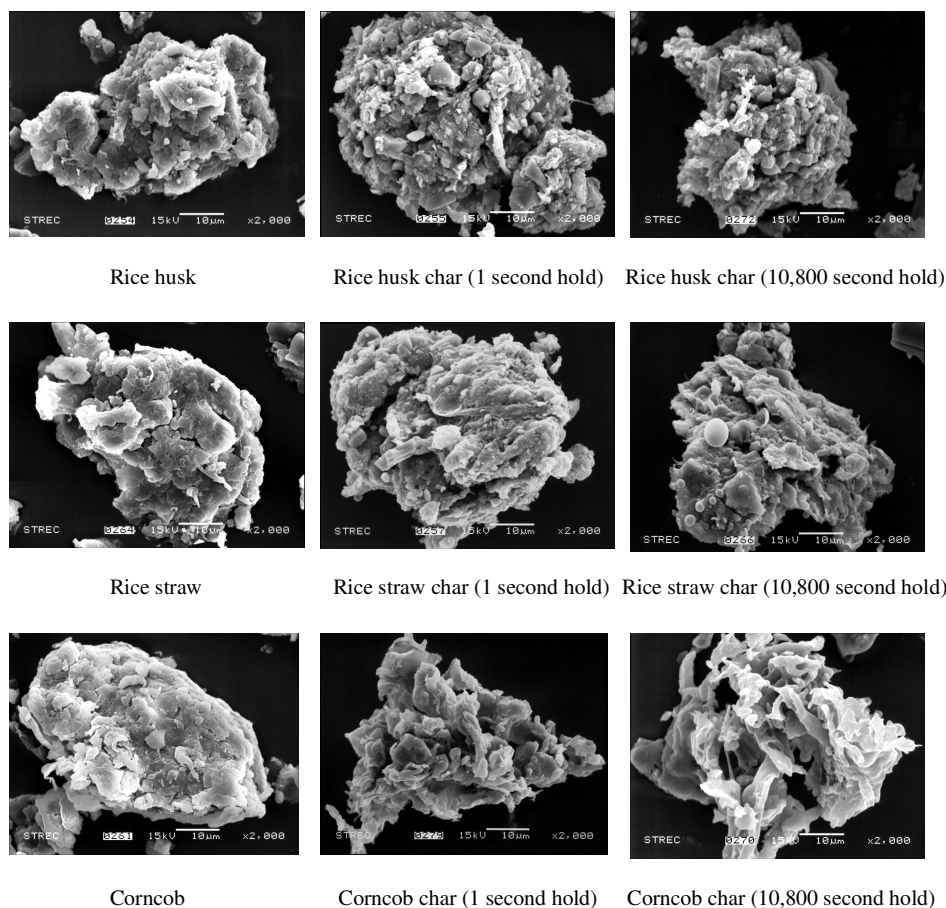
Figure 6. SEM photomicrographs of raw biomass samples and their chars obtained from pyrolysis at 850°C with 1 and 10,800 s holding time in the drop-tube/fixed-bed reactor

weight loss took place immediately after the sample injection (i.e. less than 1 second) for the treated biomass. However, the weight losses of treated biomass were always higher. At 1 second holding time, the weight losses on a dry-ash-free basis of the treated rice husk, rice straw and corncob were 91.1%, 92.5% and 91.2%, respectively, compared to 88.7%, 86.7% and 90.1% for the untreated samples. The increased weight loss by the removal of these metal species is due to the enhanced tar formation, which was also consistently observed by other researchers (Kershaw *et al.*, 2000; Li *et al.*, 2000; Hayashi *et al.*, 2000; Hayashi *et al.*, 2002). Suelves *et al.* (2000) suggested that the metal species disfavor the cross-linking reactions which reduce the char formation. This could also explain the largest difference in weight loss in the case of rice straw, which has the highest content of the metal species.

3.4 Char reactivities and their morphological changes during pyrolysis

As biomass is being pyrolysed to form char, all the characteristics of the samples change progressively. Figure 6 shows the SEM pictures of rice husk, rice straw, corncob and their respective chars prepared in the drop-tube/fixed-bed

reactor at 850°C. For all three samples, the original biomass particles have quite similar appearances, which could be seen as a smooth surface with some distributed pores. After only 1 second pyrolysis during which the biomass samples were subjected to heat and decomposed rapidly, each sample exhibited qualitatively different char morphologies. Rice husk and rice straw char, while retaining their particle geometries, became slightly swollen and more porous. This could be due to the immediate release of the volatiles from inside of the particles under a rapid heating up. This effect was more pronounced for rice straw compared to rice husk, which may be explained by the more rapid devolatilisation of rice straw resulting in more extensive volatile explosion and pores creation. The morphological change of corncob char was clearly different from those of rice husk and rice straw. The extensive widening of pores and changes in particle geometry were clearly observed for the corncob char. These behaviours are likely due to the significantly low lignin content but high cellulose content in corncob. The low lignin content is responsible for the weak structure of the biomass cell wall rendering the particle rupture (Saka, 2000). Moreover, the high cellulose content results in a relatively high devolatilisation rate of corncob leading to the fragmentation of its char particles. These observed developments of

Table 4. Maximum char combustion reactivities determined using a standard TGA under an isothermal condition at 500°C and the N_2 adsorption BET surface area of biomass-derived chars prepared in the drop-tube/fixed-bed reactor under fast pyrolysis at 850°C

Biomass char	Holding time (s)	R_{max} (min^{-1}, daf)	BET surface area (m^2 g^{-1})
Rice husk	0 (original)	-	5.72
	1	0.92	99.52
	600	0.71	-
	3,600	0.58	-
	10,800	0.53	72.26
Rice straw	0 (original)	-	0.15
	1	1.20	105.28
	600	1.23	-
	3,600	0.98	-
	10,800	0.94	94.53
Corncob	0 (original)	-	0.73
	1	1.23	42.21
	600	0.83	-
	3,600	0.89	-
	10,800	1.42	203.03

the char structure were confirmed by the significant increase in the surface area of chars from those of their original biomass at all preparation conditions, as will be discussed later.

The relative combustion reactivities and N_2-adsorption surface areas of chars prepared from rice husk, rice straw and corncob in the drop-tube/fixed-bed reactor at 850°C with the holding times ranging between 1 and 10,800 seconds are presented in Table 4. Although analyses were not conducted on the chars prepared at all conditions due to the insufficiently small amount of the resulting char samples, the relationships between char characteristics (reactivities and surface areas) and pyrolysis conditions can be observed. Among the three biomass samples studied, corncob chars were generally the most reactive; while rice husk chars were the least reactive. As suggested in the previous section, the difference in biomass reactivities could be due to the proportion of chemical components of each biomass, especially cellulose and lignin.

Char reactivities generally decreased with an increase in the holding time during pyrolysis. This decrease could be explained by the following reasons. One is the char annealing or the loss of char active sites due to a long-time exposure to high temperatures. The effect of high-temperature annealing has been studied and well explained by Marsh and Kuo (1989). The thermal annealing from the heat treatment results in the reduction of carbon structural defects. These defects are normally where the main active sites are located, resulting in reduced carbon reactivity. The other reason is the progressive reduction of the char surface area due to the pore overlapping and pore widening as the conversion proceeds. This

could also lower the intrinsic reactivity of the pyrolysis chars. The study of biomass pyrolysis by Liu *et al.* (2008) showed that the surface area of the pyrolysis char reached a maximum at the conversion of around 0.35 and then decreased. They also explained that during the initial step, the blocked pores are opened up and new micropores are created increasing the surface area. However, those pores are later enlarged and finally merged lowering the char surface area. This latter implication is evidently supported by the decrease of the N_2-adsorption surface areas with conversion at the extended holding times (see Table 4).

3.5 Composition analysis of pyrolysis product gas

The derived product gas from the reaction zone was swept into a mass spectrometer for a real-time gas analysis. Helium gas was used instead of N_2 in order to prevent the overlapping of the peaks representing the gas species of the same molecular weight, e.g. CO and N_2. Although, with the current setup, the estimated signal delay was around 5 seconds, the evolution trends of each gas species could still be interpreted with reasonable accuracy.

Figure 7 shows the instantaneous evolution rates as a function of time of the product gases H_2, CH_4, CO and CO_2 from isothermal pyrolysis at 850°C. The rates are presented per gram of sample. Due to the rapid evolution of gases by the fast heating rate condition, the maximum evolution rates of all gases were approximately at the same time. Under the conditions used and the current setup, almost complete evolution of the product gases was also found within 60 sec-
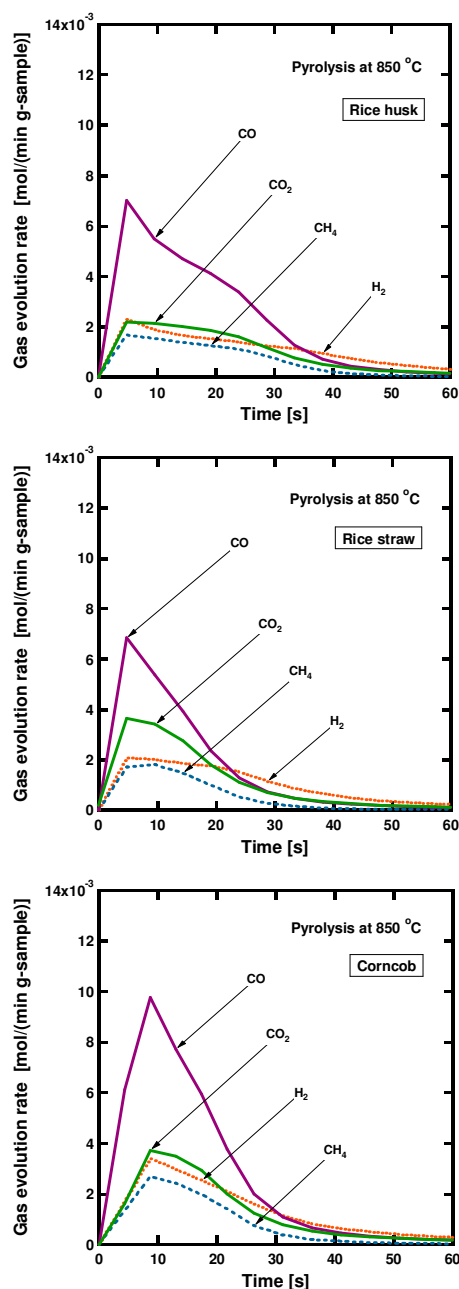
Figure 7. Evolution rates of H_2, CH_4, CO and CO_2 against time during pyrolysis at 850°C of rice husk, rice straw and corncob

Figure 8. Evolution rates of H_2, CH_4, CO and CO_2 against time during pyrolysis at 850°C of cellulose and lignin

onds for all three samples, after which the gas evolution was insignificant, i.e. < 1 % of the total gas formed.

Different gas evolution behaviours were clearly observed among the three biomass samples studied. Corncob gave higher gas evolution than rice husk and rice straw. This could be explained by the considerably high cellulose and hemicellulose contents in corncob. The results of gas evolution from cellulose and lignin pyrolysis carried out under otherwise similar conditions, as shown in Figure 8, confirm that cellulose decomposition produces significantly higher gas yield compared to li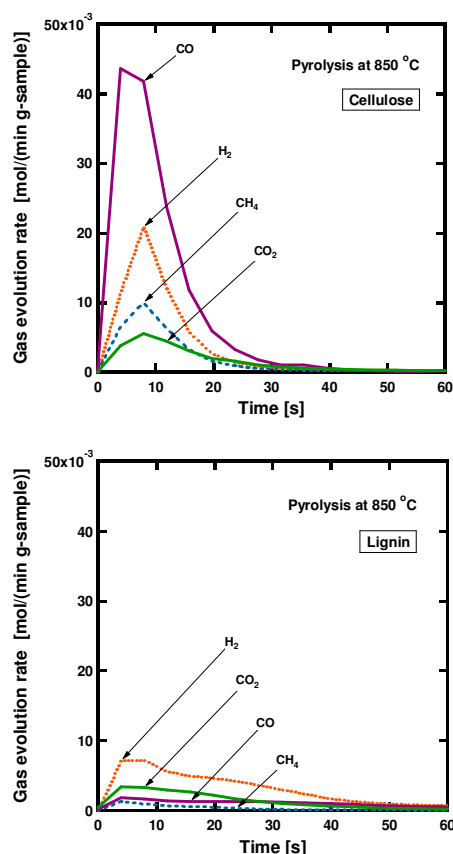gnin. These gas yield trends are in good agreement with other studies on pyrolysis experiments on different types of biomass (Graboski, 1981; Worasuwannarak *et al.*, 2007).

Among the four gas species of interest, CO had the highest evolution rate for all three biomass samples. The CO evolution is thought to mainly come from the decomposition of cellulose. As can be seen in Figure 8, CO is the main product of cellulose decomposition; while the majority of product gases from lignin is H_2. Previous studies have shown that CO is formed during the primary decomposition of hemicellulose and cellulose with a smaller proportion of CO coming from lignin by the cracking of carbonyl (C-O-C) and carboxyl (C=O) in biomass (Fitzer *et al.*, 1971; Yang *et al.* 2007). Other gases, including H_2, CH_4 and CO_2, exhibit similar evolution rate profiles for rice husk and corncob; while the CO_2 evolution rate is double that of H_2 and CH_4 for rice straw.

From this study, the effect of chemical components in biomass on the pyrolysis gas yields as well as the gas compositions could be clearly observed. However, the effect of the metal species could not be eliminated. Bridgwater *et al.* (2003) suggested that, in addition to the biomass chemical components, the inorganic matters, especially the metal species which are abundant in biomass, can play a role as nature-existing catalysts in biomass. This favours the formation of gas and char, while depressing the formation of liquid.

However, no correlation between the metal species content and the gas evolution behaviour was found.

4. Conclusions

The high temperature (i.e. > 700°C) fast pyrolysis of biomass was focused in this study. Under the conditions studied, the weight losses from rice husk, rice straw and corncob exhibited similar trends. The major weight loss occurred within only 1 second after the biomass was injected into the reactor and accounted for 70-90% of the initial weight. Although the weight loss continued throughout the range of holding times used, the rate was extremely slow. Moreover, within the range of holding times in the same order of magnitude as the typical particle residence time inside the fluidised bed reactors, i.e. 1-2 minutes, the weight loss is considered unchanged.

The pyrolysis rates were found to be influenced by the proportion of the biomass chemical components as well as the metal species contents. The higher the lignin content (which normally corresponds to the lower content of cellulose), the lower the pyrolysis weight loss. The presence of metal species in biomass increased the weight loss by enhancing the tar formation as well as depressing the cross-linking reaction to form char. The longer holding times reduced the char reactivities, which could be explained by thermal annealing as well as the reduction of the surface area as the conversion proceeded. Corncob, which contains the highest cellulose content, gave the highest total gas yield. CO is the major product gas from pyrolysis of all biomass samples as well as of the cellulose.

Acknowledgements

References

Bayarsaikhan, B., Hayashi, J-I., Shimada, T., Sathe, C., Li, C-Z., Tsutsumi, A. and Chiba, T. 2005. Kinetics of steam gasification of nascent char from rapid pyrolysis of a Victorian brown coal. Fuel. 84, 1612-1621.

Blanco Lopez, M.C., Blanco, C.G., Martinez-Alonso, A. and Tascon, J.M.D. 2002. Composition of gases released during olive stones pyrolysis. Journal of Analytical and Applied Pyrolysis. 65, 313-322.

Bridgwater, A., Czernik, S., Diebold, J., Meier, D., Oasmaa, A., Peacocke, C., Piskorz, J. and Radlein, D. 2003. Fast Pyrolysis of Biomass: A Handbook. 1, CPL Press, UK.

Caballero, J.A., Conesa, J.A., Font, R. and Marcilla, A. 1997. Pyrolysis kinetics of almond shells and olive stones considering their organic fractions. Journal of Analytical and Applied Pyrolysis. 42 (2), 159-175.

Caballero, J.A., Front, R. and Marcilla, A. 1996. Study of the primary pyrolysis of kraft lignin at high heating rates: yields and kinetics. Journal of Analytical and Applied Pyrolysis. 36 (2), 159-178.

Cao, Q., Xie, K-C., Bao, W-R. and Shen, S-G. 2004. Pyrolytic behaviour of waste corncob. Bioresource Technology. 94, 83-89.

Carpenter, A.M. and Skorupska, N.M. 1993. Coal Combustion-Analysis and Testing, IEA Coal Research, London.

Clemens, A.H., Damiano, L.F. and Matheson, T.W. 1998. The effect of calcium on the rate and products of steam gasification of char from low rank coal. Fuel. 77 (9-10), 1017-1020.

Demirbas, A. 2004. Effect of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. Journal of Analytical and Applied Pyrolysis. 72, 243-248.

Di Blasi, C., Buonanno, F. and Branca, C. 1999. Reactivities of some biomass chars in air. Carbon. 37 (8), 1227-1238.

Fitzer, E., Mueller, K. and Schaefer, W. 1971. Chemistry and Physics of Carbon, P.L. Walker Jr., editor. no. 7, Marcel Dekker Ltd., New York, pp. 237-383.

Gani, A. and Naruse, I. 2007. Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. Renewable Energy. 32 (4), 649-661.

Graboski, M. 1981. Biomass Gasification Principles and Technology, T. B. Reed, editor, Energy Technology Review No. 67, Noyes Data Corporation, New Jersey.

Hayashi, J-I, Iwatsuki, M., Morishita, K., Tsutsumi, A., Li, C-Z. and Chiba, T. 2002. Roles of inherent metallic species in secondary reactions of tar and char during rapid pyrolysis of brown coals in a drop-tube reactor. Fuel. 81 (15), 1977-1987.

Hayashi, J-I. and Li, C-Z. 2004. Structure and properties of Victorian brown coal. Advances in Science of Victorian Brown Coal, C-Z. Li, editor, Elsevier, UK. pp. 11-84.

Hayashi, J-I., Takahashi, H., Doi, S., Kumagai, H., Chiba, T. and Yoshida, T. 2000. Reactions in brown coal pyrolysis responsible for heating rate effect on tar yield. Energy & Fuels. 14 (2), 400-408.

Jakab, E., Faix, O. and Till, F. 1997. Thermal decomposition of milled wood lignins studied by thermogravimetry/mass spectrometry. Journal of Analytical and Applied Pyrolysis. 40-41, 71-186.

Kershaw, J.R., Sathe, C., Hayashi, J-I., Li, C-Z. and Chiba, T. 2000. Fluorescence spectroscopic analysis of tars from the pyrolysis of a Victorian brown coal in a wire-mesh reactor. Energy & Fuels. 14 (2), 476-482.

Kristiansen, A. 1996. Understanding Coal Gasification, IEA Coal Research, London.

Kumabe, K., Hanaoka, T., Fujimoto, S., Minowa, T. and Sakanishi, K. 2007. Co-gasification of woody bio-

mass and coal with air and steam. Fuel. 86 (5-6), 684-689.

Li, C-Z., Sathe, C., Kershaw, J. R. and Pang, Y. 2000. Fates and roles of alkali and alkaline earth metals during the pyrolysis of a Victorian brown coal. Fuel. 79 (3-4), 427-438.

Liu, T-F., Fang, Y-T., and Wang, Y. 2008. An experimental investigation into the gasification reactivity of chars prepared at high temperatures. Fuel. 87 (4-5), 460-466.

Luo, Z., Wang, S., Liao, Y., Zhou, J., Gu, Y. and Cen, K. 2004. Research on biomass fast pyrolysis for liquid fuel. Biomass and Bioenergy. 26, 455-462.

Marsh, H. and Kuo, K. 1989, Kinetics and catalysis of carbon gasification, Introduction to Carbon Science, H. Marsh, editor, Butterworths & Co. Ltd., UK.

Messenbock, R.C., Dugwell, D.R. and Kandiyoti, R. 1999. CO_2 and steam-gasification in a high-pressure wire-mesh reactor: the reactivity of Daw Mill coal and combustion reactivity of its chars. Fuel. 78, 781-793.

Orfão, J.J.M., Antunes, F.J.A. and Figueiredo, J.L. 1999. Pyrolysis kinetics of lignocellulosic materials-three independent reactions model. Fuel. 78 (3), 349-358.

Pütün, A.E., Özbay, N., Önal, E.P. and Pütün, E. 2005. Fixed-bed pyrolysis of cotton stalk for liquid and solid products. Fuel Processing Technology. 86 (11), 1207-1219.

Raveendran, K., Ganesh, A. and Khilart, K.C. 1995. Influence of mineral matter on biomass pyrolysis characteristics. Fuel. 74 (12), 1812-1822.

Rosillo-Calle, R., Bajay, S.V. and Rothman, H. 2000. Industrial Uses of Biomass Energy, Taylor & Francis, London and New York.

Saka, S. 2000. Chemical composition and distribution. Wood and Cellulosic Chemistry, D. N-S. Hon and N. Shiraishi, editor, 2nd edition, revised and expanded, Marcel Dekker Ltd., New York, 2000, pp. 51-82.

Sánchez, J.L., Gea, G., Gonzalo, A., Bilbao, R. and Arauzo, J. 2004. Kinetic study of the thermal degradation of alkaline straw black liquor in nitrogen atmosphere. Chemical Engineering Journal. 104 (1-3), 1-6.

Shafizadeh, F. 1981. Biomass Conversion Processes for Energy and Fuels, S.S. Sofer and O.R. Zaborsky, editor, Plenum Press, New York.

Sharma, R.K., Wooten, J.B., Baliga, V.L., Lin, X., Chan, W.G, and Hajaligol, M.R. 2004. Characterization of chars from pyrolysis of lignin. Fuel. 83, 1469-1482.

Suelves, I., Moliner, R. and La´zaro, M.J. 2000. Synergetic effects in the co-pyrolysis of coal and petroleum residues: influences of coal mineral matter and petroleum residue mass ratio. Journal of Analytical and Applied Pyrolysis. 55, 29-41.

Thailand Research Fund. 2007. Policy Research on Renewable Energy Promotion and Energy Efficiency Improvement in Thailand Project - Final Report

Tsai, W.T., Lee, M.K. and Chang, Y.M. 2007. Fast pyrolysis of rice husk: Product yields and compositions. Bioresource Technology. 98 (1), 22-28.

Utistham, T., Soontornrangsan, W. and Piyakuldumrong P. 2007. Energy potential from residual biomasses in Thailand. Proceedings of the 3rd Energy Technology Network of Thailand (ENETT), Bangkok, Thailand, May 23-25, 2007, 1-6.

Uzun, B.B., Pütün, A.E. and Pütün, E. 2007. Composition of products obtained via fast pyrolysis of olive-oil residue: Effect of pyrolysis temperature. Journal of Analytical and Applied Pyrolysis. 79 (1-2), 147-153.

Vamvuka, D., Kakaras, E., Kastanaki, E. and Grammelis, P. 2003. Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite. Fuel. 82, 1949-1960.

Vamvuka, D., Troulinos, S. and Kastanaki, E. 2006. The effect of mineral matter on the physical and chemical activation of low rank coal and biomass materials. Fuel. 85 (12-13), 1763-1771.

Wang, G., Li, W., Li, B. and Chen, H. 2008. TG study on pyrolysis of biomass and its three components under syngas. Fuel.87 (4-5), 552-558.

Williams P.T. and Besler, S. 1993. The pyrolysis of rice husks in a thermogravimetric analyser and static batch reactor. Fuel. 72 (2), 151-159.

Worasuwannarak, N., Sonobe, T., Tanthapanichakoon, W. 2007. Pyrolysis behaviors of rice straw, rice husk, and corncob by TG-MS technique. Journal of Analytical and Applied Pyrolysis. 78 (2), 256-271.

Xiao, B., Sun, X.F. and Sun R-C. 2001. Chemical, structural, and thermal characterizations of alkali-soluble lignin and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw. Polymer Degradation and Stability. 74, 307-319.

Yang, H., Yan, R.,Chen, H., Lee, D.H. and Zheng, C. 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel. 86, 1781–1788.

Yang, R.T. 2003. Adsorbents: fundamentals and applications, Wiley-Interscience, Hoboken, New Jersey.