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Influence of temperature on the distribution of gaseous products from pyrolyzing palm oil wastes

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Abstract

This study concerns the various gaseous products released during the pyrolysis of palm oil wastes. For this a thermogravimetric analyzer, coupled with Fourier transform infrared analysis (TGA-FTIR), identified the gases produced when pyrolyzing palm oil wastes under different conditions. An FTIR spectrum was scanned in 5 s. The influence of temperature was investigated by repeated experiments at 250, 280, 300, 325, 355, 400, and 450 °C. The kinetics of weight loss (evaluated by the TGA) and of the production of gases (determined by FTIR) at the selected temperatures were evaluated. The different profiles of gases produced at low (<355 °C) and high temperatures (>355 °C) suggest that different reaction pathways (or mechanisms) are involved. Simulations of thermodynamic equilibrium for the pyrolysis of palm oil wastes were performed for 200–1200 °C. As predicted, H₂, CO₂, CH₄, and CO are the dominant gaseous species from pyrolysis. This study provides clearer insight into the effects of temperature on the gases produced by pyrolyzing a biomass.

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Keywords: Palm oil wastes; Pyrolysis; Temperature; Effect; Gas products

1. Introduction

Recently, owing to environmental and economic considerations, interest in utilizing biomass for the production of energy and chemicals is increasing. Palm oil wastes are the main agriculture wastes in Southeast Asia. In Malaysia alone, 9.9 Mte of solid wastes consisting of the oil-palm empty fruit bunch (EFB), fiber, and shell are generated every year [1].

Novel technologies with improved efficiency and reduced environmental impacts are required to treat these wastes, and also to convert them to energy. Pyrolysis is one of the most promising thermo-chemical techniques for recovering energy from biomass. Operating parameters (such as temperature, type of biomass, heating rate, pressure, and reactor configuration) are believed to influence significantly the pyrolysis of a biomass. Temperature is one of the most important operating variants [2–13]. So far, various experimental studies have investigated the influence of temperature on pyrolysis [2–12], focusing on eval-

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Table 1
Proximate and ultimate analyses of palm oil wastes

	Proximate analysis (wt%)				Ultimate analysis (wt%)					LHV (MJ/kg)
	M _{ad}	V _{ad}	A _d	FC _{ad}	C	H	N	S	O ^a	
Fiber	6.56	76.0	5.33	12.5	50.3	7.07	0.42	0.63	36.3	20.6
Shell	5.73	73.7	2.21	18.4	53.8	7.20	0.00	0.51	36.3	22.1
EFB	8.75	79.7	3.02	8.80	48.9	7.33	0.00	0.68	40.2	19.0

M, moisture content; V, volatile matters; A, ash; FC, fixed carbon; ad, on air-dried basis; d, on dry basis.

^a The O content was determined by difference.

uating the yields of different products as a function of temperature. The experiments were mostly performed in bench-scale reactors at high temperatures (500–900 °C), and only the total yields of the main gaseous products were taken into account. A high temperature is found to generally favor the yield of gaseous products [3–6]. Studies on the distribution and release of various gaseous products at different pyrolysis temperatures have seldom been carried out [5,9]. Nevertheless, the pyrolysis of biomass involves various sequential and parallel reactions [12]; the mechanism of pyrolysis is still not fully understood. A better understanding of the effect of temperature on the distribution of products is needed to establish a model of pyrolysis and to produce biofuels with improved yields and higher quality.

Numerous models [14–17] have been developed to describe the pyrolysis of biomass; they are mainly based on considerations of kinetics, as well as heat and/or mass transport. However, these models contain parameters, which make them difficult to apply to different reactors. Models based on thermodynamic equilibrium [17–22] are independent of the reactor. However, thermodynamic equilibrium may not be achieved at low temperatures, so the calculations may not represent the real situation, when kinetic constraints become the major factor. Nevertheless, models based on thermodynamic equilibrium have been used for predicting the thermal conversions of methane [18], plastics [19], and coal [20–22]. As for biomass, they have mostly been used for combustion or gasification and only recently has equilibrium modeling been used in the pyrolysis of biomass [17] with a focus on the release of the elements K and Cl, rather than the main gaseous products. In general, pyrolysis involves endothermic reactions and so occurs at high temperatures. In this study, equilibrium modeling is introduced to outline the distribution of gaseous species, as a function of temperature.

In addition, the pyrolysis of palm oil wastes was investigated using TGA-FTIR. The weight loss was measured in a TGA and the gases evolved were detected on-line by FTIR. The influence of temperature, particularly on the distribution of gaseous products, was analyzed.

2. Materials and methods

2.1. Materials

Samples of three palm oil wastes (shell, fiber, and empty fruit bunches) were obtained from Malaysia. They were ground in a laboratory-scale centrifugal mill (Rocklabs, New Zealand) and sieved in a Retsch test sieve with a 1-mm screen (Retsch, Fisher Scientific Company, USA); i.e., all the samples studied here were <1 mm in size. The proximate and elemental analyses were carried out in a TGA (TA 2050, USA) and CHNS/O Analyzer (Perkin-Elmer 2400II), respectively. The results are listed in Table 1. Palm oil wastes have a very high volatile content (V), >70 wt%, and contain low amounts of fixed carbon (FC), <20 wt%. The lower heating value (LHV) of the samples studied (~20 MJ/kg) was measured in a bomb calorimeter (Parr 1260, Parr Instrument Company, Moline, IL); this is lower than that of coal, possibly due to the low fixed-carbon and high oxygen contents in the samples [23]. The ultimate analysis indicates that palm oil waste is environmental friendly, with trace amounts of nitrogen, sulfur, and mineral matter.

2.2. Experimental apparatus and methods

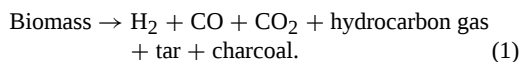
The pyrolysis of biomass was studied in a thermogravimetric analyzer (Model TA 2050, from TA). Details of the flow rate and mass of sample have been published [24]. The experimental procedure was briefly as follows. First, the sample was heated up at 10 °C/min to 150 °C from the ambient temperature and kept isothermal for 5 min to remove moisture. Generally, after removing any moisture, a flat baseline for a weight loss curve could be observed. Then, it was heated up to 900 °C and kept there for 3 min. To mitigate any problems caused by heat and mass transfer, the sample size was maintained at ~20 mg for every experiment. To remove gaseous and condensable products from the TGA furnace and minimize any secondary vapor-phase interactions, the flow rate of carrier gas (N₂) was kept at 120 ml/min; this is the largest flow rate permitted by the TGA.

The gases released in the TGA were swept immediately to a gas cell, followed by the FTIR (BioRad Excalibur Series, Model FTS 3000) analysis using a deuterated triglycine sulfate (DTGS) detector. The transfer line and gas cell were heated to an internal temperature of 230 °C, to avoid condensation or adsorption of semivolatile products. Each IR spectrum was obtained in 5 s and the IR scanning range was from 4000 to 500 cm^{-1} .

For an in-depth investigation of the influence of temperature, a biomass was pyrolyzed in the TGA at 250, 280, 300, 325, 355, 400, and 450 °C. The samples were heated up separately from the ambient to the selected temperature at a much higher rate of 30 °C/min, to minimize any potential influence of heating. The selected temperature was maintained for 120 min, i.e., when generally no more weight loss was observed because pyrolysis was complete. After that, the sample was continuously heated up to 900 °C to record any further weight loss.

2.3. Thermodynamic calculation

The thermodynamic calculations were performed using HSC-Chemistry 4.0 software, based on the minimization of the Gibbs free energy of the system [25], subject to the usual constraint of mass being conserved for each chemical element. The palm oil wastes studied have negligible ash contents (see Table 1), so to simplify the computations, only the main elements C, H, O, N, and S were taken into account [26]. Inorganic elements such as Si, Ca, Mg, K, Al, Cl, and P, were regarded as the nonprocess elements and so were not involved in the calculations, because of their trace contents and lack of reactivity with organic components [27,28]. The pyrolysis of biomass can be simplified to



In the calculations, the following species were considered: H, H₂, C, CO, CO₂, CH₄, C₂H₂, C₂H₄, CH₃OH, CH₂O, HCOOH, CH₃COOH, CH₃OCH₃, CH₃CHO, C₃H₆O, C₆H₅OH, C₄H₄O, C₄H₈O, C₃H₄O₂, C₃H₆O₂, C₂H₄O₃, C₅H₆O, C₅H₈O, C₄H₄O₂, C₄H₆O₂, C₅H₄O₂, C₆H₈O, C₅H₆O₂, C₅H₈O₂, C₅H₁₀O₂, C₆H₆O₂, C₅H₆O₃, C₅H₈O₃, C₅H₈O₄, C₆H₁₂O₂, C₆H₆O₃, C₆H₁₂O₆, O, O₂, H₂O, OH, N, N₂, NH₃, NO, NO₂, CN, HCN, S, H₂S, SO₂, SO₃, CS, COS. All gaseous products were assumed to behave ideally, and all condensed products were treated as pure phases; carbon (as graphite) was the only solid species considered [29]. The elements C, H, O, N, and S were taken as inputs. Temperatures of 200–1200 °C and a pressure of 1 atm were considered. Fiber was selected as the representative palm oil

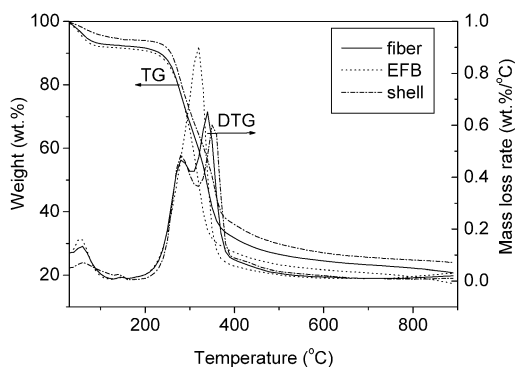


Fig. 1. The curves of weight loss for the palm oil wastes being heated up.

wastes, because it contains some nitrogen and sulfur, so facilitating an investigation of the effects of S and N being present. The composition of the fiber is C, 1 mol; H, 1.69 mol; O, 0.54 mol; N, 0.007 mol; and S, 0.005 mol.

3. Results and discussion

3.1. TGA-FTIR analysis of palm oil wastes pyrolysis

Fig. 1 shows the TGA pyrolysis curves of the three palm oil wastes. About 20–30 wt% of the sample was left as charcoal residues at 900 °C and the rest (~70 wt% of the sample) was evolved into the gas phase. As for the rate of mass loss (Fig. 1), the fiber and shell have similar patterns with two peaks, whereas only one big peak was found with EFB. The degradation of palm oil wastes happened at relatively low temperatures (200–500 °C), similar to other types of biomass [13,16].

The gaseous products of pyrolysis have a typical IR spectrum as in Fig. 2 for the fiber being pyrolyzed at 344 °C. The main gas components (CO₂, H₂O, CH₄, CO, and some organics) are shown. In fact, the “organics” are a mixture of acids, aldehydes, alkanes, ethers, etc. They are possibly formaldehyde (CH₂O), acetaldehyde (CH₃CHO), methanol (CH₃OH), formic acid (HCOOH), phenol (C₆H₅OH), acetone (CH₃COCH₃), etc., according to our database search and the literature [30,31]. Because of the low sulfur and nitrogen contents of the fiber (see Table 1), no N- or S-containing compounds were detected. In addition, some gases like H₂, N₂, O₂, and H₂S have weak or no IR absorption and so are undetectable by FTIR [30]. However, H₂ is of major interest and will be quantified using micro-GC in the future.

Fig. 3 shows the FTIR profile of gaseous products from pyrolyzing the fiber in the TGA at a heating rate

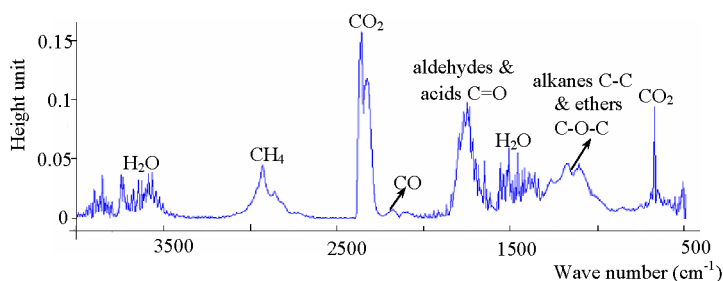


Fig. 2. A typical IR spectrum of the products from pyrolyzing the fiber at 344 °C.

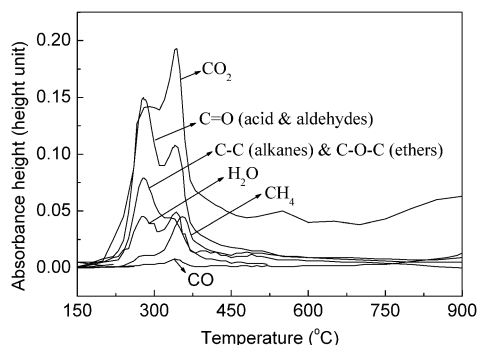


Fig. 3. FTIR profiles of fiber pyrolysis.

of 10 °C/min from 150 to 900 °C. Below 150 °C, no gas, except for water vapor, is produced. The height of an IR peak was used to qualitatively describe the changing concentration of each gas with respect to temperature. Fig. 3 shows that CO₂, CH₄, CO, and some C_{1–2} hydrocarbons are the main gaseous products, released at 220–400 °C. This corresponds well with the previous observation of weight loss in Fig. 1. The release of CO₂ first increases with temperature and reaches a first small peak at 290 °C; with a further increase of temperature it continuously increases and gets its second peak and maximum at 340 °C. The FTIR profiles of organics in Fig. 3 are different from CO₂. They start to appear at lower temperatures and have a maximum at about 280 °C. The production of CH₄ and CO happens, compared to CO₂ and organics, at higher temperatures of 320–400 °C, with maxima at about ~360 and 345 °C, respectively.

Although Fig. 3 is only qualitative, it provides sufficient information to understand the appearance of each gas from fiber pyrolyzing at different temperatures. For a clearer analysis, the relative area under every peak was calculated, based on Fig. 2, according to the following: the area for CO₂ was calculated from 2400 to 2260 cm⁻¹, organics from 900 to 1900 cm⁻¹, H₂O from 4000 to 3600 cm⁻¹, CH₄ from 2700 to 3200 cm⁻¹, and CO from 2400 to 2260 cm⁻¹ [30]. However, the area obtained between 900 and 1900 cm⁻¹ for organics might also include a

minor contribution from water, which also absorbs at ~1500 cm⁻¹ (see Fig. 2).

As the pyrolysis of palm oil wastes happens mainly at 200–500 °C (see Figs. 1 and 3), the total yield of gaseous products was calculated for this same temperature range (Table 2). The yields of CO₂, CO, and H₂O from EFB are the highest from the three wastes (highlighted in bold), whereas the highest yield of CH₄ was found with the fiber and the highest organic yield was from the shell, no doubt due to their different chemical compositions. EFB has the highest amounts of O and H, probably causing the higher yields of CO, CO₂ and H₂O. Fiber has a lower H content than shell, but the latter has the highest C content of the three palm oil wastes.

3.2. Influence of temperature on palm oil waste pyrolysis

An in-depth investigation of the effect of temperature was carried out at 250, 280, 300, 325, 355, 400, and 450 °C. The pyrolysis curves of the fiber from palm oil wastes, at different isothermal temperatures, are plotted in Fig. 4 (TGA curves) and Fig. 5 (DTG curves). In Fig. 4, the result of pyrolyzing the fiber from ambient to 900 °C at 30 °C/min (dotted line) is also shown for comparison with the other 7 cases, where different isothermal temperatures are selected. For case 1, with an isothermal temperature of 250 °C, ~30 wt% of fiber was decomposed for 120 min at 250 °C. After that, further weight loss (~35 wt%) was observed when the temperature was continuously increased to 900 °C. With an isothermal temperature of 355 °C, more weight was lost during the isothermal period (120 min) and even in the ramping period from the ambient to the selected temperatures (for cases 4 and 5), so that less weight was lost in the follow-ups. The plots in Fig. 4 for cases 6 and 7 are very close to that observed when the temperature rose from ambient directly to 900 °C without an isothermal period.

In Fig. 5, it can be seen that after the sample was kept isothermal for 10–12 min, pyrolysis at the selected temperature was completed because no more obvious weight loss occurred (mass loss rate

Table 2

Yields of gas products from palm oil waste pyrolysis (200–500 °C)

Sample	Total relative area of absorbance peaks (area unit/g of waste)				
	CO ₂	Organics	CH ₄	CO	H ₂ O
Fiber	72239	184425	27489	2902	44474
Shell	74561	194734	25358	3309	47704
EFB	82260	193380	23339	4879	48525

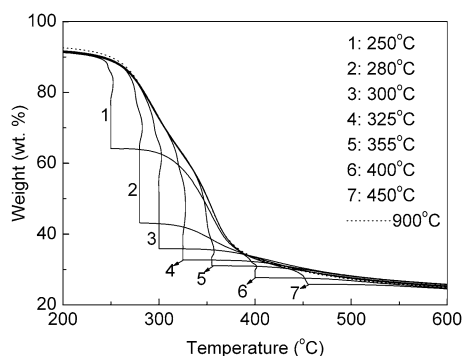


Fig. 4. TG curves of fiber pyrolysis at different temperatures.

<0.85 wt%/min). Thus, isothermal conditions for 120 min is far in excess of that required for complete pyrolysis at the selected isothermal temperature. Fig. 5 shows that at 250 °C, the rate of mass loss is very slow (<1.5 wt%/min). At 325 °C, it is ~13 wt%/min and only one peak is observed at or below 325 °C. However, when the isothermal temperature was increased to over 355 °C (cases 5, 6, and 7), two peaks were found, indicating a different mechanism of decomposition. It seems that at low temperatures (<355 °C), pyrolysis of the fiber is mostly likely controlled by kinetics, so the temperature has a big effect.

The yields of gas and the residues after pyrolysis at different temperatures are listed in Table 3. In this study, the yield of liquid oil (tar), although it was partly deposited inside the outlet tubing of the TGA, was not considered separately due to the smallness of the sample. With the current equipment, it proved almost impossible to collect and quantify the tar formed. Therefore, the yield of gas in Table 3 actually includes both gas and oil. The yield of gas increased greatly with temperature, whereas the yield of char decreased sharply. This is consistent with previous observations [4–7], even though those operating temperatures were much higher (550–900 °C).

The gaseous products from pyrolyzing the fiber at different isothermal temperatures are shown in Fig. 6. The IR scan started at 150 °C and lasted for 40 min; a spectrum was recorded every 5 s. On changing the isothermal temperature, CO₂ and organics demonstrate almost similar profiles for their release, while

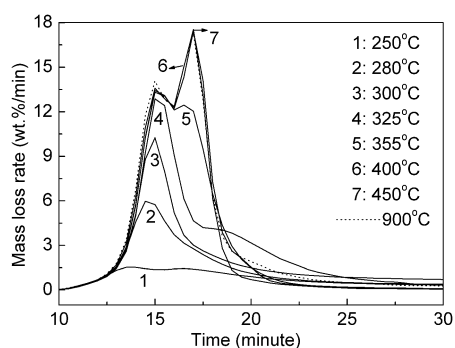


Fig. 5. DTG curves of fiber pyrolysis at different temperatures.

CO and CH₄ are also quite similar. For the first pair (CO₂ and organics), little was released at 250 °C (case 1). Up to 355 °C (cases 2 to 5), the release of CO₂ and organics increased sharply. Above 355 °C (cases 6 and 7), the total amount of these two components decreased relative to case 5; their release profiles are similar to that observed when the temperature was raised directly from ambient to 900 °C (not shown here). It is noteworthy that the profiles for CO₂ and the organics showed two peaks for cases 6 and 7; this is consistent with the DTG curves in Fig. 5.

As for CO and CH₄ in Fig. 6, their release at low temperatures (250–325 °C) is generally insignificant. However at or over 355 °C, significantly more of them appear. CO has its highest release at 355 °C; CH₄ has its at 400 °C. Only one big peak is observed for CO and CH₄, different from CO₂ and organics.

The similarity of the DTG curves in Fig. 5 to the FTIR profiles for CO₂ and organics in Fig. 6 suggests that the formation of these two components might dominate pyrolysis. There is a difference between the observations at 250–325 °C and those over 355 °C, when two peaks appear instead of one. Maybe this implies two different mechanisms with the temperature of 355 °C being a boundary. One possibility is that primary thermal decomposition happens below 355 °C, whereas secondary thermolysis above 355 °C involves aromatization [10]. Although the rate of pyrolysis (see Fig. 5) could be larger above 355 °C, the release of CO₂, organics, and CO is greatest at 355 °C, except for CH₄ which maximizes at a slightly higher temperature 400 °C.

Table 3
Gas and char yields of fiber pyrolysis at different temperatures (wt%)

Reaction temperature (°C)	250	280	300	325	355	400	450	900
Gas yield	26.8	49.1	56.4	59.5	61.1	63.0	65.8	70.6
Char + ash	65.2	42.9	35.7	32.5	31.0	28.8	25.8	21.4

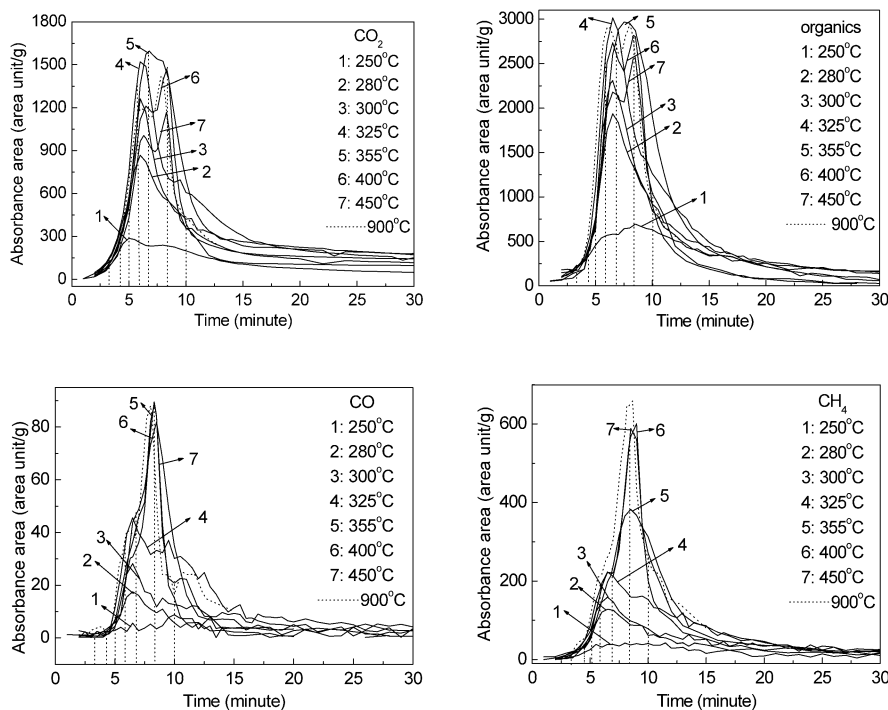


Fig. 6. Gaseous products from pyrolyzing the fiber at different temperatures.

In Fig. 6, from left to right the 7 vertical dotted lines mark the time when an isothermal period started and the temperature stopped being increased at 30 °C/min. It will be seen that the profiles of different gases to the left of a dotted line almost overlapped, due to the temperature being the same. However, big differences at the right-hand side demonstrate the significant influence of the isothermal temperature on the distribution of the products from pyrolysis. For cases 6 and 7, most mass was lost during the temperature ramp.

The total yield of every gas was estimated from the integrals of their FTIR spectra. The initial time was taken at 150 °C in the TGA and lasted for 40 min; the results are listed in Table 4. The yields of CO₂, CH₄, CO, and organics increased with temperature to 355 °C, when all the gases reached their highest yields. This might be accounted for by the fiber containing mostly hemicellulose and lignin. At 300–350 °C, the former gives off mostly CO₂, CH₄, and CO, while the latter releases almost only CO₂ during pyrolysis. From 355 to 450 °C, the yield of CO₂

and organics (the two major gas components) decreased sharply, while those of CH₄ and CO increased slightly. However, the total amount of gas released (as evaluated by TGA in Table 3) increased monotonically from 250 to 450 °C, different from the results using FTIR (see Table 4). It accordingly seems that other gases, which cannot be detected by FTIR, are released above 355 °C. Most possibly, H₂ is evolved at high temperatures, as indicated by other experiments [4–6]. This will also be confirmed in the following thermodynamic calculations.

3.3. Thermodynamic calculations

The first thermodynamic calculation considered the elements C, H, O, N, and S and ~50 species; the results for pyrolyzing the fiber are plotted in Fig. 7. The species present in significant amounts are H₂, H₂O, CO, CO₂, CH₄, and solid carbon. None of the hydrocarbons considered, other than CH₄, is thermodynamically stable under these pyrolysis conditions. Although some organics such as acetylene, ethylene,

Table 4
Yields of gas products of fiber pyrolysis at different temperatures

Temperature (°C)	Total absorbance area (area unit/g)			
	CH ₄	CO ₂	CO	Organics
250	560	3347	65	9719
280	1101	7014	145	13946
300	1379	9241	233	15467
325	2075	10814	340	18316
355	2752	11643	350	19921
400	2478	9226	253	14585
450	2781	6968	273	13959

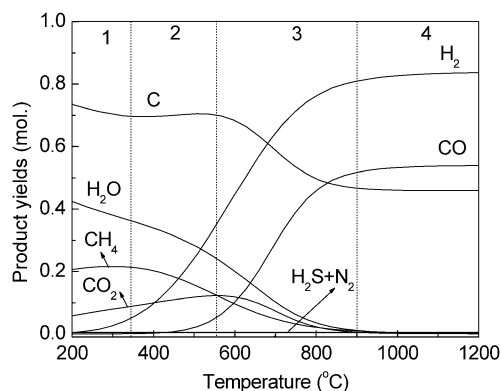


Fig. 7. Calculated species from the pyrolysis of fiber.

and higher hydrocarbons are produced in pyrolysis or gasification reactors [4–6], they are not thermodynamically favorable species [32]. Therefore, in the following calculations, the hydrocarbons with two or more C atoms per molecule will not be taken into account.

The traces of nitrogen and sulfur in biomass are released as N₂ and H₂S, respectively; their concentrations are trivial, so N and S were excluded in subsequent calculations, which considered only H₂, CO, CO₂, CH₄, H₂O, and solid carbon. Additional calculations were carried out with EFB and shell at the following conditions: pressure 1 atm, temperature 200–1000 °C, inputs of shell, C, 1 mol; H, 1.61 mol; O, 0.51 mol, and inputs of EFB, C, 1 mol; H, 1.8 mol; O, 0.62 mol. The results for the three wastes are plotted in Fig. 8, which shows that the three wastes produce the same patterns of gaseous products when plotted against temperature. The reactions involved in pyrolysis are generally [12,33,34] listed as

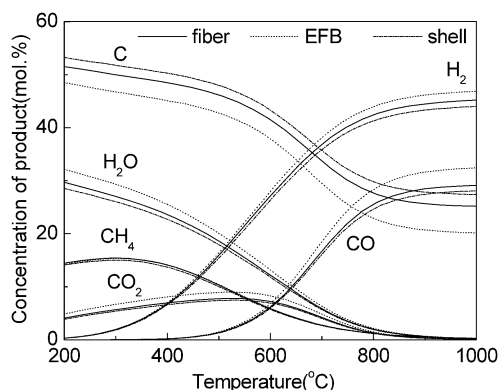
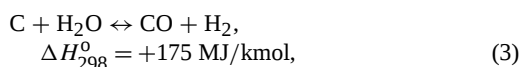
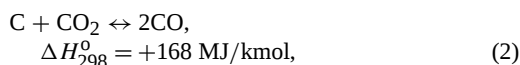
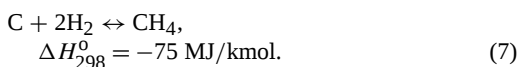
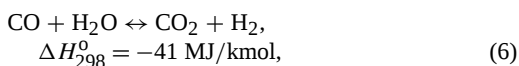
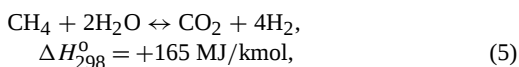
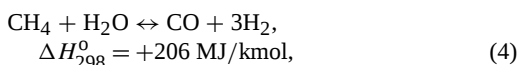


Fig. 8. Calculated species from the pyrolysis of palm oil wastes.



The pyrolysis of palm oil wastes can be divided into four temperature zones, as in Fig. 7. In the first zone (<340 °C), biomass becomes dehydrated; also water vapor, CO₂, and volatile organics (CH₄) are given off. Most likely they react with carbon (the major component in Zone 1) in reactions (2) and (3) and form H₂ and CO at higher temperatures (600–1000 °C). Nevertheless, the slightly exothermic reactions of CO with H₂O (reaction (6)) and of H₂ with C (reaction (7)) favor the steady formation of CO₂ and CH₄ at relatively low temperatures (500–600 °C). This accounts for the decrease of both C and water, but an increase of CH₄ and CO₂ in Zone 1. The second zone is for 340–560 °C, where the contents of CH₄ and water decrease, but CO₂ increases. Solid carbon remains almost constant. There is also some H₂ and CO evolved. The main reactions in Zone 2 should be (4) and (5). In Zone 3 (560–900 °C), secondary reaction occurs in (2) and (3), which control pyrolysis. Reaction (4) continuously occurs, causing the further decrease of CH₄ content. The amounts of H₂ and CO increase, but C, H₂O, CO₂, and CH₄ all fall. During the last zone (>900 °C), pyrolysis ends; almost no reaction occurs. The contents of H₂ (45 mol%) and CO (30 mol%) remain high and stable. The carbon residue can be regarded as charcoal formed by carbonization.

An increase in temperature favors endothermic reactions. Therefore, reactions (2)–(5) are shifted to the

right, whereas reactions (6) and (7) shift in the opposite direction if the temperature is increased. H_2 and CO have their highest yields at the highest temperatures, whereas most CH_4 and H_2O are obtained at the lowest temperatures. These predicted results are similar to the simulations by Zhang [10]; they are supported by the experimental results of others [4–6,13]. High temperatures do favor the production of H_2 as predicted. This supports our previous assumption of H_2 being produced above 355 °C. The predicted trend of decreasing amounts of C residue at higher temperatures is also consistent with the experiments results from the TGA (see Table 3). The corresponding temperatures used for grouping the four zones (Fig. 7) might not be the same as those found in real situations, due to the limitations of thermodynamic calculations and the big differences between an experiment in a TGA (an open system) and the calculations (for a closed system). Nevertheless, the calculation provides insight into the influence of temperature on the gases produced.

4. Conclusions

Temperature has a significant influence on the pyrolysis of palm oil wastes, particularly on the distribution of gaseous products. The different patterns of the rate of pyrolysis and the profile for evolution of gas at low (<355 °C) and high temperatures (>355 °C) indicate that different reaction pathways (or mechanisms) are involved. Pyrolysis is probably controlled by kinetics when the temperature is lower than 355 °C, where the rate of pyrolysis increased markedly with temperature. The experimental study using TGA-FTIR and thermodynamic modeling both indicate similar results: the total yield of gas increases with temperature at the expense of char residue.

As for the individual species (CO_2 , CH_4 , CO, H_2O , and some organics) identified by TGA-FTIR, the profiles of their evolution differ from each other. The major components have their maximum rate of evolution at 355 °C based on FTIR, but TGA results show a continuous increase of total yield at higher temperatures. The large amounts of H_2 produced above 355 °C are thus reasonably postulated.

Simulations of thermodynamic equilibrium indicate that H_2 , CO_2 , CH_4 , and CO are the main gaseous products. They confirm that H_2 is produced only at high temperatures. The yields of H_2 and CO increased with temperature and have maximum yields of 45 and 30 mol%, respectively, at temperatures higher than 900 °C. The yields of H_2O , CO_2 , and CH_4 decrease if the temperature increases and become essentially zero at high temperatures (>800 °C).

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