# Mechanism of Palm Oil Waste Pyrolysis in a Packed Bed

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To better understand the process mechanism, pyrolysis of palm oil wastes was investigated at different temperatures in a packed bed, with focus on the changing of chemical structure and physical characteristics of solid residues and gas-releasing properties. First, three palm oil wastes were pyrolyzed with temperature increasing from the ambient to 1000 °C, and the main products from it were solid charcoal, liquid oil, and hydrogen-rich gas. The gas component mainly consisted of $H_2$, $CO_2$, CO, and $CH_4$ together with trace $C_2H_4$ and $C_2H_6$. CO and $CO_2$ evolved out at lower temperature ($<450$ °C), while $H_2$ released at higher temperature (600−700 °C). Second, the decomposition property of biomass shell was analyzed at variable temperatures (300, 400, ..., 1000 °C). The pyrolysis products were thoroughly identified using various approaches (including micro-GC, FTIR, GC-MS, ASAP2010, SEM, and CNHS/O analyzer) to understand the influence of temperature on product properties and, thus, reaction mechanism involved. Starting from low temperature at 300 °C, CO and $CO_2$ evolved out easily because of the breaking of carbonyl and carboxyl functional groups, and the releasing of $CH_4$ increased at the price of CH alkyl breaking and diminishing. Following that, at temperature $>$ 400 °C, aromatic rings broke gradually with a lot of $H_2$ evolving out. Meanwhile, a large amount of pores in the biomass sample were opened in the course of pyrolysis, and the Brunauer−Emmett−Teller (BET) surface area increased greatly. The maximum yield of oil was achieved at 500 °C, and it is a mixture of acid, ether, phenol, etc. High temperature ($>700$ °C) was favorable for the evolving of hydrogen-rich gases, while medium temperature (500−600 °C) was recommendable for a higher generation of liquid oil and charcoal with a large BET surface area and fine pore size.

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## 1. Introduction

Recently, because of the depletion of fossil fuels and the concern on energy supply security, biomass energy has attracted increasing attention worldwide. One of the main local biomass resources in Southeast Asia is palm oil waste (including oil-palm empty fruit bunch (EFB), fiber, and shell). About 9.9 million tons of palm oil wastes are generated every year in Malaysia alone, and this keep increasing at 5% annually.[1]

Pyrolysis is one of the most promising technologies of biomass utilization, and it is also the first stage of biomass thermochemical conversion, which converts biomass resource to solid char, liquid oil, and hydrogen-rich gas. However, it is essentially a complex process. The yields and compositions of end products of pyrolysis are highly dependent on biomass species, chemical and structural composition of biomass, temperature (temperature−time history), heating rate, reactors, and others.[2−5] To achieve an advanced process for improved product yields from pyrolysis of selected biomass, in-depth investigations on the mechanism of biomass pyrolysis are needed.

Temperature is one of the most critical parameters in controlling the biomass pyrolysis performance, particularly on the yield distribution of solid, liquid, and gas products.[5] Various experimental studies have investigated the influence of temperature on pyrolysis using different reactors, such as fixed-bed,[6] fluidized-bed,[7] thermogravimetric analyzer (TGA),[8] and others,[9,10] with focuses on the yield of different products as a function of temperature. It was observed that higher temperature is in favor of production of hydrogen-rich gases.[9] Depending on temperature, the char fraction might contain inorganic

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[1] Mahlia, T. M. I. Dynamic modeling, simulation, and experimental validation of a palm oil mill boiler. In *M. Eng. Sci.*; University of Malaya: Kuala Lumpur, Malaysia, 1997.

[2] Di Blasi, C.; Signorelli, G.; Di Russo, C.; Rea, G. Product distribution from pyrolysis of wood and agricultural residuals. *Ind. Eng. Chem. Res.* **1999**, *38*, 2216−2224.

[3] Demirbas, A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers. Manage.* **2001**, *42* (11), 1357−1378.

[4] Yaman, S. Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Convers. Manage.* **2004**, *45*, 651−671.

[5] Demirbas, A.; Arin, G. An overview of biomass pyrolysis. *Energy Sources* **2002**, *24* (5), 471−482.

[6] Ates, F.; Putun, A. E.; Putun, E. Fixed bed pyrolysis of Euphorbia rigida with different catalysts. *Energy Convers. Manage.* **2005**, *46* (3), 421−432.

[7] Garcia, A. N.; Font, R.; Marcilla, A. Gas Production by Pyrolysis of Municipal Solid Waste at High Temperature in a Fluidized Bed Reactor. *Energy Fuels* **1995**, *9* (4), 648−658.

[8] Yan, R.; Yang, H. P.; Chin, T.; Liang, D. T.; Chen, H. P.; Zheng, C. G. Influence of temperature on the distribution of gaseous products from pyrolyzing palm oil wastes. *Combust. Flame* **2005**, *142*, 24−32.

[9] Chen, G.; Andries, J.; Luo, Z.; Spliethoff, H. Biomass pyrolysis/gasification for product gas production: The overall investigation of parametric effects. *Energy Convers. Manage.* **2003**, *44* (11), 1875−1884.

[10] Yu, Q. Z.; Brage, C.; Chen, G. X.; Sjostrom, K. Temperature impact on the formation of tar from biomass pyrolysis in a free-fall reactor. *J. Anal. Appl. Pyrolysis* **1997**, *40−41*, 481−489.

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**Table 1. Proximate and Ultimate Analyses of Biomass Samples**[a]

| | proximate analysis (wt %) | | | | ultimate analysis (wt %, d) | | | | | LHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|---|---|
| | $M_{ad}$ | $V_{ad}$ | $A_d$ | $FC_{ad}$ | C | H | N | S | O[b] | |
| shell | 5.73 | 73.74 | 2.21 | 18.37 | 53.78 | 7.20 | 0.00 | 0.51 | 36.30 | 22.14 |
| fiber | 6.56 | 75.99 | 5.33 | 12.39 | 50.27 | 7.07 | 0.42 | 0.63 | 36.28 | 20.64 |
| EFB | 8.75 | 79.67 | 3.02 | 8.65 | 48.79 | 7.33 | 0.00 | 0.68 | 40.18 | 18.96 |

[a] M, moisture content; *V*, volatile matters; *A*, ash; FC, fixed carbon; ad, on air-dried basis; d, on dry basis. [b] The O content was determined by difference.

materials, certain unconverted organic solid and carbonaceous residues which generally decreased with temperature increases.[4] The pyrolysis liquid is a complex mixture of oxygenated aliphatic and aromatic compounds.[11] Yu et al.[10] found that the yield of total tar and phenolic compounds decreased whereas aromatics compounds increased with temperature increasing from 700 to 900 °C. Although a number of studies on the effect of temperature have been carried out, the forming behavior of gas, liquid oil, and solid charcoal at different temperatures as well as the mechanisms related were rarely reported. However, these are necessary knowledge, which could benefit the design of biomass pyrolysis reactor and process optimization. The insufficient availability of basic information hindered the further development of biomass utilization via pyrolysis.

In this study, the devolatilization behavior of palm oil wastes was investigated in a packed-bed reactor, with focus mainly on the releasing profile and forming behavior of biomass pyrolysis products (gas product, solid charcoal, and liquid oil), and also on the related physicochemical pathway under varied temperatures. An in-depth analysis of the properties of the product generated at different temperatures is favorable for a better understanding of the mechanism of biomass pyrolysis.

## 2. Experimental Section

**2.1. Sample.** The three palm oil waste samples (shell, fiber, and empty fruit bunches (EFBs)) 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, U.S.A.); i.e., all the samples studied here were smaller than 1 mm in size. The proximate and elemental analysis results are listed in Table 1, and the details on the analytical methods can be found in our previous work.[12] The chemical structures of the original palm oil waste samples were further identified using Fourier transform infrared spectrometer (FTIR); the detailed analytical method will be introduced later in Section 2.3.2.

**2.2. Experimental Setup and Procedure.** The pyrolysis of palm oil wastes was carried out using the packed-bed reactor plotted in Figure 1. The system consisted essentially of a quartz tube (height = 390 mm, i.d. = 38 mm, and o.d. = 42 mm) with a corundum sample crucible, a cooling system for the separation of water and condensable organic vapors (tar), and a gas cleaning/drying system followed by gas-measurement devices. For every trial, ∼2 g of sample in the corundum crucible was placed into the reactor prior to heating. Inert purging gas (pure $N_2$) was provided from the bottom of the reactor at 120 mL/min to maintain the pyrolysis atmosphere.

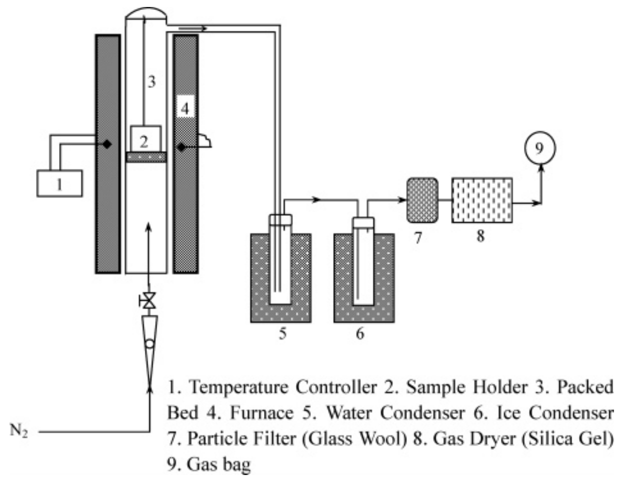

**Figure 1.** Scheme of packed-bed reactor system.

When pyrolyzing the three palm oil wastes, the furnace was heated to 1000 °C from the ambient temperature at 10 °C/min. With temperature increasing, the biomass sample decomposed and volatiles were purged out by $N_2$. Following that, the condensable volatiles were collected in the ice−water condenser, whereas those noncondensed parts were filtered and cleaned through a glass wool filter and the gas was dried using silica gel. The gas product was then collected using a gasbag and analyzed using micro gas chromatography (micro-GC). The gas generated in the course of a pyrolysis trial was collected for every 5 min. The initial gas-sampling time started as the furnace temperature reached 200 °C and continued for every 5 min until the pyrolysis was completed. In other words, the gas product was collected at several temperature ranges including 200−250, 250−300, ..., 850−900, and 950−1000 °C.

The influence of different final temperatures (300, 400, 500, ..., 900, 1000 °C) on the properties and distribution of generated solid charcoal, liquid oil, and gases from shell pyrolysis was also investigated. The experimental procedure was as follows. The ground shell sample (∼2 g) was put in the reactor. Then the furnace was heated to the selected temperature at 10 °C/min and kept isothermal for 30 min to complete the pyrolysis.[8] The gas sample was sequentially collected using a gasbag with temperature increasing from 200 °C to the selected temperature and till the end of experiment. Then, it was immediately analyzed using micro-GC. Other conditions were the same as previously mentioned.

After each trial, the furnace was cooled instantly. The pyrolysis residue was weighed and recorded as the solid char yield. Gas yield was calculated by combining all the gases collected in the whole temperature range and was converted from volume to weight percentage at ambient temperature and atmospheric pressure (the volume of 1 mol gas equals 24.45 L at 1 atm and 25 °C). The yield of liquid oil, which consisted of tar, organic oils, water, and some fine particles, was obtained by difference. To analyze the components of liquid oil, the condenser and the connecting tubes between the furnace and the condenser were washed using acetone. The collected solution was dried at 70 °C to remove the acetone and water, and the residue was mostly the liquid oil. Then, the collected organics were dissolved in fresh acetone and filtered to remove the fine particles for further analysis using gas chromatography-mass spectroscopy (GC-MS).

**2.3. Analytical Methods. 2.3.1. Gas Analysis.** Micro gas chromatography (GC) has been used to analyze qualitatively and quantitatively the gas components from biomass conversion,

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(11) Meier, D.; Faix, O. State of the art of applied fast pyrolysis of lignocellulosic materials−A review. *Biosource Technol.* **1999**, *68* (1), 71−77.

(12) Yang, H. P.; Yan, R.; Chin, T.; Liang, D. T.; Chen, H. P.; Zheng, C. G. TGA-FTIR analysis of palm oil wastes pyrolysis. *Energy Fuels* **2004**, *18* (6), 1814−1821.

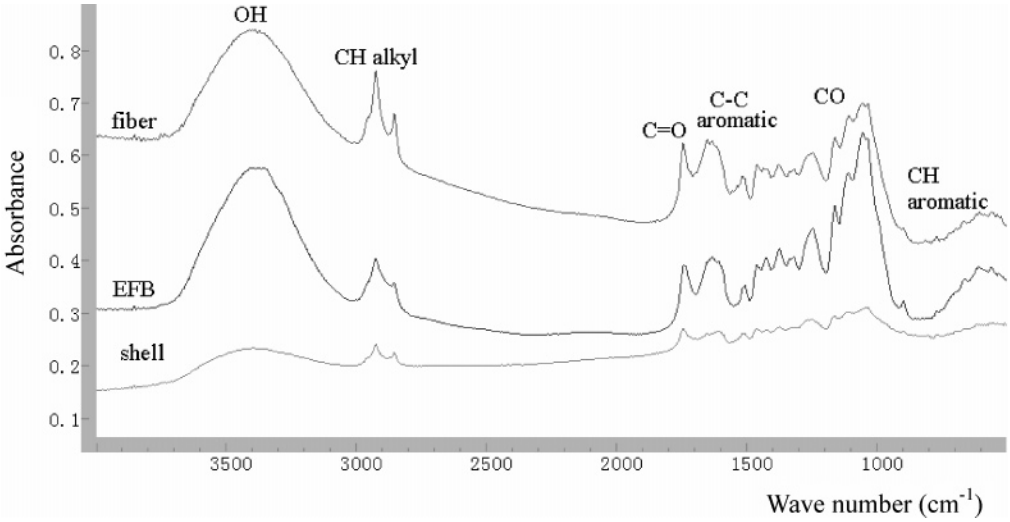

**Figure 2.** FTIR spectra of the dried palm oil waste samples.

because of the following advantages: small amount of sample ($\times 10^{-6}$ cm$^3$) needed, short retention times (~160 s), high accuracy, speed, and profitability.[13,14] In this study, the gas product from palm oil shell pyrolysis was analyzed using a dual-channel micro-GC (Varian, CP-4900) with thermal conductivity detectors (TCD). Channel A with molecular sieve 5A column (MS-5A) was set at 95 °C for determination of $H_2$, CO, and $CH_4$. Channel B with Porapak Q (PPQ) was set at 60 °C for checking $CO_2$, $C_2H_4$, and $C_2H_6$. A cylinder of standard gas (containing $H_2$ 35.89 mol %, CO 20.01 mol %, $CH_4$ 10.16 mol %, $CO_2$ 29.94 mol %, $C_2H_4$ 1 mol %, $C_2H_6$ 1 mol %, and $C_2H_2$ 2 mol %) was purchased from a commercial gas company, and the calibration was carried out regularly. Each gas sample was measured thrice to get the average. The gasbags were cleaned by $N_2$ purge and vacuumed after each trial of gas sampling.

**2.3.2. Solid Charcoal Analysis.** The collected solid charcoal from pyrolysis at different temperatures was ground to fine particles and followed by identification using different approaches. First, the charcoal sample was mixed with KBr powder to prepare the pellets for FTIR analysis. The total weight of the pellet was 150 mg, and the ratio of sample to KBr powder was kept at about 1:149. The mixture of charcoal and KBr powder was dried in the oven at 105 °C for overnight.[15] The pellet was made under the same conditions, including the sample weight, size of pellet, pelleting time, and pressure. The instrumental parameters settings were as follows: resolution 4 cm$^{-1}$, sensitivity 1, speed 2.5 KHZ, filter 1.2, UDR 2, scans to co-add 20, aperture source 4−2000 cm$^{-1}$. Prior to each measurement, the instrument was run to establish the background, for which KBr was taken as the reference. The background was then automatically subtracted from the sample spectrum. To compare with the raw biomass samples and, thus, to understand the change of chemical structure of biomass treated by different temperatures, the FTIR analysis was also conducted for the three original palm oil wastes under the same conditions.

The surface property (surface area, pore distribution, and volume) of solid charcoal was examined using an accelerated surface area porosimetry (ASAP 2010) instrument. It was detected using liquid $N_2$ at 77 K. Moreover, the main organic components (C, H, O, N, and S) of the solid charcoal were analyzed using Perkin-Elmer instruments, series II CNHS/O 2400 analyzer. Scanning electron microscopy (SEM), model JSM-5310V, JEOL (Japan), was also used to understand the pore properties of solid charcoal generated from biomass pyrolysis.

**2.3.3. Liquid Oil Analysis.** The collected liquid oil was first identified using FTIR. Oil was dissolved in 100 mL of acetone solution, and 2 mL of the solution was added on to a KBr pellet. The pellet was heated at 70 °C for 2 min to allow acetone to be fully vaporized to minimize the interference of absorbance caused by acetone. A thin film of organics was, thus, formed on the KBr pellet and absorbed IR spectra. The instrumental parameter setting is the same as that for charcoal analysis. In this case, KBr with acetone was taken as a reference for establishing the background.

The component of the liquid oil was further analyzed using gas chromatography coupled with a mass selective detector (GC6890N/MSD5973, Agilent technologies). An HP-FFAP capillary column (30 m × 0.25 mm i.d. × 0.25 $\mu$m d.f.) was used. The oven program consisted of 2 min of isothermal at 40 °C and then a ramp to 100 °C at 1 min, followed by 0.2 min of isothermal at this temperature. The oven was continuously heated to 105 °C at 2 °C/min, and then it was heated to 250 °C at 30 °C/min and maintained for 2 min. Helium was taken as a carrier gas at a 1.2 mL/min constant flow rate. The injector was pulsed splitless at 200 °C; pulsed pressure and time were set at 25.0 psi for 1 min, purge flow and time were set at 50.0 mL/min for 0.25 min, and gas saver flow and time were set at 20 mL/min for 3 min.

## 3. Results and Discussion

**3.1. Chemical Structure of Palm Oil Wastes.** The IR spectra of the dried palm oil wastes are shown in Figure 2. The spectra contain not only the characteristic signals of carbohydrates but also those of lignin.[16,17]— They are (1) O−H stretching vibration

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(13) Rapagna, S.; Jand, N.; Foscolo, P. U. Catalytic gasification of biomass to produce hydrogen rich gas. *Int. J. Hydrogen Energy* **1998**, *23* (7), 551−557.

(14) Schmieder, H.; Abeln, J.; Boukis, N.; Dinjus, E.; Kruse, A.; Kluth, M.; Petrich, G.; Sadri, E.; Schacht, M. Hydrothermal gasification of biomass and organic wastes. *J. Supercrit. Fluids* **2000**, *17* (2), 145−153.

(15) Xie, K.-C. Coal structure and its reactivity. Science Press: Beijing, 2002; p 119 (in Chinese).

(16) Bilba, K.; Ouensanga, A. Fourier transform infrared spectroscopic study of thermal degradation of sugar cane bagasse. *J. Anal. Appl. Pyrolysis* **1996**, *38*, 61−73.

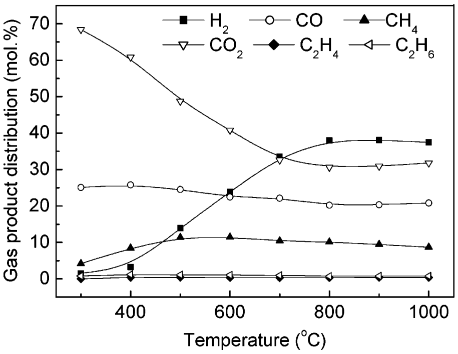

**Figure 3.** Gas product evolving profile from shell pyrolysis.

(3100−3600 cm$^{-1}$), O−H bending (1333 cm$^{-1}$), and O−H association (1108 cm$^{-1}$); (2) C−H$_n$ (alkyl and aromatic) stretching vibration (2860−2970 cm$^{-1}$), C−H bending vibration (1400−1460 cm $^{-1}$), and aromatic hydrogen (700−900 cm$^{-1}$); (3) C=O stretching vibration (1700−1730 cm$^{-1}$ and 1510−1560 cm$^{-1}$); (4) C−O stretching vibration (1279−1060 cm$^{-1}$), C−O−C aryl−alkyl ether linkage (1232 cm$^{-1}$), C−O−C stretching vibration (1170 cm$^{-1}$), and C−O−C pyranose ring skeletal vibration (1082 cm$^{-1}$); (5) C=C stretching vibration of the benzene ring (1632 cm$^{-1}$); and (6) others, such as aromatic skeletal mode (1608, 1516, and 1450 cm$^{-1}$), C−H deformation (1402 and 835 cm$^{-1}$), and CO deformation (1108 and 1060 cm$^{-1}$).

The most intense band of the spectra could be due to an aromatic skeletal mode, significantly intensified by the presence of oxygen-containing polar substitutes. The spectra of the shell of the present work revealed a much smaller amount of IR absorbance than that for fiber and EFB, possibly because of its low volatile content. Fiber contained more CH alkyl bonds, while EFB showed more C−O−H absorbance. From Figure 2, it also can be known that a large amount of oxygen functional groups (such as −COOH and −OH) existed in palm oil wastes, possibly attributed to their low calorific values (Table 1, ~$^1/_2$ that of petroleum oil). Therefore, it is desired to develop an efficient method of treating the palm oil wastes as resources for energy and chemicals generation, rather than the direct combustion.

**3.2. Pyrolysis Characteristics of Palm Oil Wastes.** A typical profile of gas evolving from shell pyrolysis with temperature increasing from ambient to 1000 °C is plotted in Figure 3. It can be observed that $CO_2$ and CO were mainly evolved out at lower temperature ($<$450 °C) and displayed almost the same pattern. Their evolving rates increased with temperature increasing and reached their peaks (3.5 mL/min/(g of $CO_2$), 1.58 mL/min/(g of CO)) at 300 °C. With temperature increasing further up to 500 °C, the $CO_2$ and CO evolving rates decreased instantly and kept constant till 1000 °C. $H_2$ evolved out at a much higher temperature ($>$450 °C), and as temperature increased, the evolving rate of $H_2$ increased greatly and reached the maximum value (1.96 mL/min/g) at ~700 °C. After that, it decreased gradually to ~0.5 mL/min/g at 1000 °C. According to ref 15, the evolving of CO and $CO_2$ at low temperature is mainly caused by the breaking of C=O in biomass (300−400 °C), and the cracking and reforming of aromatic rings gives rise to $H_2$ releasing at higher temperature ($>$400 °C). $CH_4$ started to evolve out at temperature $>$ 300 °C, then it increased as temperature increased and reached the maximum evolving rate at 400−500 °C but decreased gradually to zero at 750−800 °C. The maximum evolving rate of $CH_4$ was much lower than that of CO and $CO_2$. With regards to $C_2H_4$ and $C_2H_6$, their releasing was mainly at 350−550 °C, and their evolving rates are very low.

For the other two palm oil wastes (fiber and EFB), they showed similar pyrolysis characteristics with shell. Fiber achieved the maximum evolving rate of gases as the following: $H_2$ 1.83 mL/min/g at 650−700 °C, CO 1.45 mL/min/g at 250−300 °C, $CH_4$ 0.44 mL/min/g at 450−500 °C, and $CO_2$ 3.36 mL/min/g at 300−350 °C. EFB achieved its maximum evolving rate of gases as the following: $H_2$ 1.93 mL/min/g at 650−700 °C, CO 3.5 mL/min/g at 250−300 °C, $CH_4$ 0.48 mL/min/g at 450−500 °C, and $CO_2$ 3.86 mL/min/g at 300−350 °C.

The yields of solid, liquid, and gas products from pyrolysis of three palm oil wastes are listed in Table 2. Gas yields covered only ~15 wt % of the total products. The liquid part was the largest, and it took more than half the weight of the biomass sample. The yields of different gas species are also listed in Table 2. The yield of $H_2$ accounted for ~40 mol % of the total gas product. $CO_2$, which was the second largest one, covered ~30 mol % of gas products. However, it is the final product of carbon conversion; thus, it has no more energy value. CO and $CH_4$ also accounted for a big portion, and they could provide energy (heat) when being burnt. By comparing the gas compositions of the three palm oil wastes, it can be observed that fiber has the highest $H_2$ (41.30 mol %) and $CO_2$ (35.62 mol %) yields but the lowest CO yield (15.24 mol %). EFB has the highest CO content (23.24 mol %), and shell shows the highest methane content (9.29 mol %). The minor difference of the gas components observed among the three wastes might be attributed to their different structures (FTIR spectra in Figure 2), and the details will be discussed later in Section 3.3.2. As previously mentioned, the chemical structure of palm oil wastes consists of a large amount of O-bearing functional groups, which generally have low thermal stability. As a result, palm oil wastes are very easy to decompose at low temperature.[12] It is noteworthy that, in Table 2, the product contents in three phases were quite stable after temperature becomes $>$700 °C, indicating that the kinetics of biomass pyrolysis is no longer the control phenomenon. It is most likely attributed to the primary pyrolysis having reached equilibrium at that temperature, and an even higher temperature is required for starting secondary pyrolysis.

**3.3. Shell Pyrolysis at Different Temperatures.** The yields of solid charcoal, liquid oil, and gas product from shell pyrolysis at different temperatures (300, 400, ..., 900, 1000 °C) are listed in Table 3. The charcoal content was reduced greatly from 36.7 to 28.5 wt % as temperature increased from 300 to 600 °C. After that, with temperature increasing further, the charcoal yield decreased slightly, and only 1.5 wt % more of shell mass was lost when the final temperature increased from 600 to 1000 °C. It can be seen that the devolatilization of shell was focused at lower temperatures (300−600 °C). Gas yields also increased greatly with temperature increasing from 300 to 700 °C; then with temperature increasing further, the extent of gas yield increasing was lowered and reached its maximum value (16.32 wt %) at 1000 °C. In terms of the liquid part, the liquid yield covered ~57 wt % of biomass sample mass and showed a slight increase with temperature. The yields of the three products at 1000 °C in Table 3 are quite close to that found in Table 2 for shell pyrolysis; the higher gas yield (16.32%) and lower charcoal yield (27.1%) of the former accounts for the only

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(17) Kuo, M. L.; McClelland, J. F.; Luo, S.; Chien, P L.; R. D. W. Applied of infrared photoacoustic spectroscopy for wood samples. *Wood Fiber Sci.* **1988**, *20* (1), 132−145.

**Table 2. Pyrolysis Product of Palm Oil Waste Samples**

| | pyrolysis product (wt %) | | | gas product composition (mol % $N_2$-free and $H_2O$-free) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| sample | char | gas | liquid | $H_2$ | CO | $CH_4$ | $CO_2$ | $C_2H_4$ | $C_2H_6$ |
| shell | 27.57 | 14.88 | 57.55 | 37.76 | 20.99 | 9.29 | 31.03 | 0.20 | 0.73 |
| EFB | 24.21 | 15.91 | 59.88 | 37.26 | 23.24 | 5.21 | 33.30 | 0.18 | 0.80 |
| fiber | 27.62 | 13.93 | 58.45 | 41.30 | 15.24 | 6.83 | 35.62 | 0.21 | 0.81 |

**Table 3. Yield of Pyrolysis Products of Shell at Different Final Temperatures**

| temp (°C) | | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 |
|---|---|---|---|---|---|---|---|---|---|
| pyrolysis products (wt %) | char | 36.7 | 32.54 | 29.96 | 28.57 | 28.23 | 28.5 | 27.25 | 27.1 |
| | gas | 10.07 | 11.19 | 12.73 | 13.77 | 14.88 | 15.23 | 15.63 | 16.32 |
| | liquid | 53.23 | 56.27 | 57.31 | 57.66 | 56.89 | 56.27 | 57.12 | 56.58 |

difference of the temperature program operated (30 min isothermal at 1000 °C).

**3.3.1. Influence of Pyrolysis Temperature on Gas Products Property.** The gas species distribution profile from shell pyrolysis at different final temperatures is plotted in Figure 4. At lower temperatures (300−400 °C), only minor $H_2$ (~1.5 mol %) evolved out. The gas products mainly contain $CO_2$ (68 mol %) and CO (25 mol %) together with some methane (4.2 mol %). As temperature increased from 400 to 800 °C, $H_2$ content increased significantly from 3.2 to 38 mol % while $CO_2$ content decreased sharply from 68 to ~30 mol %. From 800 to 1000 °C, the $H_2$ (38 mol %) and $CO_2$ (~30 mol %) contents kept stable. In the whole temperature range studied, CO content (25−20 mol %) decreased slightly with temperature increasing. $CH_4$ behaved differently from the other gas species. With temperature increasing from 300 to 600 °C, $CH_4$ content increased linearly from 4 to 11.42 mol %. After that, with the temperature increased further, it decreased slightly to 8.71 mol % at 1000 °C. $C_2H_4$ and $C_2H_6$ contents are very low ($C_2H_4$ < 0.5 mol % and $C_2H_6$ < 1.5 mol %). Their contents did not show an obvious change with temperature variance.

Although Figures 3 and 4 were obtained under different temperature-varying conditions, it is clear that temperature is indeed a critical parameter in terms of not only the biomass decomposition rate (Figure 3) but also the final gas product distribution (Figure 4). The high evolving rates of $CO_2$, CO, and methane at low temperature (<400 °C) accounted for their high yields at the same temperature range, which is most likely due to the primary pyrolysis of biomass and is mainly controlled by temperature. As for $H_2$ generation, two temperature points were important: 400 and 800 °C. Above 400 °C, $H_2$ started to evolve and its yield increased with temperature till 800 °C. When temperature was above 800 °C, the $H_2$ yield kept steady regardless of the decreased evolving rate. Overall, temperature increasing is favorable for $H_2$ upgrading, which is consistent with our previous experimental result and also confirmed the simulation work.[8] As thermal cracking and secondary pyrolysis of biomass tar are generally favored at higher temperature (1000 °C),[18] it can be concluded that $H_2$ production from biomass is mainly dependent on the secondary pyrolysis of biomass.

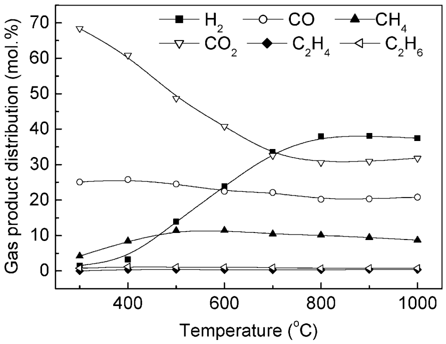

**Figure 4.** Gas species distribution profile at different final temperatures.

**3.3.2. Influence of Pyrolysis Temperature on Solid Charcoal Property.** The thermal decomposition of biomass represents the chemical bonds presenting in biomass to break and release volatile gases as temperature increases to a specific point. Therefore, there might be a relationship between the chemical structure of solid charcoal (identified by FTIR) and the composition of released gases at different final temperatures. The FTIR spectra of solid charcoal from shell pyrolysis at different final temperatures are plotted in Figure 5, which shows similar IR absorption characteristics to that from the dried shell sample (Figure 2). It can be observed in Figure 5 that the peak of OH absorbance diminished sharply to zero with final temperature increasing to 400 °C, which might be attributed to the dehydration of biomass, and at the same time a large amount of water was released.[12,16] The C−H (alkenes) absorbance amount also decreased to zero as temperature increased to 500 °C, possibly caused by the break of the weak bonds between C and H of alkyl. The breaking of C−H functional groups brought some $CH_4$, $C_2H_e$, and $C_2H_4$ releasing and gave a rise to the content of $CH_4$ and $C_2$ hydrocarbon in the gas products (refer to Figure 4).

The functional groups of C=O in biomass are easy to break with a large amount of CO and $CO_2$ evolving out (300−400 °C), and the absorbance of C=O (1700 $cm^{-1}$) decreased promptly as temperature increased.[16] Contrarily, the IR absorbance of other functional groups such as C=C aromatic ring (1690 $cm^{-1}$), C−O (1196 $cm^{-1}$), and C−H aromatic ring, i.e., C−H ar. (1439 $cm^{-1}$, 813 $cm^{-1}$), increased when shell is pyrolyzed at 300 °C, compared to 100 °C. It might be caused by the great decrease of peaks of OH and CH alkyle. However, with final temperature increasing further to 400, 500, and 600 °C, the peaks of C=C ar. (1690 $cm^{-1}$), C−H ar. (813 $cm^{-1}$) start to break stepwise to form volatiles. The cracking and reforming of aromatic rings give rise to $H_2$; thus, $H_2$ yield increased as temperature increased (400−600 °C). As final temperature increased to 800−1000 °C, almost no organic functional groups were left in the solid charcoal residue. From Figure 5, it can be concluded that the pyrolysis of shell is focused at 300−800 °C. According to refs 16 and 19, the pyrolysis process of palm oil shell can be divided into two ranges: (1) decomposition (~300−400 °C) with a large amount of CO and $CO_2$ evolved out at the price of C=O diminishing, which mainly involved dehydration, decarbonylation, and decarboxylation reactions; and (2) aromatization (>400 °C) where low molecular compounds ($H_2$ and $CH_4$) evolved out and functional groups disappeared, consequently leaving only solid residue charcoal.

Because of the thermal cracking of organic functional groups and evolving of volatiles, the elements (C, H, O, N, and S) in

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(18) Devi, L.; Ptasinski, K. J.; Janssen, F. J. J. G. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenergy* **2003**, *24* (2), 125−140.

(19) Fisher, T.; Hajaligol, M.; Waymack, B.; Kellogg, D. Pyrolysis behavior and kinetics of biomass derived materials. *J. Anal. Appl. Pyrolysis* **2002**, *62*, 331−349.

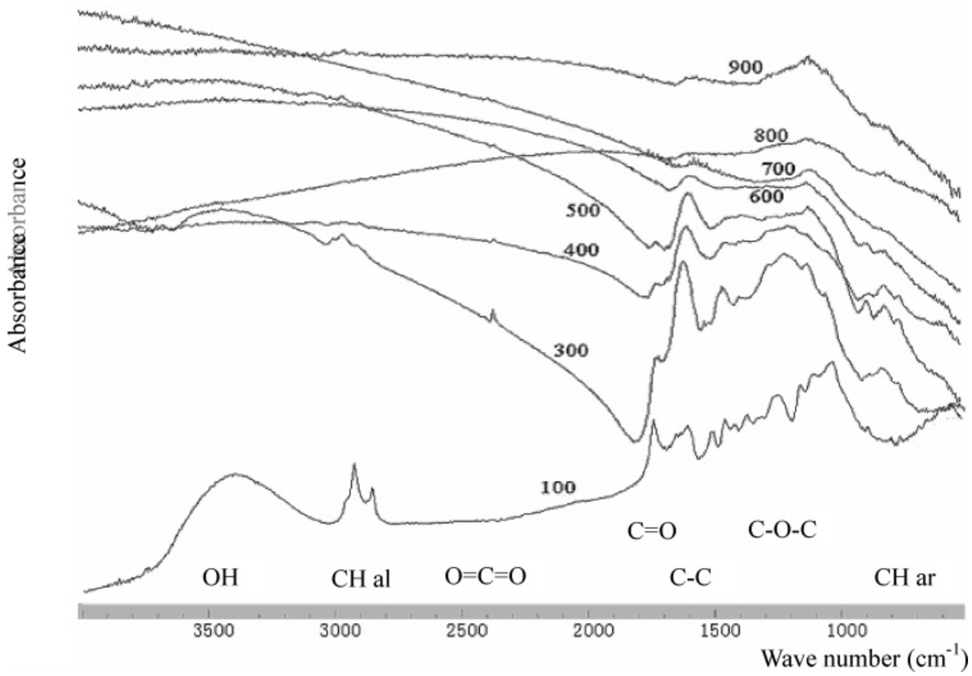


**Figure 5.** FTIR spectra of solid charcoal from shell pyrolysis at different temperatures.

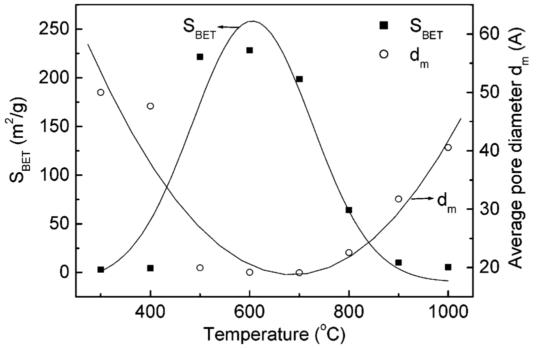


**Figure 6.** Surface property of solid charcoal at different temperatures.

**Table 4. Ultimate Analysis of Solid Charcoal from Shell Pyrolysis under Different Temperatures (wt %, Dry Basis)**

| temp (°C) | C | H | N | S | O |
|---|---|---|---|---|---|
| 300 | 67.38 | 3.63 | 1.97 | 0.48 | 14.54 |
| 400 | 75.63 | 2.96 | 2.43 | 0.43 | 11.77 |
| 500 | 75.09 | 2.01 | 2.63 | 0.34 | 12.56 |
| 600 | 76.81 | 1.46 | 2.32 | 0.22 | 11.47 |
| 700 | 76.91 | 0.88 | 2.25 | 0.13 | 12.01 |
| 800 | 77.34 | 0.67 | 2.14 | 0.10 | 12.01 |
| 900 | 78.39 | 0.44 | 2.05 | 0.05 | 10.97 |
| 1000 | 79.08 | 0.3 | 1.99 | 0.03 | 10.45 |

solid charcoal are varied at different temperatures. The chemical components of solid charcoal were analyzed using a CNHS/O analyzer, and the results are listed in Table 4. Carbon is the main element (67−79 wt %) in charcoal, which is higher than that detected in dried biomass (see Table 1) and increased with treated temperature. From 300 to 400 °C, because of the dehydration and decarbonylation/ decarboxylation reactions, the contents of O and H decreased greatly. With temperature increasing further, the aromatization of solid charcoal led to the evolving of $H_2$ and light molecular hydrocarbon ($CH_4$ and $C_2$); thus, the content of H in charcoal decreased significantly and there is almost no H left at 1000 °C. However, O content is kept at ∼10−12 wt % in the temperature range of 400−1000 °C, indicating that most of the O-bearing compounds are decomposed at 300−400 °C if considering the high O content detected in shell (Table 1, ∼30−40 wt %). It is consistent with the FTIR result (Figure 5). At higher temperatures, there are only carbon and some oxides left in the solid charcoal.

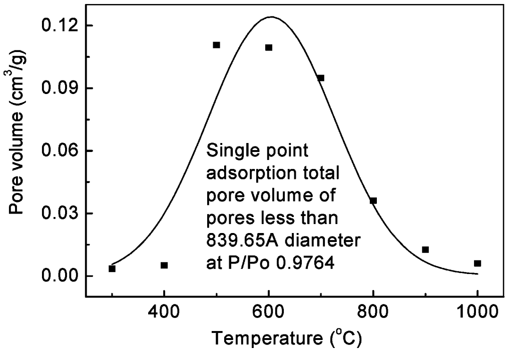
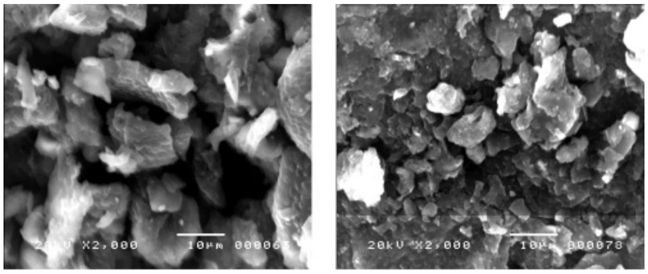
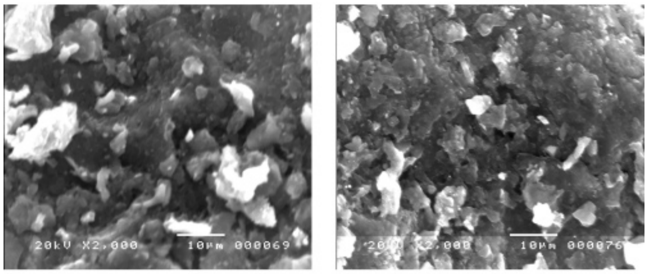


**Figure 7.** Pore volume of solid charcoal at different temperatures.



a: 400°C

b: 600°C



c: 800°C

d: 1000°C

**Figure 8.** SEM pictures of solid charcoal from shell pyrolysis at different temperatures.

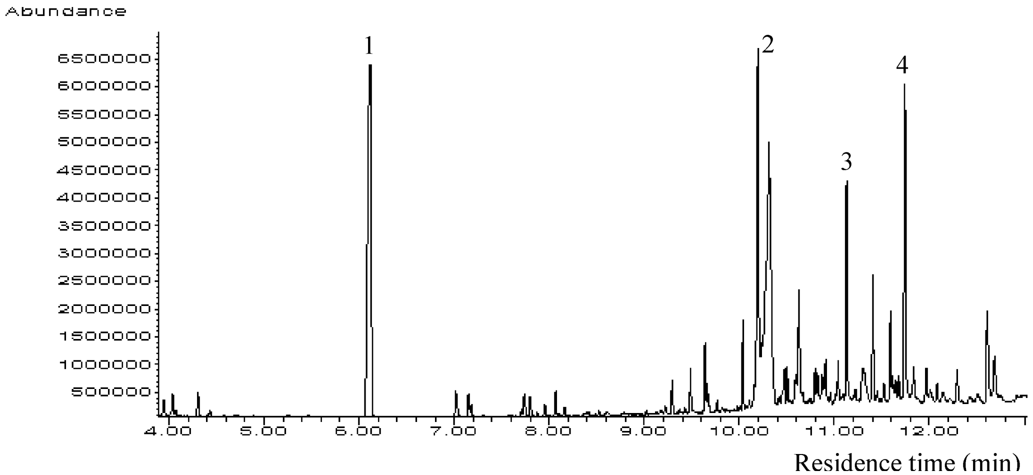


**Figure 9.** Typical total ion chromatogram of liquid oil from shell pyrolysis.

**Table 5. FTIR Functional Group Composition of Palm Shell Pyrolysis Oil**

| frequency ($cm^{-1}$) | group | class of compound |
|---|---|---|
| 3300−3600 | O−H stretching | polymeric O−H, water impurities |
| 3050−2800 | C−H stretching | alkanes |
| 1750−1650 | C=O stretching | ketones, aldehydes, carboxylic acids |
| 1650−1580 | C=C stretching | alkenes |
| 1470−1350 | C−H bending | alkanes |
| 1300−950 | C−O stretching | primary, secondary, and tertiary alcohol |
| 915−650 | O−H bending | phenol, esters, ethers, and aromatic compounds |

In the original biomass sample, the contents of N and S elements are very low (Table 1). After pyrolysis, the N content in solid charcoals became ~2 wt %, possibly attributed to the adsorption of $N_2$ or the forming of N-bearing organic groups on the surface of solid charcoal, because a large amount of $N_2$ is available during shell pyrolysis. With temperature increasing, S content decreased linearly while that of N increased first with temperature going up to 500 °C and then decreased linearly at higher temperature. Higher temperature (>500 °C) was more favorable for N-bearing compounds degrading. Nevertheless, in this study, evolving of N and S compounds in the gas phase was not analyzed, because their amount is too low to be detected using either FTIR or micro-GC.

With the releasing of various volatile gases, surface structures of charcoal are also variable. These were analyzed using ASAP 2010 with liquid $N_2$ at 77 K. The results (including Brunauer−Emmett−Teller (BET) surface area, the mean diameter of pore, and pore volume) are plotted in Figures 6 and 7. Compared with the original shell sample (1.33 $m^2$/g, 42.6 Å), the measured BET area and average pore size did not show great change when the final temperature is very low (<400 °C); this might be attributed to the low decomposition of volatile matter in shell. However, with temperature increasing to 500 °C, the BET surface area increased greatly from ~4 to 221.55 $m^2$/g, whereas the average pore size ($d_m$, adsorption average pore diameter, 4 V/S by BET,) decreased greatly from 50 to 20 Å. It might be attributed to the quick volatile decomposition and gas releasing (CO and $CO_2$) at this temperature. The significant increase of surface area and pore volume is accompanied by the opening of a large amount of fine pores, so the average pore diameter decreased and the pore structure became more uniform. When temperature increased to 600 °C, surface area increased slightly to 228.27 $m^2$/g, but with temperature increasing further to 900 °C, $S_{BET}$ decreased quickly to 3 $m^2$/g while $d_m$ increased greatly from 20 to 40 Å. It might be attributed to the blocking of some surface pores due to the plasticity of solid charcoal and the releasing of tar; thus, the surface area and pore volume of solid charcoal decreased. The blockade and merging of fine pores brought a great increase to $d_m$. The curves of $S_{BET}$ and volume of charcoals are almost in line with Gaussian profiles: the maximum points are (605 °C, 258.82 $m^2$/g) and (610 °C, 0.124 $cm^3$/g), respectively, while that of $d_m$ agreed with the parabolic profile; the peak point is at (672 °C, 18.81 Å). It can be concluded that the medium final temperature (~600 °C) is favorable for solid charcoal to get higher BET surface areas with a large amount of fine pores, to hopefully develop to chemical adsorbent.

The SEM picture (Figure 8) displayed the result similar to those found with $S_{BET}$ in Figure 6. As the space is limited, only the SEM photos of solid charcoals at 400, 600, 800, and 1000 °C are shown. At 300 °C, only a few fine pores were found, and thus, the $S_{BET}$ are very low. With final temperature increasing to 400 °C, the pore size increased significantly; however, the pore number did not show great change. With temperature increasing further to 500−600 °C, there are a number of fine pores developed (Figure 8b), and the surface area increased greatly (Figure 6). After that, with temperature increased to 800−1000 °C, the pore number shrunk largely; consequently, $S_{BET}$ decreased greatly from ~200 to several $m^2$/g. This is possibly due to the melting and combination of minerals, which gave rise a significant decrease of surface area in charcoals.

**3.3.3. Influence of Pyrolysis Temperature on Liquid Oil.** The details of functional group compositional analysis for liquid oil from shell pyrolysis, obtained from the FTIR spectra, are represented in Table 5. The pyrolysis oil is possibly a mixture of alcohols, phenols, acids, aldehydes, alkanes, ethers, ketones, and esters.[20] With temperature increasing, the absorbance of these functional groups increased till the final temperature reached 500 °C and they achieved their maximum absorbance value. With final temperature increased further, the IR absorbance of these functional groups decreased slightly. The break of functional groups at higher temperature is attributed to the great increase of gas yields ($H_2$, CO, $CO_2$, etc.).

The liquid oil from shell pyrolysis at different temperatures was also investigated using GC-MS. The typical total ion count (TIC) chromatogram liquid oil from shell pyrolysis is shown in Figure 9. There are more than 10 obvious separated peaks

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(20) Das, P.; Sreelatha, T.; Ganesh, A. Bio oil from pyrolysis of cashew nut shell-characterisation and related properties. *Biomass Bioenergy* **2004**, *27*, 265−275.

observed and among them; the 4 largest peaks were further identified and listed respectively as follows: (1) $m/z$ =146, 2-pentanone-4-hydroxy-4-methyl; (2) $m/z$ = 137, phthalic acid diisooctyl ester; (3) $m/z$ = 154, phenol, 2,6-dimethoxy; and (4) $m/z$ = 158, nonanoil acid, $CH_3(CH_2)_7COOH$. The yield of compound 1 increased as the final temperature increased from 300 to 600 °C and reached the maximum value at 600 °C; after that, it decreased continuously as the temperature increased further. For compound 2, the yield was enhanced linearly with the final temperature increasing as it is lower than 700 °C, and then with temperature increasing further, it started to decrease. Compounds 3 and 4 showed a similar changing tendency as that of compounds 1 and 2; they reached their maximum values at 500 and 700 °C, respectively. The composition and quality of liquid oil will be studied in-depth soon, with the aim to obtain the best process condition for improved oil quality and yield.

## 4. Conclusions

The process of biomass pyrolysis was investigated in detail and deeply from the viewpoint of chemical and physical structure of solid residue, liquid oil, and gas product. The knowledge gained facilitates our understanding to the mechanism of biomass pyrolysis and the process optimization, which can also assist the design of an industrial-scale reactor for future exploitation of palm oil wastes as energy sources. The main conclusions obtained from this study are listed as follows.

Temperature played a great role on the yield and quality of different products (gas, liquid, and solid charcoal) from biomass pyrolysis. Devolatilization of palm oil shell mainly happened at lower temperatures (400−800 °C). At temperature $< 300$ °C, dehydration is the main reaction involved. When temperature was increased slightly (~300 °C), CO and $CO_2$ evolved out easily because of the breaking of carbonyl and carboxyl functional groups followed by reforming, and the releasing of $CH_4$ increased at the price of CH alkyl breaking and diminishing. Following that, with temperature increasing further ($>$400 °C), aromatic rings broke gradually with a lot of $H_2$ evolving out. Meanwhile, a large amount of pores in biomass sample were opened, and the BET surface area increased greatly. Simultaneously, with the devolatilization of organic functional groups in biomass samples, large molecular organics condensed and formed liquid oil. The maximum yield of oil was achieved at 500 °C, and it is a mixture of acid, ether, phenol, etc. The thermal cracking of organic functional groups present in biomass differentiates the elemental components of solid charcoal, and their surface structures are also various. Medium temperature (~600 °C) is in favor of producing charcoal with higher surface area, pore volume, and fine pore size.

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