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Pvrolysis of Palm Oil Wastes for Biofuel Production

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Abstract: Purpose of the work: About 80% of world's palm oil is produced in Southeast Asia. With the sharp expansion of palm oil demand and production, palm oil wastes from palm oil production increased markedly. Current practice of waste incineration is generally low in efficiency and has aggravated environmental problems. These wastes are potential biomass energy sources that are CO2 neutral. Pyrolysis is considered as one of the promising thermo-chemical approaches to convert biomass to energy. However, it is a highly complex process influenced not only by the properties of biomass feedstock, but also by the operating conditions. This study aims to determine the pyrolysis characteristics and gas product properties of palm oil wastes, so as to promote the general idea of converting the wastes to an energy source, in an effective and environmentally-favorable way.

Approach and methodology: To understand better the fundamentals of palm oil wastes pyrolysis, this study focuses mainly on the effect of sample properties (composition and particle size of three samples - empty fruit bunches, fiber, and shell) and operating conditions (temperature, kinetics, decomposition process) on the pyrolysis characteristics and gas products distribution. TGA-FTIR is used for on-line identification of gas products releasing from pyrolysis. A thermodynamic equilibrium model was employed to predict the dominant gas products during the pyrolysis of three palm oil wastes under different operating conditions.

Scientific innovation: A better understanding of the mechanism of biomass pyrolysis was achieved based on determining the trends of various gas products releasing from pyrolysis of palm oil wastes.

Results: Thermal analysis demonstrated that palm oil wastes are easily decomposed, most of their weight loss happened at 220-350^{0}C. The pyrolysis process could be divided into four stages: moisture evaporation, hemicellulose decomposed, cellulose decomposed and lignin degradation. The influence of temperature on pyrolysis of palm oil wastes was investigated at 250, 280, 300, 325, 355, 400, and 450 ^{0}C, respectively. The weight loss kinetics (evaluated by TGA) and gas product releasing profiles (determined by FTIR) at the selected temperatures were evaluated and discussed in depth. The different patterns related to pyrolysis rate and gas evolving profile at low (<355^{0}C) and high temperatures (>355^{0}C) suggest the different reaction pathway (or mechanism) involved.

Conclusions: Palm oil wastes are ideal energy sources for biofuel generation. This fundamental study provides a basic insight of the palm oil wastes pyrolysis, which can benefit to our current work in developing an advanced thermal process for high-yield biofuel production from palm oil wastes.

Keywords: Palm Oil Wastes, Pyrolysis, TGA-FTIR, Temperature Effect, Characteristics, Gas Products, Mechanism.

Introduction

Palm oil wastes are highly-potential biomass energy sources in Southeast Asia. Pyrolysis is considered as one of the promising thermal approaches in converting biomass to energy [1]. Nevertheless, pyrolysis is a highly complex process influenced not only by the properties of biomass feedstock, but also by the operating conditions. Fundamentals of biomass pyrolysis have been widely investigated using fluidized bed, fixed bed, and/or thermogravimetric analyzer (TGA). The use of TGA has the advantages of a fast and repeatable data collection of pyrolysis rate, which facilitates a deep investigation of kinetic parameters. Among various operating parameters, temperature is one of the most important concerns. So far, a number of experimental studies have been carried out to investigate the influence of temperature [2-5], focusing on product yields evaluation. The experiments were mostly performed in bench-scale reactors at high temperatures (500 – 900 ^{0}C), and only the total yields of main gas species were taken into account. The gas components at different pyrolysis temperatures were studied only in few cases [2,3]. Moreover, pyrolysis involves a number of sequential and parallel reactions [4]. The mechanism and the real-time gas release in the course of pyrolysis, which should be closely related to the pyrolysis temperature, are rarely studied. A better understanding of the fundamentals and mechanisms in pyrolysis and of the effect of temperature is thus essential to achieve the high yields of the targeted products. In this study, the pyrolysis of palm oil wastes, the representative biomass in the region, was carried out. The characteristics of three palm oil wastes pyrolysis were determined and the real-time evaluation trends of gas products were investigated using an integrated system of TGA and Fourier transform infrared spectrometer (FTIR). After that, the influence of final temperature on palm oil wastes pyrolysis was determined in depth through either experiment or thermodynamic calculation. A better understanding of the biomass pyrolysis process is achieved and the fundamentals in the pyrolysis of palm oil wastes are further explored.

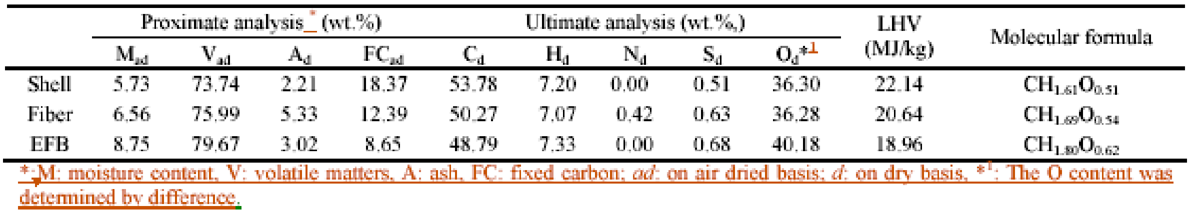
Experimental Materials and Methods

Materials

The three palm oil wastes — shell, fiber, and empty fruit bunches (EFB), were obtained from Malaysia. They were ground and sieved with a 1-mm screen. The particle size distribution of the samples was analyzed using Malvern instruments Mastersizer 2000. It was found that the average particle size of shell is much larger than those of fiber and EFB, with most of its particle size located at 500-600 µm. EFB and fiber particles are finer, with their peaks of particle size distribution located at 100 ฒm and 150 µm, respectively. Almost 90% of their particles are smaller than 500 µm.

The proximate analysis of palm oil wastes was carried out in TGA (TA 2050, USA) and the ultimate analysis was conducted using Perkin Elmer 2400II CHNS/O Analyzer. The results are listed in Table 1. The low heating value (LHV) of the studied samples, measured in a Bomb Calorimeter (Parr 1260, Parr Instrument Company Moline, IL USA), is ~ 20

Table 1 Proximate and ultimate analyses of biomass samples



	Proximate analysis* (wt.%)				Ultimate analysis (wt.%,)					LHV (MJ/kg)	Molecular formula
	M_{ad}	V_{ad}	A_d	FC_{ad}	C_d	H_d	N_d	S_d	O_d*[1]		
Shell	5.73	73.74	2.21	18.37	53.78	7.20	0.00	0.51	36.30	22.14	$CH_{1.61}O_{0.51}$
Fiber	6.56	75.99	5.33	12.39	50.27	7.07	0.42	0.63	36.28	20.64	$CH_{1.69}O_{0.54}$
EFB	8.75	79.67	3.02	8.65	48.79	7.33	0.00	0.68	40.18	18.96	$CH_{1.80}O_{0.62}$

*: M: moisture content, V: volatile matters, A: ash, FC: fixed carbon; *ad*: on air dried basis; *d*: on dry basis, *[1]: The O content was determined by difference.

Experimental equipment and procedures

Pyrolysis of palm oil wastes was performed in a thermogravimetric analyzer (TGA 2050, TA, USA). The sample was first heated up at 10 ^{0}C/min to 150 ^{0}C from the ambient temperature, and kept isothermal for 5 minutes to remove moisture. Then, it was heated to 900 ^{0}C and kept it for 3 minutes to complete the pyrolysis. The flow rate of purging gas (N2) for kinetic analysis of biomass in TGA was set at 40 ml/min.

The gas products were on-line analyzed using FTIR with DTGS detector (Bio Rad Excalibur Series FTS 3000) which is connected with TGA. The gas products were swept directly by the carrier gas (120 ml/min N2) to a gas cell. The transfer line and gas cell were heated to an internal temperature of 230 ^{0}C to minimize secondary interactions and avoid the condensation or adsorption of semi-volatile products. IR scanning range is from 4000 to 500 cm-1 wave number.

For an in-depth investigation to the influence of temperature on the pyrolysis of palm oil wastes, pyrolysis was carried out at different temperatures (250, 280, 300, 325, 355, 400, and 450 ^{0}C). The samples were heated up separately from the ambient to the selected temperature at a much higher rate of 30 ^{0}C/min, to minimize the influence potentially caused by the heating process. The selected temperature was kept for 120 minutes where generally no more weight loss was observed, i.e., the pyrolysis at that temperature was completed. After that, the sample was continuously heated up to 900 ^{0}C to record the further weight loss, if any, at higher temperatures. FTIR identification of the gaseous species released from the pyrolysis at different temperatures was conducted at 1 scan per 5 seconds.

Thermodynamic calculation

The simulation of biomass pyrolysis and gasification was performed on the basis of minimized Gibbs free energy of thermodynamic equilibrium using HSC Chemistry — a commercial computation code for windows. With only the main elements (C, H, O) considered for the biomass sample, similar as previous work [6], only the species (H_2, CO, CO_2, CH_4, H_2O and solid carbon), defined as final products of biomass pyrolysis, are considered in the computation systems. The condition considered for HSC simulation is as MJ/kg. The results indicate that palm oil wastes are environment friendly with trace content of N and S and mineral matters. If only considering the main elements (C, H, O), the molecular formula of the studied samples based on one C atom can be written as CHxOy, as listed in Table 1. follows: temperature is in the range of 200 - 1200 ^{0}C, and pressure is at 1atm. For the studied palm oil wastes, the input (in mol) is following those given in Table 1, shell (C: 1, H: 1.61, O: 0.51), fiber (C: 1, H: 1.69, O: 0.54), and EFB (C: 1, H: 1.8, and O: 0.62).

Results and Discussion

Biomass pyrolysis in TGA

The pyrolysis characteristics, both TG (in weight %) and DTG (in %/^{0}C) curves of the three palm oil waste samples (shell, fiber and EFB) are shown in Fig. 1. The samples start to degrade at ~220^{0}C and the weights lose sharply after that. When temperature is over 340^{0}C, no obvious weight loss is observed. Differences among the three samples are mainly found with their DTG curves: shell and fiber have two peaks, but EFB has just one. It is possibly related to the different volatile and fixed carbon contents found in the wastes (see Table 1). EFB has a much higher volatile and lower fixed carbon, compared to the other two, the release of volatilesmight cause an earlier degradation of carbon resulting one big peak. However, shell and fiber contain a much higher content of fixed carbon, and therefore are more difficult to degrade. Their two separated peaks represent, respectively, the volatile release and the carbon degradation. It is known that cellulose, hemicellulose, and lignin are the main components of lignocellulosic biomass samples, generally, 40-60 wt.% cellulose, 20-40 wt.% hemicellulose, and 10-25 wt.% lignin on dry basis are found in biomass [7]. The three components played individually significant roles in determining the pyrolysis characteristics and generally no interaction happened among them [8]. As for the studied palm oil wastes, although there existed some differences in terms of the onset and end temperatures of pyrolysis, their degradation can be separated into several stages as follows: ~220^{0}C, moisture evolution, 220-300^{0}C predominantly hemicellulose decomposition, 300-340^{0}C mainly cellulose decomposition, >340^{0}C, mainly lignin decomposition.

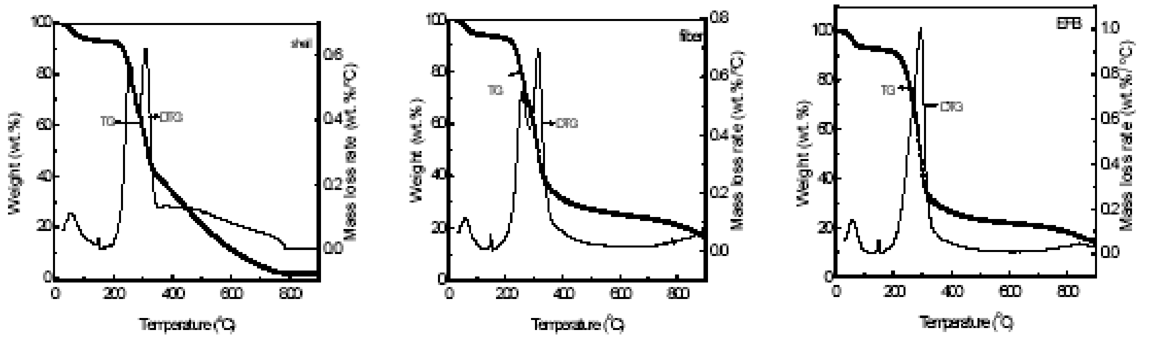


Fig. 1 Pyrolysis curves of shell, fiber and EFB.

Table 1 Proximate and ultimate analyses of biomass samples

Biomass Samples	Temperature Range (°C)	n	E (kJ/mol)	A (s^{-1})	R*	Weight loss (wt.%)	E_m (kJ/mol)
Shell	220-300	1	55.64	28.2	0.9936	32.0	62.85
	300-340	1	75.72	2427.6	0.9991	17.9	
Fiber	220-300	1	51.82	10.3	0.9967	32.3	58.64
	300-340	1	67.68	364.4	0.9980	24.4	
EFB	220-300	1	59.50	77.4	0.9868	46.1	61.35
	300-340	1	67.58	619.7	0.9953	13.6	

R*: correlation coefficient

Calculation of kinetic parameters

Kinetic parameters (activation energy - E, and the preexponential factor - A) were calculated at selected conditions (sample mass: 20-25 mg and flow rate: 40 ml/min) where only chemical reaction is considered as the control step whilst the internal/external diffusion and mass transfer are negligible. The weight loss of the studied palm oil wastes occurred mainly at 220-340^0C, this temperature range was thus considered for the calculation of kinetic parameters, i.e., only the decomposition of hemicellulose (220-300^0C) and cellulose (300-340^0C) were calculated. To determine the kinetic parameters, different reaction orders (n = 0, 0.5, 1, 2, and 3) were assumed and the reaction order is ascertained on the basis of best-fit criteria. In Table 2, n = 1 is the best fit for the pyrolysis of palm oil wastes where the correlation coefficients are all over 0.99. Em is the weight-based mean activation energy from those calculated in different temperature ranges. The activation energy of biomass in pyrolysis was reported to be around 70-100 kJmol-1 [9], and our result shows that pyrolysis of palm oil wastes could be effective with a slightly lower activation energy demanded.

TGA-FTIR analysis of gas products

A typical spectral output from the TGA-FTIR of fiber pyrolysis is shown in Fig. 2, as a stack plot.

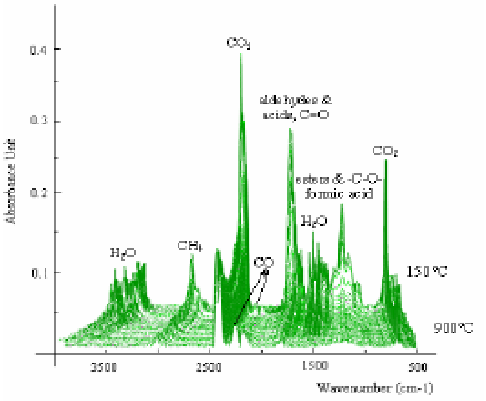


Fig. 2 IR stack plot from fiber pyrolysis in TGA-FTIR.

The infrared spectra taken from 150^0C to 900^0C every minute in the experiment are plotted one on top of the other; totally 75 IR scans formed the 3D spectra indicating the evolving of gas products in the course of pyrolysis of fiber, as function of both wave number and time or temperature. The main gas products of palm oil wastes are: CO2, H2O, CH4, CO and some organics. The gas products begin to evolve at about 230^0C, and most gas species evolve out at 260 - 350^0C. It corresponds with the previous results of weight loss obtained from the thermoanalysis (Fig. 1). The releasing of CO2 and CH4 first increases as temperature increased and reaches their maximum yields at ~ 330^{0}C and 340^{0}C, respectively. CO has demonstrated similar performance as CO2 except it gets its maximum evolution at about 270^{0}C. Among the gas species, only CO2 is evolved when the temperature is higher than 350^{0}C. For the other two samples (EFB and shell), similar results are observed except that their CH_4 evolution is very small; almost no CH_4 yield is observed for EFB and shell.

There are also a few organics (C_2 acids, ether, and other hydrocarbon compounds) in the evolved gas, but their concentrations are often too low to be detected. In addition, those gases such as H_2, N_2, O_2, and H_2S have no or weak IR absorption, so they are impossible to be detected using FTIR. Nevertheless, this approach provides a rapid FTIR scan within seconds, which facilitates our research on the kinetics and gaseous species evolution.

The influence of final temperatures

The pyrolysis curves of fiber, a representative of palm oil wastes, at different isothermal temperatures are plotted in Fig. 3 (TGA curves) and Fig. 4 (DTG curves). A case of fiber pyrolysis with temperature changing from ambient to 900 ^{0}C at 30 ^{0}C /min (dot line) is also present to compare with the other cases. For case 1 where the isothermal temperature is 250 ^{0}C, ~30 wt% of fiber is decomposed during the 120 min of isothermal period. After that, further weight loss (~35 wt%) is observed as the temperature continuously goes up to 900 ^{0}C. With the increase of isothermal temperature from 250 to 355 ^{0}C, more and more weight loss happens during the isothermal period (120 min) thus leaving less weight lost in the follow-ups. Pyrolysis patterns of cases 6 and 7 are very close to that observed for temperature rising from ambient directly to 900 ^{0}C without isothermal period.

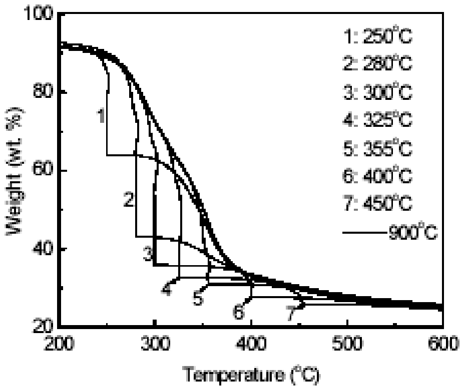


Fig. 3 TG curves of fiber pyrolysis at different temperatures.

In Fig. 4, it can be seen that for all isothermal temperatures, after the sample is kept isothermal for ~10-12 minutes the pyrolysis at the selected temperature is completed as no more obvious weight loss happened (mass loss rate < 0.85 wt.%/min). That-is-to-say, 120 min of isothermal time is far in excess of that required for a complete pyrolysis at the selected isothermal temperature. At 250 ^{0}C, the sample mass loss rate is very slow (<1.5 wt%/min). With the increase of isothermal temperature from 250 to 325 ^{0}C, the mass loss rate increased sharply to ~13 wt%/min and only one peak is observed in these cases. However, when the isothermal temperature increased to over 355^{0}C (cases 5, 6,7), two peaks are found indicating a completely different decomposition mechanism compared to cases 1 to 4. Again, cases 6 and 7 are very close to that observed for temperature rising from ambient to 900 ^{0}C (the dot line). That-is-to-say, the fiber pyrolysis at low temperature (< 355 ^{0}C) is most likely controlled by kinetics thus temperature has demonstrated a big effect. After analyzing the yields of gas and residues, it can be observed that the gas yield increased greatly as temperature increased, at the price of char yield decreased sharply. It is consistent with previous reports [2, 5], although the operating temperatures in their studies were much higher (550-900 ^{0}C)

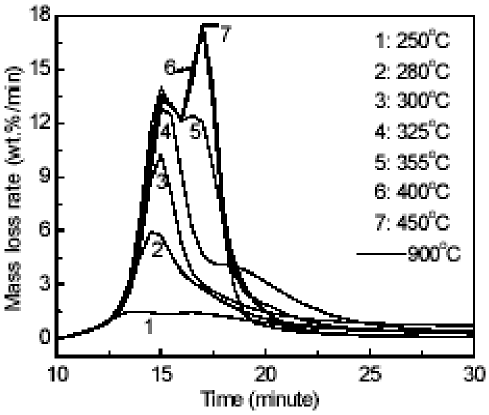


Fig. 4 DTG curves of fiber pyrolysis at different temperatures.

The gas products released from fiber pyrolysis at different isothermal temperatures were also analyzed by FTIR. Figures are not shown here due to the space limit. With changing of the isothermal temperatures, CO_2 and organics demonstrate almost similar releasing profiles while those of CO and CH_4 are also quite close. For the first pair (CO_2 and organics), both of their releasing at 250 ^{0}C is very low. With the isothermal temperature increase to 355 ^{0}C, the releasing of CO_2 and organics increased sharply. When the temperature continuously goes up to over 355 ^{0}C, the total releasing of the two components are decreased and their releasing patterns are similar with that observed with temperature heated directly from ambient to 900 ^{0}C. As for another pair (CO and CH_4), their releasing under low temperature (250 – 325 ^{0}C) is generally insignificant, although a slight increase of their releasing amount is still observed with the temperature increasing. But when the temperature goes up to over 355 ^{0}C, both of their releasing is improved significantly. CO gets its highest releasing at 355 ^{0}C while CH_4 gets its at a higher temperature (400 ^{0}C). Only one big peak is observed for CO and CH_4 in their releasing profile, different to those found with CO_2 and organics.

The similar patterns of DTG curves and FTIR releasing profile of CO_2 and organics suggest that the formation and releasing of the two components dominate the overall fiber pyrolysis process. The different patterns of these curves at lower temperatures (250 – 325 ^{0}C) and higher temperature (over 355 ^{0}C) where one peak and two peaks are respectively associated, implies two different mechanisms involving in fiber pyrolysis. The temperature 355 ^{0}C could be a boundary.

The total gas yields were estimated based on integrating the FTIR spectra from 150 ^{0}C for 40 minutes. Yields of CO_2, CH_4, CO and organics increased straightly with temperature increasing to 355 ^{0}C. At 355 ^{0}C, all the gas products reach their highest yields. Based on a mass balance point-of-view, it can be deduced that there must be other gases released above 355 ^{0}C, which however cannot be detected by FTIR. Most increase tendency of H_2 evolving with temperature has been testified formerly by experiment [1].

Thermodynamic calculations

Thermodynamic predictions of gas products at different temperatures were extensively conducted using HSC software but the figures are not present here due to the space limit. It could be known from the calculation that the releasing patterns of gas products from pyrolysis of shell and EFB are similar with that from fiber. The pyrolysis of palm oil wastes could be divided into four zones, according to temperatures. In the first zone (T <340 ^{0}C), biomass become dehydrated, and along with water vapor, CO_2 and volatile organics (CH_4) are given off. They are most likely react with carbon (the major component in Zone 1) to form H_2 and CO. Nevertheless, the slight exothermic reactions of CO with H_2O and H_2 with C are in favor of the steady formation of CO_2 and CH_4. It accounts for the decrease of C and water but increase of CH_4 and CO_2 in Zone 1. The second zone is for temperature at 340-560 ^{0}C. The contents of CH_4 and water are decreased in Zone 2 but CO_2 content increased, carbon keeps almost constant. There is also some H_2 and CO evolving out. In zone 3 (T: 560 – 900 ^{0}C), the formation of CO and H_2 becomes predominant of fiber pyrolysis. The content of H_2 and CO increase at the price of C, H_2O, CO_2, and CH_4 diminishing. During the last zone (>900^{0}C), pyrolysis reaches the end. Almost no reaction occurs. The contents of H_2 (45 mol.%) and CO (30 mol.%) keep high and stable.

An increase in the reaction temperature favors endothermic reactions. Thus, higher yields of H_2 and CO and lower yields of CH_4 and H_2O are obtained at higher temperatures. The predicted changing tendency of gas products with respect to temperature is similar to the simulation work done by Zhang [10], and also supported by other experimental results [2, 5]. As predicted, high temperature is in favor of the production of H_2 during pyrolysis of palm oil wastes, supports at certain extent our experimental observation with TGA-FTIR where H2 production at over 355^{0}C was suggested based on mass balance, although the direct measurement of H_2 was not conducted in this study. The trend of decreasing C residue as predicted, is also consistent with the experiments results from TGA. The corresponding temperatures used for grouping the 4 zones might not be the same with those found in real situation, due to the limitation of thermodynamic calculation. Nevertheless, this simulation approach provides a better understanding to the influence of temperature on pyrolysis products.

Conclusions

The following conclusions could be reached:

1. Palm oil wastes are easily degraded and their pyrolysis can be divided into four stages: moisture evolution (<220^{0}C), hemicellulose decomposition (220~300^{0}C), cellulose decomposition (300~340^{0}C), and lignin decomposition (>340^{0}C). The weight loss of the studied palm oil wastes is focused at 220-340^{0}C. The activation energy is only about 60 kJ/mol and the degradation of palm oil wastes is in general first order reaction at the studied conditions: sample mass (20-25 mg), flow rate (40 ml/min).
2. Gaseous products, identified by FTIR, are mainly CO_2, CO, CH_4, H_2O, and a few organics. Most gaseous product evolved at 250-350^{0}C, which is consistent with the observation obtained from the thermoanalysis.
3. Temperature has demonstrated significant influence on pyrolysis of palm oil wastes. The different patterns related to pyrolysis rate and gas evolving profile at low (<355^{0}C) and high temperatures (>355^{0}C) are observed and it indicates the different reaction pathway (or mechanism) involved. The experimental study using TGA-FTIR and thermodynamic modeling of gas product releasing showed similar results: gas yield is increased with temperature at the expense of char residue.

4. Thermodynamic equilibrium simulation of palm oil wastes pyrolysis show that the main gas products are H_2, CO, CH_4, and CO. It confirmed the evolving of H_2 at higher temperatures. Yields of H_2 and CO are increased as temperature increasing to 900 ^{0}C, and they get their stable yield of 45 mol.% and 30 mol.%, respectively.

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