Thermogravimetry Study on Pyrolysis of Various Lignocellulosic Biomass for Potential Hydrogen Production

S.S. Abdullah, S. Yusup, M.M. Ahmad, A. Ramli, L. Ismail

Abstract—This paper aims to study decomposition behavior in pyrolytic environment of four lignocellulosic biomass (oil palm shell, oil palm frond, rice husk and paddy straw), and two commercial components of biomass (pure cellulose and lignin), performed in a thermogravimetry analyzer (TGA). The unit which consists of a microbalance and a furnace flowed with 100 cc (STP) min^{-1} Nitrogen, N_2 as inert. Heating rate was set at 20°C min^{-1} and temperature started from 50 to 900°C. Hydrogen gas production during the pyrolysis was observed using Agilent Gas Chromatography Analyzer 7890A. Oil palm shell, oil palm frond, paddy straw and rice husk were found to be reactive enough in a pyrolytic environment of up to 900°C since pyrolysis of these biomass starts at temperature as low as 200°C and maximum value of weight loss is achieved at about 500°C. Since there was not much different in the cellulose, hemicelluloses and lignin fractions between oil palm shell, oil palm frond, paddy straw and rice husk, the T-50 and R-50 values obtained are almost similar. H_2 productions started rapidly at this temperature as well due to the decompositions of biomass inside the TGA. Biomass with more lignin content such as oil palm shell was found to have longer duration of H_2 production compared to materials of high cellulose and hemicelluloses contents.

Keywords—biomass, decomposition, hydrogen, lignocellulosic, thermogravimetry

I. INTRODUCTION

BEING the most dependable supply of renewable energy, biomass become the major resources of bio-energy to deal with depletion of fossil fuel resources and global warming crisis [1]. Various conversion techniques such as physical, thermal, chemical and biological schemes have been utilized in order to make use of biomass as energy resources.

Among these, thermal conversion methods such as combustion, pyrolysis, co-firing and gasification of biomass have been universally employed to generate heat, syngas, biofuels, power, etc [1],[2]. In recent years, many studies have been done to utilize biomass in various systems at their utmost efficiency. For this, biomass is characterized to study their behavior during thermal conversion.

Valuable information regarding characteristics of gas-solid and gas-liquid systems can be obtained from thermogravimetry analyzer (TGA), i.e. reaction mechanism, kinetic parameters, thermal stability and phase transformation. Besides, this analysis also gives useful data on specific temperatures where various heterogeneous reactions occur throughout the pyrolysis of biomass inside the TGA [3].

The aim of this paper is to perform a thermogravimetry study to observe the pyrolytic behavior of four lignocellulosic biomass widely available in Malaysia at wide temperature range, and to observe gas production profiles throughout the process.

II. EXPERIMENTAL

A. Samples Preparation and Characterization

Four types of biomass were selected as the raw materials to be tested; they were oil palm shell, oil palm frond, rice husk and paddy straw. These biomass came from two major agricultural sectors in Malaysia, which were oil palm and paddy. The proximate, elemental and heating value analyses of these materials are as listed in Table 1.

Biomass were dried in a drying oven at 105^{0}C, and weights were recorded every 1 h until they became constant. From this, original moisture contents (as received basis) of each biomass were obtained. After drying, raw materials were grinded and sieved to a maximum particle size of 0.25mm. Samples with particle size of less than 0.25mm were collected and kept in desiccators at room temperature prior to further analyses. Elemental analysis was carried out using Leco CHNS elemental analyzer, proximate analysis was conducted using a Seiko SII TG/DTA 6300 thermogravimetry analyzer (TGA) and the calorific value was determined using IKA Werke C5000 bomb calorimeter. These analyses were done in accordance with the procedure of American Society for Testing and Materials (ASTM).

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TABLE I
CHARACTERIZATION OF FOUR BIOMASS MATERIALS

		Oil palm shell	Oil palm frond	Rice husk	Paddy straw
Proximate analysis (wt%, dry basis)	Volatiles	81.03	83.19	64.20	72.48
	Fixed carbon	14.52	12.66	12.57	8.08
	Ash	4.44	4.15	23.24	19.45
Moisture (wt%, as received basis)		17.50	71.43	13.08	8.47
Elemental analysis (wt%, dry basis)	C	49.65	42.10	38.74	33.48
	H	6.13	5.46	5.83	6.01
	N	0.41	0.70	0.55	1.46
	S	0.48	0.13	0.06	0.15
	O (by difference)	38.89	47.46	31.58	39.45
Fiber analysis (wt%) [4]-[7]	Cellulose	20.80	30.40	42.20	40.50
	Hemicelluloses	22.70	40.40	18.47	23.00
	Lignin	50.70	21.70	19.40	16.00
High heating value (MJ/kg)		20.40	15.59	14.79	13.74

Two commercially available components of biomass, namely pure cellulose and lignin (both purchased from Sigma Aldrich) were also used in the experiment to give an insight on decomposition of individual biomass components.

B. Gas Analysis

An Agilent 7890A Gas Chromatograph (GC) was connected to a Seiko SII TG/DTA 6300 thermogravimetry analyzer (TGA) to enable an online analysis of the gases produced during pyrolysis. The GC used consists of packed columns for fast refinery gas analysis for samples up to C6, with 2 thermal conductivity detectors (TCD) and 1 flame ion detector (FID). Intensities of the gases produced during pyrolysis were captured every 4 minutes by GC Chemstation software. Integrations of these intensity peaks give the amount CO, CO_2, CH_4, and H_2.

C. Non-catalytic pyrolysis in TGA

Pyrolysis was conducted in a TGA, which resembled a fixed bed reactor. A ceramic crucible loaded with approximately 5mg ($\pm$0.5 mg) biomass sample was placed inside the analyzer. The sample weight was continuously measured and recorded together with the time and temperature profile inside the TGA. To create an inert environment for pyrolysis , nitrogen was used as a carrier gas and the flow rate was fixed at 100 cc (STP) min^{-1}. Experiment started after allowing inert purging for 30 min. The heating rate was controlled at 20^{0}C min^{-1} and the temperature ranged from 50 to 900^{0}C. This wide temperature range is advantageous to characterize the behavior of samples at various temperatures of interest.

The TGA and GC were periodically calibrated to ensure the reproducibility and quality of the measured data. TGA gives data in the forms of thermogravimetry (TG) curve and its first derivative known as differential thermogravimetry (DTG) curve, whereas GC quantifies the emitted gases during pyrolysis in percent.

III. RESULTS AND DISCUSSION

The behavior of cellulose, hemicelluloses and lignin, which form the three major components of biomass must be well-known in order for researcher to understand more on biomass pyrolysis [8].

Among these three major fractions of biomass, hemicelluloses are the easiest to be pyrolyzed due to its linear polymer structure with short side chains [9]. In contrast, cellulose is constructed of semicrystalline arrays chains associated with one another which makes it thermally. As for lignin, it is a complicated structure of phenolic polymer encasing the polysaccharides of the cell walls that produces strong and durable composite materials [2],[10]. According to [9] and [11], the most reactive compound, hemicelluloses decomposes at between 200 to 350^{0}C, whereas cellulose from 305 to 375^{0}C and lignin steadily over of 250 to 500^{0}C. However, some reported that pyrolysis of heavier volatiles such as lignin occurs from temperature as low as 150 up to 900^{0}C since it is more thermally stable in contrast to cellulose and hemicelluloses [12].

A. Thermogravimetric analysis

Lignocellulosic structure of biomass can be qualitatively identified from thermogravimetry analysis. According to [2] and [3], weight losses observed in TG and DTG curves are found to be relevant to the composition of cellulose, hemicelluloses, and lignin fractions in biomass. TG curves of all samples tested in this study are presented in Fig. 1.

Sample-01 (Oil palm shell) — Sample-02 (Oil palm frond)
Sample-05 (Cellulose) — Sample-03 (Rice husk)
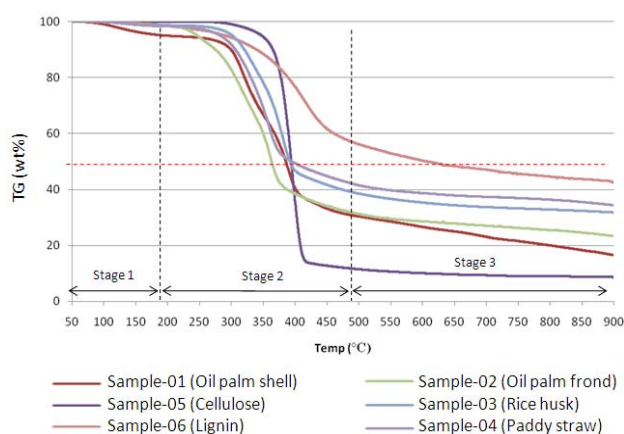Sample-06 (Lignin) — Sample-04 (Paddy straw)

Fig. 1 TG distribution of various materials in pyrolysis environment

Generally, three different regions can be distinguished from a particular TG curve, in spite of materials tested. Weight change of a sample is recorded as a function of time or temperature and portrayed by a TG curve. This curve conveys information on thermal behavior of solid fuels in pyrolytic conditions. On the other hand, DTG emphasizes the zone of reaction where various reaction steps are taking place over the entire temperature range. In Fig. 1, different stages of decomposition curves were clearly shown by the dotted vertical lines. The first stage (temperature below 200°C) corresponds to the drying period where light volatiles, mainly water were liberated throughout the procedure. Slender decay of sample weight can be observed as illustrated in Fig. 1,

where the weight losses of all six tested materials were less than 10% at this early stage.

Devolatilization is the major step in all thermochemical conversion process involving biomass. This step is represented by the second stage of decomposition, occurring at temperature between 200 to 500^{0}C, where remarkable slope of the TG curves are observed, corresponding to significant drop in weight of samples due to liberation of volatile hydrocarbon from rapid thermal decomposition of hemicelluloses, cellulose and some part of lignin. At this stage; weights of the tested materials are reduced to below 50%, except for the commercial lignin sample. This is primarily due to the fact that 80 wt% of biomass is formed by volatile fraction, and only around 20 wt% is in form of solid carbonaceous residue [8]. This shows that volatile products play a very important part in pyrolysis of biomass materials and product gas composition.

For stage 3, weight loss is not as momentous as in stage 2, primarily due to the steady decomposition of the remaining heavy components mainly from lignin.

Two indicators, T-50 and R-50 were anticipated to confer a more depth assessment of weight loss between all tested samples [9],[10]. T-50 (°C) represents the temperature at 50% weight loss whereas R-50 (% min^{-1}) represents the reactivity at T-50. The values obtained from the experiment were plotted in Fig. 2.
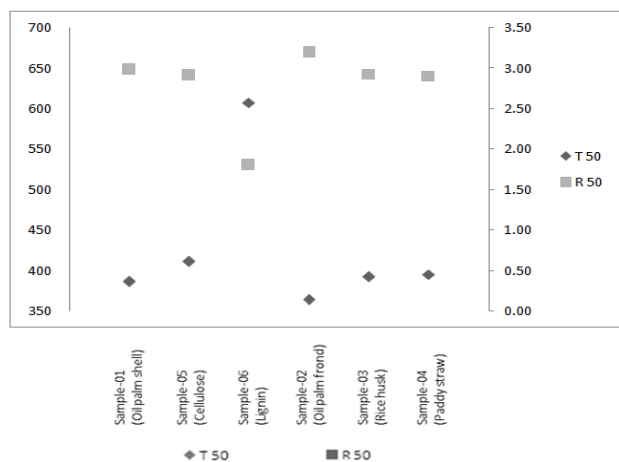

Fig. 2 Profiles of T-50 and R-50 of various materials in pyrolytic environment

From Fig. 2, values of T-50 ranges from 363 to 410°C for all materials except for commercial lignin, where its T-50 is at 607°C, which is very much higher than the others. Corresponding to T-50, values of R-50 are between 2.90 and 3.19% min^{-1} for all materials except lignin where it has a lower R-50 at 1.80% min^{-1}. Larger value of R-50 suggests that the materials are relatively active at T-50. This reveals that at temperature between 363 to 410°C, 50% of weight is loss from all samples except for lignin, which losses 50% of its weight at higher temperature, 410°C.

B. TG/DTG and GC analysis

For a more depth insight on behaviors of these samples during pyrolysis, TG/DTG curves and gas profiles of all six samples in pyrolysis environment are plotted separately and presented in Fig. 3(a)-3(f).
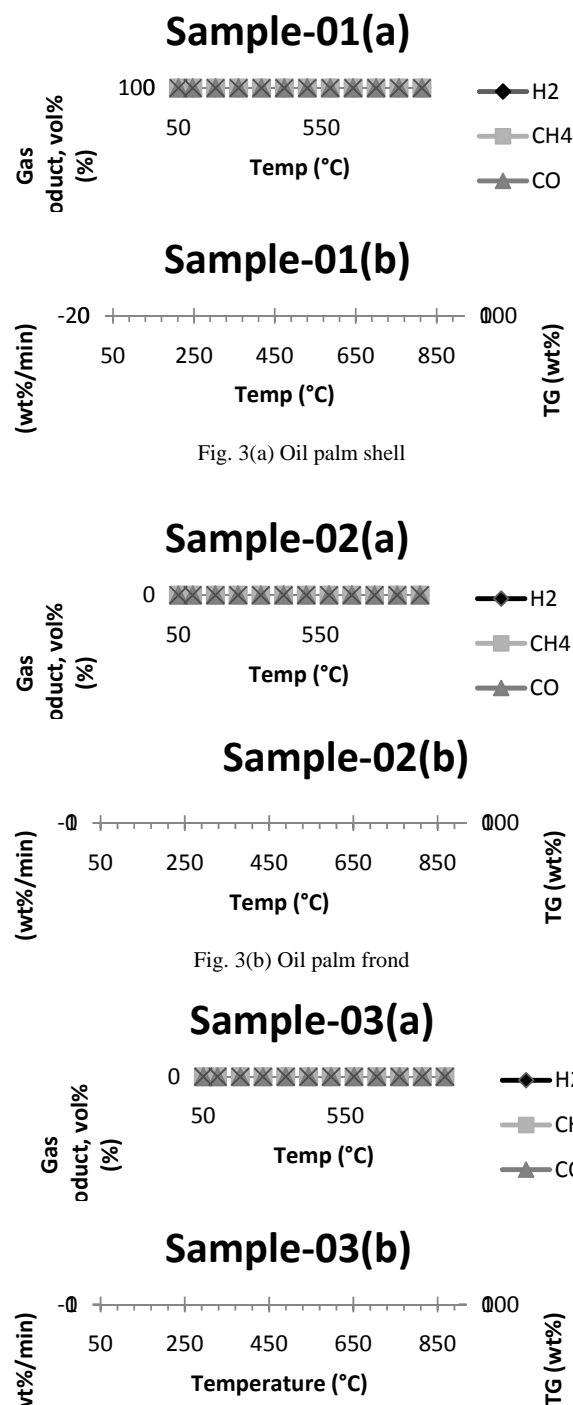

Fig. 3(a) Oil palm shell
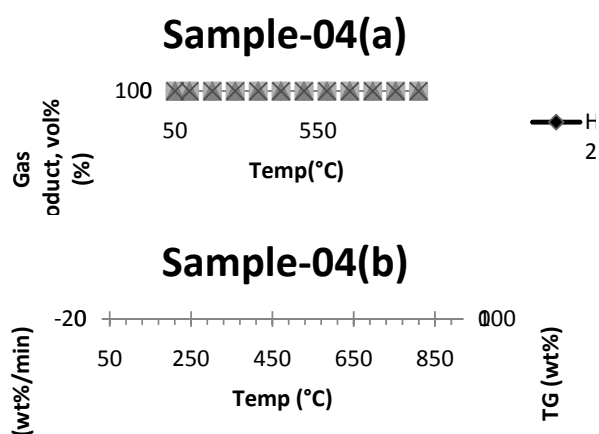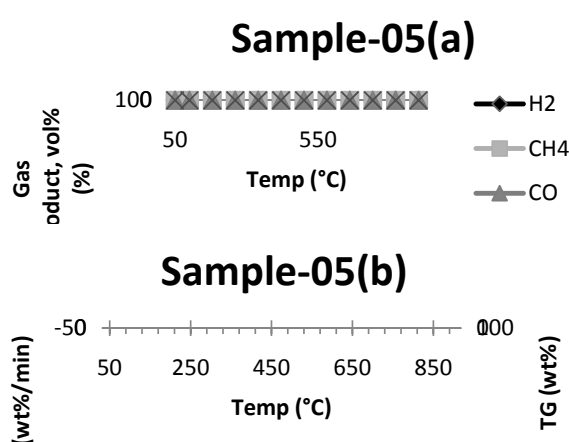

Fig. 3(b) Oil palm frond

Fig. 3(c) Rice husk

Sample-04(a)

Sample-04(b)

Fig. 3(d) Paddy straw

Sample-05(a)

Sample-05(b)

Fig. 3(e) Cellulose
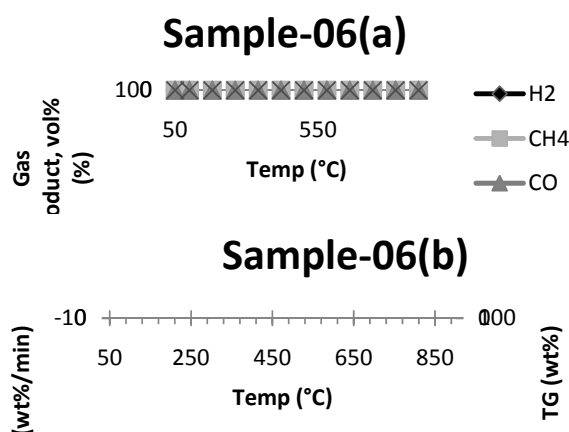
Sample-06(a)

Sample-06(b)

Fig. 3(e) Lignin

Fig. 3(a)-(f) Distributions of TG/DTG and gas profiles of (a) Oil palm shell, (b) Oil palm frond, (c) Rice husk, (d) Paddy straw, (e) Cellulose, and (f) Lignin in a pyrolytic environment

Pyrolysis process of biomass materials is s complex phenomenon due to involvement of several reactions in series.

As suggested by [8], performing pyrolysis study on decomposition mechanism of each individual biomass fractions independently will assist in understanding behavior of biomass as a whole, throughout the wide temperature range in pyrolytic conditions.

The temperature at which there is a first sign of weight loss in the sample is denoted as initial temperature, T_i. At the beginning of the first inverse curve on the DTG line, start-point temperature, $T_{s.p}$ is recorded whereas $T_{e.p}$ is recorded at the end of the curve to denote the end-point temperature, From DTG curve also, temperature at which maximum rate of reaction occurs is denoted as T_{max}. These values and remaining weights of each sample at 900°C were as recorded in Table 2.

TABLE II
DEVOLATILIZATION TEMPERATURES OF ALL TESTED SAMPLES

Sample ID	01	02	03	04	05	06
T_i (°C)	103.67	103.67	106.00	105.33	115.67	103.50
$T_{s.p}$ (°C)	213.33	213.33	248.00	242.67	275.33	215.67
$T_{e.p}$ (°C)	483.33	406.33	421.33	408.67	437.33	562.67
T_{max} (°C)	323.67 393.67	255.00 322.00 365.00	334.00 385.00	363.00	401.00	421.33
Wt_{900} (%)	16.48	23.30	31.73	34.34	8.61	42.74

For oil palm shell (Fig. 3(a)), a double-peak distribution in the curve is obviously exhibited. The first peak (323.67°C) and the second peak (393.67°C) stand for hemicelluloses and cellulose, respectively. The wavy curve with very low intensity at temperature higher than 500°C indicates the pyrolysis of lignin composition in oil palm shell.

When oil palm frond (Fig. 3(b)) is tested, one sharp peak is displayed. The peak develops at 365°C from the decomposition of cellulose, while another two peaks with lower intensity are observed at 255°C and 322°C.

For rice husk and paddy straw (Fig. 3(c) and 3(d) respectively), the peak of cellulose is located at almost similar temperatures (385 and 365°C, respectively) and the peaks of hemicelluloses (334°C) overlap that of cellulose. In addition, it is observed from the smooth tailing of the curves that lignin decays steadily as temperature increases.

For pure cellulose purchased from Sigma-Aldrich, the pyrolysis proceeds very rapid between 300 to 410°C (Fig. 3(e)). Entering the second stage at 500°C, its weight loss reaches at 85 % and the remaining residue is 8.61 wt% at the end of the process (900°C). Only one sharp peak (401°C) is observed from DTG curve which stands for decomposition of cellulose, and thus confirming the purity of the tested material.

For commercial lignin (Fig. 3(f)), the decomposition is quite slow and occurs gradually from 250 to 500°C. One broad peak is observed at 421.33°C. Smaller peaks in stage 3 (500 to 900°C) indicate that steady decomposition of lignin is still happening and high amount of residue (40%) is observed at the end of the experiment.

As a consequence of moisture liberated from the biomass, a bump develops at temperature around 100°C can be observed

in TG of all samples. Compared to cellulose, percentage of hemicelluloses contained in both rice husk and paddy straw are relatively small causing the peak of hemicelluloses to merge greatly with peak of cellulose. In contrast, percentage of hemicelluloses and cellulose contained in oil palm shell are very much similar to each other, resulting in an obvious double-peak in the curve. As for oil palm frond, two obvious peaks developed before the peak of cellulose is due to a relatively high percentage of hemicelluloses composition in the material as compared to cellulose.

For oil palm shell and frond, the residues left after pyrolysis until 900°C are less than 25 wt%. However, for paddy straw and rice husk residues left are higher (more than 30 wt%) compared to the first two samples. For cellulose, only 10 wt% is left after pyrolysis since it decomposes easily throughout the temperature range. On the other hand, lignin gives the highest remaining char (50 wt%) due to its complex and thermally stable nature.

For gas profile obtained from GC analysis, significant amount of H_2 started to be produced at temperature around 350°C for all samples. However, the time taken for H_2 percentage to drop varies between samples. This may depend on the decomposition rate of the samples.

Sample like lignin decomposes at low rate, thus permitting H_2 to be released at longer time. In contrast, production of H_2 finished very soon for cellulose mainly due to its rapid decomposition between 350 and 450°C. Permanent gases such as CO_2 and CO are dominating the amount of gases produced from the pyrolysis. These gases are released vigorously in stage 1 (below 200°C), mainly from hemicelluloses decomposition during the drying stage. Based on the decomposition profiles, this is strongly contributed by high percentage of cellulose and hemicelluloses in the samples.

IV. CONCLUSION

Pyrolysis of four biomass (oil palm shell, oil palm frond, paddy straw and rice husk) and two individual components of biomass (pure cellulose and lignin) have been performed in a TGA to study the decomposition behavior of these materials and impact on the gases produced in a pyrolytic environment up to 900°C. TG/DTA together with GC analysis provides an insight regarding the link between biomass decomposition behavior and its fiber fractions. Overall, TG/DTG and gases profiles obtained suggest effective pyrolysis temperature at which different fractions of biomass actively respond to the experimental condition.

Oil palm shell, oil palm frond, paddy straw and rice husk are found to be reactive enough in a pyrolytic environment of up to 900°C since significant decomposition of these biomass starts at temperature as low as 210°C and maximum value of weight loss is achieved at about 500°C. H_2 productions started rapidly at this temperature as well, due to the decompositions of biomass inside the TGA. However, for materials with more percentage of lignin such as oil palm shell, slightly higher operating temperature is needed in order to allow complete decomposition of lignin fractions. In contrast, materials with high hemicelluloses or cellulose fractions may need lower operating temperature as compared to lignin, to achieve complete decomposition.

Biomass with higher lignin contents such as oil palm shell shows longer duration for H_2 to completely release. Decomposition of this fraction gives off more H_2. On the other hand, biomass with more cellulose such as rice husk and paddy straw complete emission of H_2 in shorter time.

These TG/DTG and GC results are beneficial to be observed prior to selection of operating parameters for pyrolysis or any thermal treatment for these samples.

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