International Journal of Renewable Energy Resources 1 (2011) 7-10

THERMOGRAVIMETRIC ANALYSIS OF PALM OIL WASTES DECOMPOSITION

Z. Khan, S. Yusup and M.M. Ahmad
Department of Chemical Engineering, Universiti Teknologi PETRONAS
Bandar Seri Iskandar, Tronoh 31750, Malaysia
Email: drsuzana_yusuf@petronas.com.my

ABSTRACT

Thermal decomposition of palm oil wastes i.e. palm kernel shell (PKS) and palm oil fronds (POF) was studied using thermogravimetric analysis (TGA) under non-isothermal conditions. Thermogravimetric (TG) and its first derivative profiles were depicted to show different breakdown regions for PKS and POF. The decomposition region of hemicellulose, cellulose and lignin was identified. Kinetic parameters i.e. activation energy, pre-exponential factor and order of reaction were then evaluated from the weight loss profiles for the temperature range of 50-900 °C at a heating rate of 20 °C/min. Nearly 60 wt% of palm oil wastes decomposed at the temperature less than 400 °C. The thermal decomposition of palm oil wastes fitted well as first order kinetics with correlation coefficient of $R^2 > 0.99$. The activation energy of PKS and POF was 35 kJ/mol and 41 kJ/mol, respectively. This fundamental study provides the basic information on palm oil wastes decomposition which can benefit our current development work on palm oil wastes steam gasification unit.

Keywords: Palm oil wastes, Thermogravimetric analysis, Biomass, thermal decomposition, kinetic study

1. INTRODUCTION

Biomass has been upgraded as an alternative source of chemical feedstock and fuels in the last two decades due to serious environmental issues and fast depleting rate associated with conventional fossil fuel. It has been accepted as renewable, abundant and CO_2 neutral by the society. The efficient use of biomass depends on its conversion into clean and valuable energy. Thermal decomposition of biomass is an important step in its thermochemical conversion processes. The detail understanding of the biomass decomposition process and associated kinetic parameters are valuable information for the design of equipment and process operation for biomass thermal conversion processes (Guo and Lua 2001). Palm oil is the main resource for Southeast Asia particularly Malaysia and Indonesia which contributed 43% and 44% of global production in 2006, respectively (Shuit et al. 2009). In the same year, Malaysia generated 51.2 million tons of palm oil wastes including empty fruit bunch (EFB), palm oil fronds (POF), mesocarp fiber (MF), palm oil trunks (POT) and palm kernel shell (PKS) (Sumathi et al. 2008). The distribution of the wastes is given in Figure 1. Several techniques are available to understand the (in-depth) processes and reaction kinetics for biomass decomposition. Among these, thermogravimetric analysis (TGA) which is based on the observation of sample mass loss with respect to time or temperature at a specific heating rate is the most popular and simplest technique (Luangkiattikhun et al. 2008). Moreover, TGA provides high precision (Várhegyi et al. 2009), a fast rate data collection and high repeatability (Yang et al. 2004) under well-defined kinetic control region.Very few attempts have been carried out to study the thermal decomposition of palm oil wastes using TGA. Guo et al. (2001) reported the effect of heating rate on the thermal decomposition and kinetic parameters for PKS. They found a lateral shift in derivative thermograms (DTG) when the heating rate was increased.

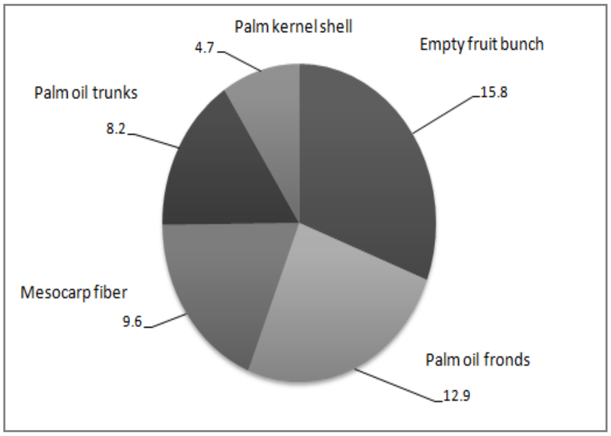


Figure 1 Palm oil wastes distribution (million tons) in Malaysia in 2006 (Sumathi et al. 2008)

Yang et al. (2004) studied hemicellulose and cellulose decompositions in PKS and EFB. They proposed the decomposition temperatures in the range of 220-300°C and 300-340°C for hemicellulose and cellulose, respectively. Hooi et al. (2009) (Hooi et al. 2009) observed the thermal decomposition of palm oil pressed fruit fibres (PFF) at temperature zones of 220-300 °C, 300-400°C and 400-700°C, and determined the kinetic parameters. Recently, Khan et al. (2011) studied the thermal decomposition of PKS and EFB and reported kinetic parameters at three different heating rates (10, 30 and 50 °C/min). They found that EFB decomposed faster compared to PKS and, observed that the decomposition of the palm oil wastes was faster and easily occurred when the heating rate was increased.

In this work, decomposition of palm kernel shell (PKS) and palm oil fronds (POF) under nonisothermal conditions was investigated using TGA. Thermogram analysis was presented to understand the decomposition of cellulose, hemicellulose and lignin as the major components in lignocellulosic biomass. Moreover, kinetic parameters i.e. activation energy, frequency factor and order of reaction were determined and compared with literature.

2. MATERIAL AND METHODS

2.1 Biomass sample preparation

Two types of palm oil wastes, i.e. palm kernel shell (PKS) and palm oil fronds (POF) were used in this study. These biomass wastes have been characterized in accordance with the procedure of American Society for Testing and Materials (ASTM) and the basic properties are summarized in Table 1(Khan et al. 2011). Biomass samples were dried at 105 °C and the weight was monitored at one hour interval, until the readings became constant. The samples were then grinded and sieved to the particle size of 150-250 µm.

Table 1 Biomass properties (wt % dry basis)

Analysis	Palm kernel shell	Palm oil fronds
Proximate analysis		
Moisture	7.73	5.99
Volatiles	81.03	83.19
Ash	4.10	3.90
Fixed Carbon (by difference)	14.87	12.91
Elemental analysis		
C	49.65	42.10
H	6.13	5.46
N	0.41	0.70
S	0.48	0.13
O (by difference)	43.33	51.61
Chemical analysis (major components)		
Cellulose	20.80	30.40
Hemicellulose	22.70	40.40
Lignin	50.70	21.70

2.2 Experimental procedure

The palm oil wastes decomposition experiments were performed under nonisothermal conditions in a standard TGA (EXSTAR TG/DTA 6300, from SII). For all experiments, N_2 was used as inert carrier gas with a constant flow rate of 100 ml/min. Biomass sample with the weight of approximately 5 mg was used in all experimental runs. Before the start of each experiment, the system was purged with N_2 gas at 100 ml/min for about 20 min (at 50 °C) to remove entrapped gases. Subsequently, the sample was heated at a constant heating rate of 20 °C/min from 50 to 900 °C after which the temperature was kept constant for 10 min. All experiments were repeated twice for reproducibly. No significant variation was observed in the repetition run.

2.3 Kinetic parameter estimation

Biomass decomposition rate under nonisothermal condition can be represented by the following equation (Zhang et al. 2006):

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-\frac{E}{RT})(1-\alpha)^n \tag{1}$$

Here α, T, A, E, R and n is sample mass fraction reacted, temperature, frequency factor, activation energy, universal gas constant and reaction order, respectively.
α can be defined as

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{2}$$

where m_0, m and m_∞ represent initial, actual and final sample weights, respectively.
By integrating, equation (1) becomes

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{A}{\beta}\int_0^T \exp(-\frac{E}{RT})dT \tag{3}$$

In eq. (3), $\int_0^T \exp(-\frac{E}{RT})$ has no exact solution. Integrating the function and neglecting high order terms, eq. (3) then becomes

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{\beta E}\left[1-\frac{2RT}{E}\right]\exp(-\frac{E}{RT}) \tag{4}$$

In logarithm form, the equation obtained is

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{ART^2}{\beta E}\left[1-\frac{2RT}{E}\right]\exp(-\frac{E}{RT})\right] \tag{5}$$

As RT/E <<1, it can assumed that 1-2RT/E ~ 1 (Ahmed and Gupta 2009), so the final form for n^{th} order reaction can be derived as

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \tag{6}$$

For first order reactions, the equation becomes

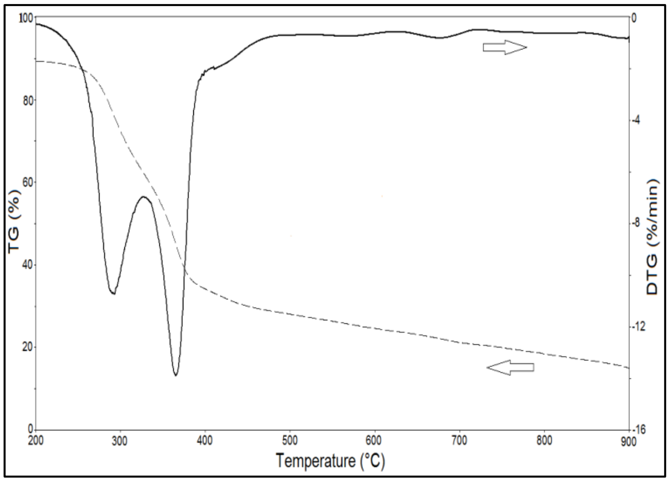
$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]=\ln\left[\frac{AR}{\beta E}\right]-\frac{E}{RT} \qquad (7)$$

By plotting the term in left hand side of eq. (6) and (7) against 1/T, for nth and first order reactions, respectively, the resultant straight line posses a slope of E/R and intercept of ln(AR/βE). The slope and intercept values are then used to determine E and A.

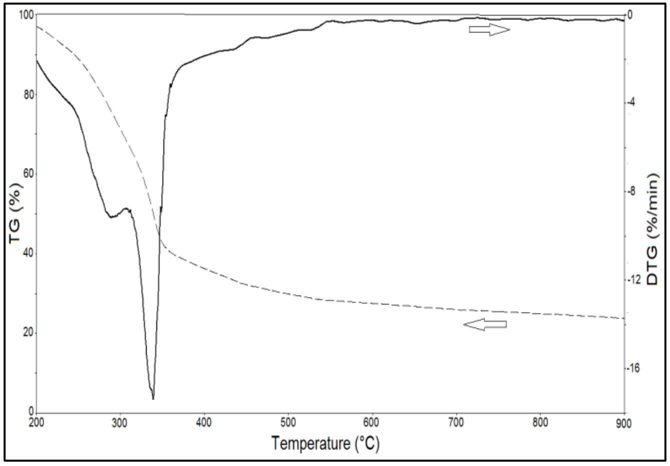
3. RESULTS AND DISCUSSIONS

3.1 Thermogram analysis

Residual weight% (TG %) and its first derivative (DTG) of PKS and POF samples with respect to temperature ranges between 200 to 900 °C at a heating rate of 20 °C/min are shown in Figure 2. Sample drying usually takes place at the temperature less than 200 °C, at which results are not shown here.



(a)



(b)

Figure 2 Thermogravimetric and derivative thermogravimetric profiles for a) palm kernel shell and b) palm oil fronds

Lignocellulosic material mainly consists of hemicellulose, cellulose and lignin. In biomass thermal decomposition, hemicellulose is first to decompose, followed by cellulose, with lignin being the last to decompose due to its heavy cross link molecules (Demirbas 2001). In Figure 2, the DTG profiles for PKS and POF mainly consist of two dominant peaks appearing at 280-300 °C and 340-360 °C, respectively. The first peak represents hemicellulose decomposition where the second peak representing cellulose decomposition. For both biomass wastes, hemicellulose decomposition occurs almost in similar temperature region. Meanwhile, in PKS, the cellulose decomposition takes place at higher temperature as compared to POF which is may be due to different cellulosic structure and chemical compositions between the palm oil wastes. The tail at temperature higher than 400 °C indicates the lignin decomposition region, similar reported by Yang et al. (2004) and Luangkiattikhun et al. (2008). In the present study, no significant lignin decomposition is observed at temperature higher than 400 to 900 °C which is consistent with findings reported by other researchers (Guo and Lua 2001; Luangkiattikhun et al. 2008). However, small lignin decomposition was observed for PKS and EFB at a higher heating rate of 50 °C/min in the temperature range of 450-530 °C and 680- 750 °C (Khan et al. 2011). Among the two palm oil wastes, POF produces residual fraction of 24% as compared to 15% by PKS. In the DTG profiles, maximum decomposition rate of -17 %/min and -14 %/min at temperature of 360 °C and 345 °C can be observed from PKS and POF, respectively. It is important to note that 60 wt% of PKS and POF are decomposed at 374 °C and 361 °C. This high weight loss at low temperature may be attributed to the high volatile material content i.e. more than 80% in the palm oil wastes.

3.2 Kinetic parameter determination

The kinetic parameters are determined based on sample mass fraction reacted (α) of palm oil wastes against temperature at a heating rate of 20 °C/min. Activation energy (E), frequency factor (A) and order of reaction (n) with their respective correlation coefficients are evaluated and listed in Table 2. The correlation coefficient (R^2) is higher than 0.990 for both palm oil wastes. The activation energy evaluated for PKS and POF are 35.02 kJ/mol and 41.23 kJ/mol, and the frequency factor are 2.81 and 10.81 s^{-1}, respectively, for first order kinetics. Yang et al. (2004) proposed the first order reactions kinetics for the decomposition of palm oil wastes i.e. PKS, EFB, palm oil fibers, and reported high activation energy of 60 kJ/mol which is higher compared to the values reported in the present work. High activation energy for palm oil wastes decomposition was also reported by Khan et al. (2011), Guo et al. (2001) and Luangkiattikhun et al. (2008). This deviation may be due to different properties and approach used to calculate the kinetic parameters.

Table 2 Kinetic parameters

Biomass	Kinetic parameters			R^2
	E (kJ/mol)	A (s^{-1})	n (-)	
Palm kernel shell (PKS)	35.02	2.81	1.0	0.991
Palm oil fronds (POF)	41.73	10.01	1.0	0.997

4. CONCLUSION

Thermal decomposition of palm kernel shell and palm oil fronds was carried out in TGA to identify the decomposition regions and to evaluate kinetic parameters i.e. activation energy, frequency factor and reaction order. Based on the decomposition profiles, hemicellulose was first to be decomposed at 280-300 °C, followed by cellulose decomposition at 340-360 °C for both palm oil wastes. No lignin decomposition was observed, which was consistent with literature. The decomposition rate of PKS was found higher as compared to POF. Palm oil wastes decomposition profiles fitted well to first order reactions kinetics. Nevertheless, in the present study, activation energy and frequency factor determined are observed to be lower compared to the values reported in the literature. This may be due to the different properties of palm oil wastes and the approach used for kinetic parameters evaluation.

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