

## Estimating Combustion Kinetics of UAE Date Palm tree Biomass using Thermogravimetric Analysis

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### Abstract

Palm tree consists of different parts among which are the leaflet, rachis and fibers. All these parts constitute lignocellulose biomass components capable of producing value added end products.

A kinetic study of thermal decomposition of UAE date palm tree of *phoenix dactylifera* species was carried out using thermal gravimetric analysis (TGA) at heating rates 10 °C/min, 15 °C/min and 20 °C/min. Most of the lignocellulose material decomposed between 300 °C and 650 °C at each heating rate. The rachis decomposed in three phases while the leaflet and fibers decomposed in two phases. The apparent activation energies increased from 54 to 476 kJ/mol, 55 to 458 kJ/mol and 84 to 329 kJ/mol for leaflet, rachis and fibers, respectively for conversion ranging from 10-% to 80-%. Results from this study are fundamental in optimizing operational conditions of a reactor for production of furfural, levulonic acid, dihydroeugenol, DHE and 2,6-dimethoxy-4-propyl phenol, DMPP as high value chemicals.

**Key words:** UAE Palm tree biomass, Thermogravimetric analysis, Combustion kinetics, Activation energy

### 1. Introduction

United Arab Emirates and the surrounding Gulf nations are home to millions of date palm trees and in particular the phoenix *dactylifera* species. Palm tree has a rich survival history and is perhaps one of the oldest trees in the world, although its base origin remains uncertain with some reports suggesting it was domesticated 5000 years ago in Mesopotamia, Iraq and Arab regions (Zohary and Hopf, 2000). The degree of certainty about the origin of date palm was obtained from the oldest radiocarbon that showed the discovery of seeds was from United Arab Emirates' Dalma Island. The two seeds obtained in 1998, the oldest was 5110 BCE and the second one was 4670 BCE (Jain and Priyadarshan, 2009). For a long time, date palm trees have played a significant role in the society and the environment of UAE and the Gulf region. Widely cultivated date palm trees are used both for their delicious fruit and for landscaping. Currently UAE has over 30 million date palm trees and each palm tree, on average produces around 12-15 new leaves every year and the same amount is usually cut from the tree (Barrevel, 1993). Each dried leaf weighs about 2-3 kg. Therefore, on average each date palm tree produces approximately 25-30 kg of waste from the leaves and the surface fibers around the trunk and additional 10-15 kg of waste from the fruit-bearing bunches summing to 40 kg of total waste per tree (Mallaki and Fatehi, 2014). Considering that UAE has over 30 million date palm trees (both productive and non-productive), the amount of waste they generate is huge (about 1.2 million tons annually). Moreover, many other trees are grown for landscape design in UAE which also generate significant amount of waste. Palm tree leaves even after drying do not naturally fall off like many leaves of other trees, they must instead be manually removed, which preserves them from being blown away by wind and in turn making their collection and potential distribution easier for

feedstock applications. However, once leaves are in excess on the mother tree, this can render the date palm tree and surrounding trees vulnerable to environmental hazards such as pests, insects, disease and wild fires.

Most of the waste from palm trees is currently turned into compost or burned to generate heat despite their high content of cellulose, hemicelluloses and lignin that can be processed into more valuable products such as fuel generation, bio-based chemical production and all these through controlled thermochemical techniques would cause less environmental impact. Research is ongoing to convert the different date palm tree parts to value added products considering lignocellulose components as a base feed stock. For instance the lignocellulose from palm tree fibers have been studied for its potential application as a source of reinforcing fiber in composite materials, pulp and paper in addition to production of other bio-refinery products (Sbiai et al., 2008; Khiari et al., 2010; Saadaoui et al., 2013; Bendhaou et al., 2009; Agoudjil et al., 2011; El may et al., 2012). The rachis contain high holocellulose and hemicellulose content (Saadaoui et al., 2013; Bendhaou et al., 2009) and these are precursors for production of high value chemicals (HVC) such as 5-hydroxymethylfurfural (5-HMF) and furfural (Chuntanapum et al., 2008; Riansa-ngawong and Prasertsan, 2011; Yong et al., 2016; Aleid, 2013; Karimi et al., 2006) which are used in food, oil refineries, pharmaceutical as well as agricultural industry (Dias et al., 2005; Dias et al., 2006). The HVC from palm tree leaflets such as bio-succinic acid (Tan et al., 2017) and other copolymers (Beyaz et al., 2018) have potential to compete favorably with similar chemical compounds from petrochemical industry to positively impact food, pharmaceutical and other industrial applications.

Date palm residues represent a major quantity of biomass as lignocellulosic materials. This biomass is mostly made up of carbohydrates including cellulose and hemicellulose, bonded with lignin (Nakhshiniev et al., 2012). The lignocellulose content in palm biomass varies from species to another. A review study on *Elaeis Guineensis* species (Hossain et al., 2016) commonly cultivated in south East Asia, Central and West Africa showed various results of different palm tree parts and their lignocellulose content. For instance for palm fibers, a hemicellulose- 17.1–33.5 wt.%, cellulose- 42.7–65 wt. % and lignin- 13.2–25.31 % content was reported (Shinoj et al., 2011), while another study on *Phoenix dactylifera L.* species showed hemicellulose- 55 wt.%, cellulose- 20 wt.% and lignin- 23 wt.% content (Briones et al., 2011). The former is common species found in many parts of UAE; however, to our knowledge, the thermo decomposition kinetic study of leaflet, rachis and fibers of UAE date palm using thermogravimetric analysis (TGA) has not been reported before. TGA has been employed as a potential method for determining thermal decomposition mechanisms of plant biomass (Carrier et al., 2011).

Therefore, the purpose of this study is to determine the kinetics of combustion of UAE date palm tree (*Phoenix dactylifera L.*) using TGA analysis, with an aim of providing an insight on lignocellulose thermodecomposition trends for future production of high value chemicals from the same biomass. TGA can quantitatively resolve complex mixtures because of the characteristic thermal decomposition temperature of each component (Barneto et al., 2009). It was well established for instance that the pyrolytic decomposition of palm fibers in a closed reactor occurred at mild temperature region for hemicelluloses around 220 °C and for cellulose around 315 °C; -, however, the lignin peak was not displayed in that study (Ly et al., 2013). The combination of TGA and Differential Thermogravimetric analyses (DTG) provides the lignin content and particularly its influence during the combustion process. Finally, in the description of the biomass pyrolysis cellulose and lignin contents of some biomass (such as pulp and paper) have been determined by TGA; however, the method registered high errors for hemicelluloses contents due to complex varying nature of hemicellulose in different biomass (Cozzani et al., 1997). Therefore, in this study the TGA and DTG analysis were used to predict the thermo decomposition of leaflet, rachis and date palm fibers. In addition, the hemicellulose, cellulose and lignin contents were determined using established standard methods.

## 2.0 Methods

### 2.1 Materials

The Leaflet, Rachis and Fibers of *Phonenix dactylifera L.* used in this study as shown in **Figure 1**, were collected from local adult size (10-15 years old) date palm trees in Al-Ain, UAE (24122 N, 554441 E).



Figure 1. The different components of lignocellulose wastes of UAE date palm tree.

This lignocellulose biomass was collected as naturally dried samples with less than 9 wt.% moisture content; however, they were washed clean to remove any field contaminants and then dried under shade. The particle size of all samples used in this work was below 60 mesh.

## 2.2 Experimental procedures

The heating values of the samples were determined using bomb calorimeter model IKA C 2000 according to DIN 51900 method; where 0.5g crushed biomass sample was pelletized and placed in a quartz crucible connected with a fuse wire (15 cm), the crucible was placed inside the bomb calorimeter and charged with oxygen to approximately 200 Psi for about 10 seconds. The heat of combustion was computed from the temperature observations before ( $T_o$ ), during and after combustion ( $T_{max}$ ), taking into care for thermochemical and heat transfer corrections. The calorimeter was calibrated by combusting a standard known mass,  $m$ , of benzoic acid with a known heat of combustion (26.453 MJ/kg). Calibration and analysis samples were done in triplicates and the calibration factor for the bomb calorimeter,  $H$ , was calculated from benzoic acid calibration as follows:

$$H = (m * 26.453)/(T_{max} - T_o) \quad (1)$$

In three triplicates, the bulk density was determined as mass per unit volume using 500 ml graduated measuring cylinder according to the reference method (Oberberger and Thek, 2004). The proximate analysis of the biomass samples was determined according to ASTM D3173 (inherent moisture content); where triplicate samples were dried for 24 hours and 2 g in triplicates was weighed and kept in desiccator for 12 hours. The difference in weight before and after signified inherent moisture content; 2 g sample in triplicates was accurately weighed in a clean dry crucible and samples placed in a furnace at 575 °C for 3 hours, cooled under desiccator conditions for 1 hour and the difference in weight before and after expressed as a percentage signified ash content according to ASTM D3174 (ash); Volatile matter was determined according to ASTM D3175 in which 1 g sample was weighed in an empty crucible and then placed in a furnace, set and operated at 950 °C for exactly 7 minutes. Loss in weight after cooling was calculated and the deduction of inherent moisture off the weight loss, gave the volatile matter. from [100- (moisture content + Ash + volatile matter)], fixed carbon was determined as stated in ASTM D3172-07a (Fixed carbon) methods (ASTM, 2013). The component contents of C, H, O, and N were analyzed by the automatic elemental analyzer (Flash EA1112, CE Instruments) from Petroleum Institute, UAE, to determine the ultimate analysis of the sample.

Thermo-gravimetric analysis of all the three date palm parts in this study was carried out using TGA (Q500, TA Instrument). For each experiment, a sample weight of 6.0 mg ( $\pm 1.0$ ) was used for thermo-gravimetric analysis.

Nitrogen was used as a carrier gas with a flow rate of 20 mL/min. The heating rate was controlled at 10, 15 and 20 °C/min from 25 to 900 °C. During the thermo-decomposition process, the initial weight was recorded continuously as a function of temperature and time. The derivative (DTG) curve showed the weight loss of sample per unit time against temperature.

### 3.0 Results and Discussion

#### 3.1 Material Characterizations and Elemental Analysis

The bulk density and High Heating Values (HHV) characteristics of the samples are presented in **Table 1**. For the different parts of the palm tree, the moisture content of the leaflet, rachis and the fibers was 4.3, 5.7 and 5.4 wt%, respectively (see **Table 2**). The ash content of the leaflet was 12.7 wt.% and that of rachis and fibers was 6.1 wt.% and 8.2 wt.%, respectively. This ash content can be detrimental to the process as it has a tendency of reducing heat transfer during reactor operations such as heat transfer loss during pyrolysis, on the other hand once this ash is incinerated to obtain Oil Palm Ash (OPA), it can be used as a source of fertilizer due to its high potassium content (Sumathi et al., 2008). Some research groups have utilized OPA to synthesize absorbents targeting toxic gas removal (sulfur dioxide, SO<sub>2</sub>). It is believed that the active compound (calcium, silica, potassium, alumina, and hydrated water) in the absorbent prepared from OPA is responsible for the high absorption capacity of SO<sub>x</sub> (Zainudin et al., 2005; Mohamed et al., 2005).

Table 1. Bulk Density and Calorific Values of palm biomass (leaflet, rachis and fibers)

Biomass	Bulk Density (kg/m <sup>3</sup> )		Calorific value, HHV (MJ/kg)	
	This study	Literature	This study	Literature
Leaflet	426±4	411 <sup>a</sup>	15.5±0.1	17.9 <sup>b</sup>
Rachis	425±4	635 <sup>a</sup>	15.5±0.1	10.9 <sup>b</sup>
Fibers	387±9	209 <sup>a</sup>	14.8±0.1	16.4 <sup>c</sup>

<sup>a</sup>(Almi et al., 2015); <sup>b</sup>(Sait et al., 2012); <sup>c</sup>(Asadullah et al., 2014)

Table 2. Proximate analysis of palm biomass (leaflet, rachis and fibers)

Biomass	Moisture (wt.%)	Volatile matter (wt.%)	Ash content (wt.%)	Fixed carbon (wt.%)
Leaflet	4.3±0.3	75.8±1.2	12.7±1.2	7.2±0.2
Rachis	5.7±0.2	84.6±1.8	6.1±1.0	3.6±1.0
Fibers	5.4±0.1	77.4±0.6	8.2±0.3	9.0±0.8

The carbon (C) content of palm leaflet, 44.1±0.2 % was slightly higher than that of rachis and fibers, 43.6 % and 43.2 ±0.1%, respectively. Results for this study were in the same range with other reported lignocellulose biomass (Maiti et al., 2007), making UAE phoenix *dactyloflifera* palm specie equally competitive for fuel and as a chemical source precursor. The Nitrogen (N) content and results of other ultimate analysis are shown in **Table 3**.

Table 3. Ultimate analysis of palm biomass (leaflet, rachis and fibers) (as % on dry basis)

Biomass	C	H	N	S	O	O/C	H/C
Leaflet	44.1±0.2	5.9±0.0	1.5±0.2	0.0	48.5±0.4	1.1±0.2	0.1±0.2
Rachis	43.6±0.0	6.1±0.1	0.0±0.0	0.0	50.3±0.2	1.2±0.2	0.1±0.1
Fibers	43.2±0.1	5.7±0.1	0.8±0.0	0.0	50.3±0.2	1.2±0.2	0.1±0.2

The concentrations of phosphorous (P), calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) are shown in Table 4. Date palm tree is a representative of biomass consisting of mainly; cellulose, hemicellulose, and lignin. There is more lignin (21 wt.%) and cellulose (33 wt.%) content in fibers than in leaflet (20 wt.%, 21 wt.%, respectively) and rachis (11 wt.%, 32 wt.%, respectively). Rachis has the highest hemicellulose content (19.0 wt.%) (See Table 4.).

Table 4. Chemical composition (wt. %) of the different lignocellulosic parts of date palm.

Component	Leaflet	Rachis	Fibers
Hemicellulose (wt. %)	11.0±1.6	19.0±1.0	17.0±0.3
Cellulose (wt.% )	21.0±2.6	32.0±1.0	33.0±1.2
Insoluble Lignin (wt.% )	19.0±1.0	10.0±2.0	20.0±1.2
Soluble lignin (wt. %)	1.0±0.0	1.0±0.0	1.0±0.0
Ethanol-Benzene Extractives (wt.% )	29.0±3.8	14.8±1.0	9.0±3.0
<b>Element Analysis(ppm)</b>			
K	33.0±0.6	28.9±0.6	30.8±0.0
P	10.9±0.2	16.7±1.8	6.7±1.6
Ca	196.5±8.0	158.2±20	305.9±28
Mg	24.0±2.2	21.4±3.0	46.6±8.0
Na	8.7±2.3	11.5±1.4	26.5±3.6

### 3.2 Thermogravimetric Analysis

Results of the thermogravimetric analysis were expressed as a function of conversion, X and was defined as;

$$X = (w_o - w)/(w_o - w_\infty) \quad (2)$$

Where;  $w_o$  is the initial weight of the sample;  $w$  is the weight of the pyrolyzed sample;  $w_\infty$  is the final residual weight.

The degree of conversion as a function of temperature for palm leaflet, rachis and fibers at selected heating rates of 10 °C/min, 15 °C/min and 20 °C/min is shown in **Figure.2a**, **Figure.2b** and **Figure.2c**, respectively, which was calculated from the TG data. The thermal decomposition for all investigated palm biomass parts, followed a similar trend showing an increase in conversion with increasing temperature. At lower temperatures for all the three parts of palm biomass, the small change in conversion was attributed to the vaporization of the inherent

moisture attached on the surface of the sample. A similar phenomenon was reported for other biomass including soft and hard wood, as well as microalgae (Ly et al., 2013; Kim et al., 2012; Ly et al., 2015; Liou et al., 1997). After moisture vaporization, the rate of decomposition increased with increasing heat rate, which is probably because there is more thermal energy to facilitate better heat transfer between the sample and the surroundings (Caballero et al., 1997). This increased thermal energy resulted in increased conversion. The maximum differential rate of conversion for palm leaflets occurred at 716, 718 and 725 °C at heating rates 10, 15 and 20 °C/min, respectively. On the other hand, the maximum differential rate of conversion for palm rachis occurred at 669, 683 and 698 °C at heating rates 10, 15 and 20 °C/min, respectively, and the maximum differential rate of conversion for palm fibers occurred at 715, 720 and 729 °C at heating rates of 10, 15 and 20 °C/min, respectively.

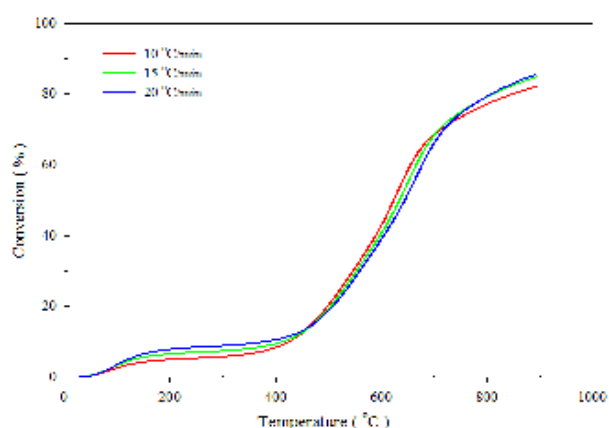


Figure 2a. Conversion of palm leaflet as a function of temperature at different heating rates.

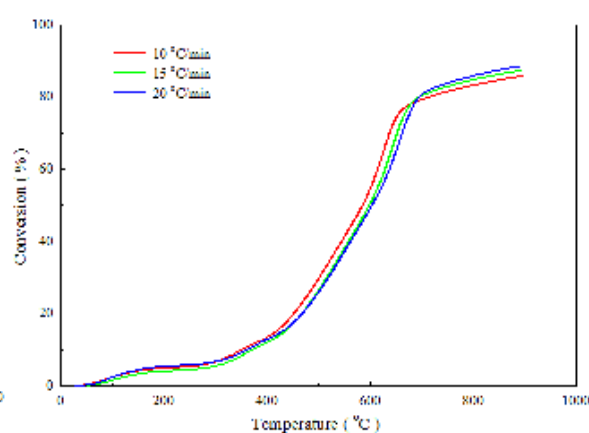


Figure 2b. Conversion of palm rachis as function of temperature at different heating rates.

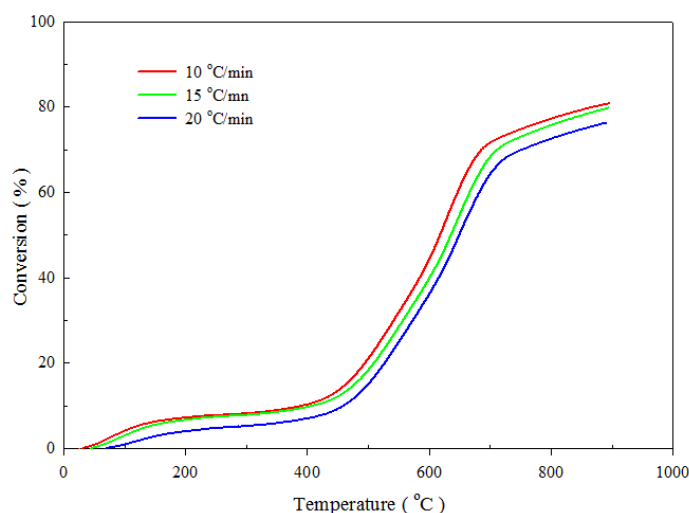


Figure.2c. Conversion of palm fibers as a function of temperature at different heating rates.

### 3.3 Differential Thermogravimetric Analysis

The differential rate of conversion,  $dX/dt$ , was obtained from differential thermogravimetric analysis (DTG) at heating rates of 10, 15 and 20 °C/min. The DTG curves of palm rachis for various heating rates of 10, 15 and 20 °C/min is shown in **Figure.3a**. A big fraction of rachis biomass decomposed between 290 °C and 700 °C, and this was attributed to decomposition of hemicellulose, cellulose and lignin fractions that make up the biggest percentage of lignocellulose biomass. The thermal decomposition peak between 290 °C and 390 °C was assigned to the decomposition of hemicellulose, and between 390 °C and 520 °C and the last peak between 520 °C and 700 °C, was assigned to the decomposition of  $\alpha$ -cellulose and  $\beta$ -cellulose, and lignin, respectively. The DTG for palm leaflet and fibers had a similar decomposition temperature profile between 290 °C and 700 °C as that of rachis (see **Figure.3b** and **Figure.3c**). However, the decomposition peaks of hemicellulose and cellulose seemed to overlap giving two major decomposition regimes as opposed to rachis where all the three components were revealed for all the three investigated heating rates. The result of hemicellulose and cellulose decomposition temperature profile for this work was in agreement with that reported in the literature by other researchers (Alvarez and Vázquez, 2004; Kim and Agblevor., 2007) based on which the peaks in the DTG profiles of the present work were assigned. In another study, the thermal decomposition of wood revealed two decomposition peak regimes at lower temperatures, which were assigned to hemicellulose and cellulose (Antal and Varhegyi, 1995). The noticeable decomposition peak at lower temperatures below 290 °C for all the three parts of palm biomass investigated at various heating rates was assigned to vaporization of the inherent adsorbed moisture on the surface of biomass. Furthermore increasing the heating rate from 10 °C/min to 20 °C/min, increased the rate of biomass decomposition but this never altered the decomposition trend, this is because increasing heating rate only provided more thermal energy in the system and the surrounding thus aiding more sample decomposition. The assignment of the three peaks to hemicellulose, cellulose and lignin is in accord with the fact that the chemical characteristics of hemicellulose are thermally labile and decompose first at relatively low temperature; cellulose is more thermally stable due to its crystalline structure and decomposes at higher temperatures compared to hemicellulose and due to its complex and relatively heterogeneous structure, lignin decomposes over a wide range of temperature, and in some cases it decomposes without showing a visible peak in the DTG curve (Müller-Hagedorn et al., 2003).

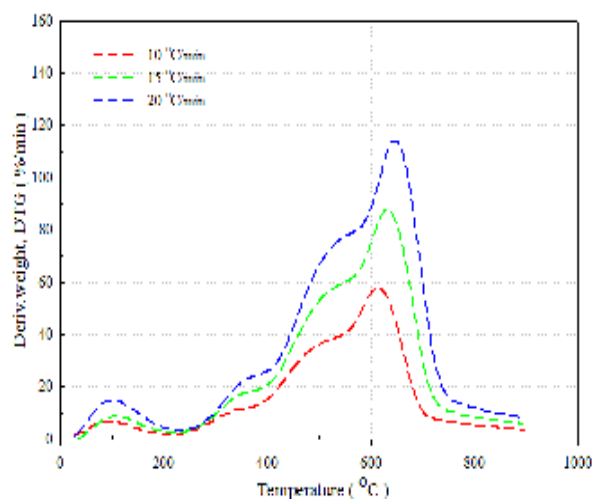


Figure 3a. Differential Thermogravimetric (DTG) curves of palm rachis at 10, 15 and 20 °C/min heating rate.

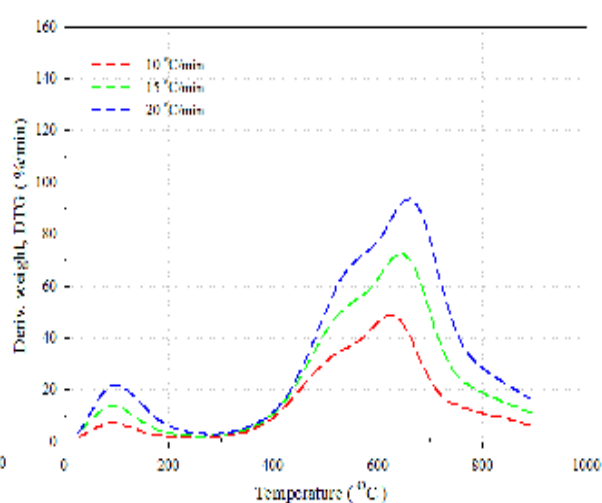


Figure 3b. Differential Thermogravimetric (DTG) curves of palm leaflet at 10, 15 and 20 °C/min heating rates.

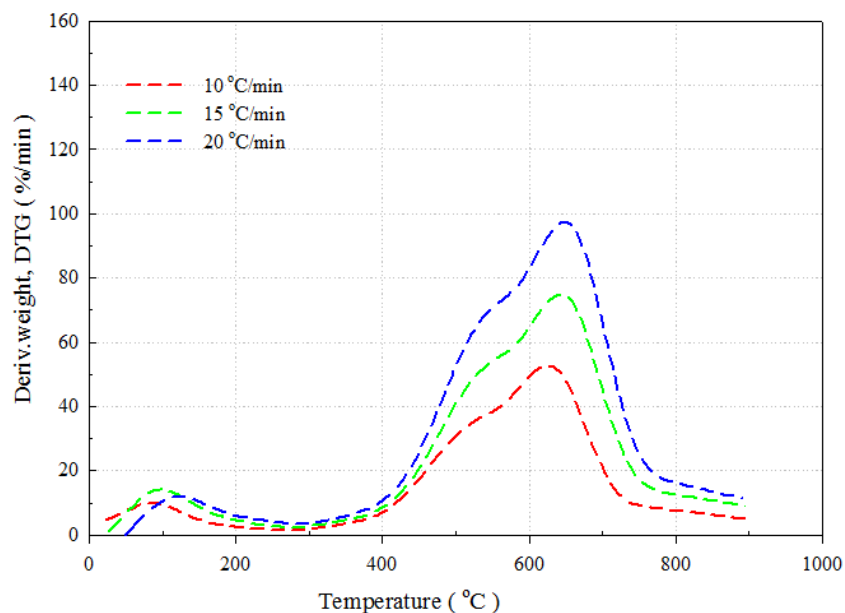


Figure.3c. Differential Thermogravimetric (DTG) curves of palm fibers at 10, 15 and 20 °C/min heating rates.

### 3.4 Kinetic parameters of Palm leaflet, rachis and fiber biomass

The thermal gravimetric analysis and differential thermogravimetric (DTG) curves are often used to assess the stability of polymeric materials. For processes like pyrolysis, the shapes of TG curves are determined by kinetic parameters such as activation energy, Arrhenius frequency factor and order of reaction. From the gravimetric data; the pyrolysis kinetic parameters were obtained using differential technique (Friedman, 1963) and the thermal decomposition rate of conversion,  $dX/dt$  was expressed as;

$$dX/dt = kf(X) \tag{3}$$

Where  $f(X)$  is the function of conversion and  $k$  is the reaction rate constant and can be expressed by the equations below;

$$f(X) = (1 - X)^n \tag{4}$$

Where  $n$  is the reaction order.

The reaction rate constant was expressed by Arrhenius equation as;

$$K = A \exp(-E_a/RT) \tag{5}$$

Substituting equations (3) and (4) in equation (2), and then introducing natural logarithms on both sides, results the following;

$$\ln(dX/dt) = \ln A + n \ln(1 - X) - (E_a/RT) \tag{6}$$

$E_a$  is the apparent activation energy and can be obtained from a linear relationship plot of equation (5) considering  $\ln(dX/dt)$  against  $1/T$ . Hence, for the different conversions different parallel straight lines with negative slope  $E_a/R$  were obtained from which apparent energies of activation were calculated. Taking an example of palm rachis, for conversion of 30%, the corresponding temperature at different heating rate was 502 °C, 516 °C and 520 °C, for heating rates of 10°C/min, 15 °C/min and 20 °C/min, respectively. The values of  $\ln(dX/dt)$  were -7.8750, -7.4984 and -7.1995 with corresponding  $1/T$  values of  $1.2902 \times 10^{-3}$ ,  $1.2665 \times 10^{-3}$  and  $1.2613 \times 10^{-3}$ , respectively were obtained for the mentioned temperatures respectively. These data and those of



leaflet and fibers are shown in **Figure.4a**, **Figure.4b** and **Figure.4c**, for different iso-conversion. The intercept  $\ln[A(1-X)^n]$  was calculated from Fig.4a, Fig.4b and Fig.4c for all conversions. Assuming the lower fixed apparent orders of 0 or 1, exponential constant can be obtained by curve fitting equation (5).

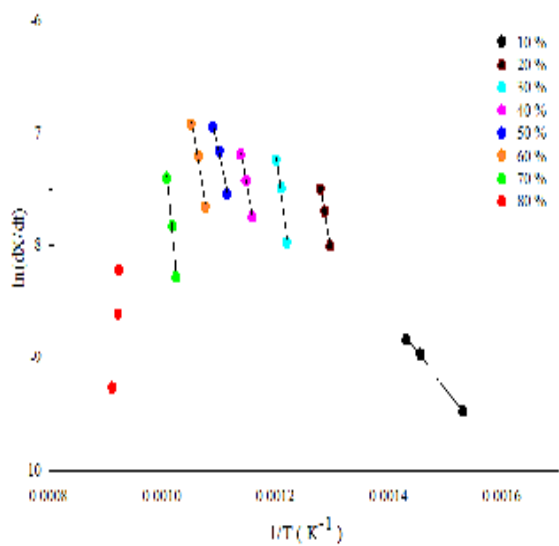


Figure.4a. Relationship between  $\ln(dX/dt)$  and  $1/T$  for palm leaflet for different conversions.

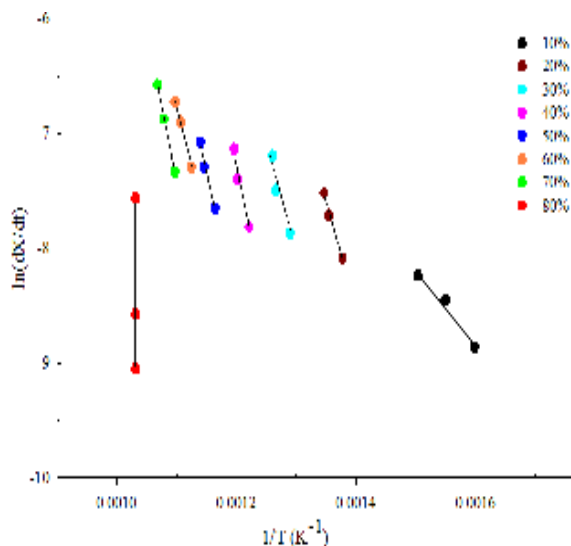


Figure.4b. Relationship between  $\ln(dX/dt)$  and  $1/T$  for Palm rachis for different conversions.

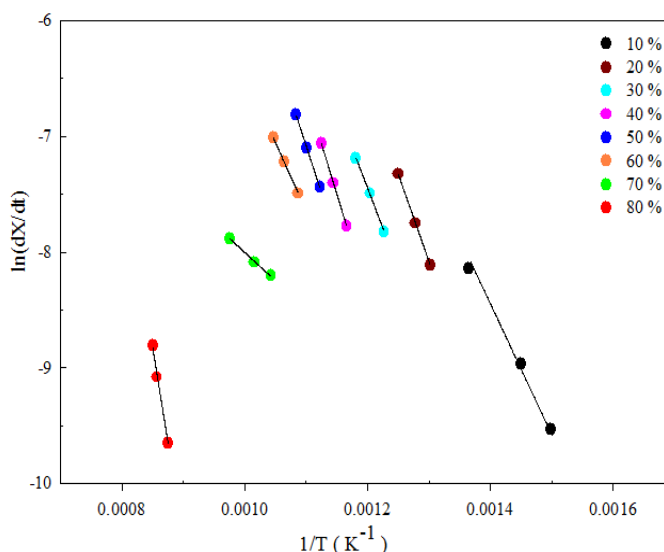


Figure 4c. Relationship between  $\ln(dX/dt)$  and  $1/T$  for palm fibers for different conversions.

The apparent activation energy as a function of iso-conversion is shown in **Figure.5** for palm leaflet, palm rachis and palm fiber biomass. From the same figure, activation energy generally has two regimes; first one for conversion from 10 % to 60 % , which depicts the energy barrier needed to decompose hemicellulose and cellulose and the second regime from conversion of 60 % to 80 % , which represents the energy barrier needed to overcome the decomposition of lignin. This apparent activation energy trend in principle is in agreement with our obtained results from DTG analysis. The average activation energy was; 252 kJ/mol, 200 kJ/mol and 164 kJ/mol, for leaflet, rachis and fibers, respectively. In comparison to other works, similar activation energy range was reported; 182.3 kJ/mol for cellulose derivatives (Alvarez and Vázquez, 2004). And the variation in activation energies was reported for a scheme consisting of independent first order parallel reactions of a biopolymer component of hemicellulose, cellulose and lignin (Vamvuka et al., 2003).

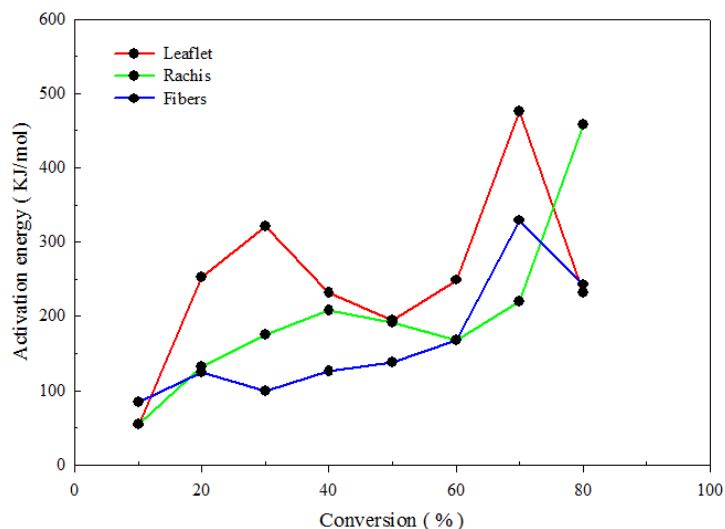


Figure 5. Calculated activation energies at different iso-conversions for thermal decomposition of Palm leaflet, rachis and fibers.

The pre-exponential factor obtained from equation (5), had a direct relationship with apparent activation energy (see Table 5). When the activation energy increased, the pre-exponential factor increased and the reverse was true, this result was in agreement with Friedman’s approach (Friedman, 1963). During the first decomposition regime, the pre-exponential factors were highest for leaflet ( $1.60 \times 10^{17} \text{ s}^{-1}$ ), followed by rachis with  $1.33 \times 10^{10} \text{ s}^{-1}$  and lastly fibers with  $3.30 \times 10^4 \text{ s}^{-1}$ , at which point the weight loss corresponded to the thermal decomposition of hemicellulose and cellulose in the palm biomass parts investigated. The pre-exponential factors for leaflet, rachis and fibers, were higher when conversion was 80%, perhaps because of devolatilization of residual char. The range of pre-exponential factors assuming the overall reaction, 0<sup>th</sup> and 1<sup>st</sup> orders for conversion ranging from 10 % to 80 % were between;  $1.57 \times 10^0 \text{ s}^{-1}$  to  $1.38 \times 10^{25} \text{ s}^{-1}$  (0<sup>th</sup> order) and  $1.74 \times 10^0 \text{ s}^{-1}$  to  $6.91 \times 10^{25} \text{ s}^{-1}$  (1<sup>st</sup> order) for leaflet,  $5.49 \times 10^0 \text{ s}^{-1}$  to  $6.61 \times 10^{26} \text{ s}^{-1}$  (0<sup>th</sup> order) and  $6.10 \times 10^0 \text{ s}^{-1}$  to  $3.30 \times 10^{27} \text{ s}^{-1}$  (1<sup>st</sup> order) for rachis and  $2.39 \times 10^2 \text{ s}^{-1}$  to  $4.64 \times 10^{15} \text{ s}^{-1}$  (0<sup>th</sup> order) and  $2.66 \times 10^2 \text{ s}^{-1}$  to  $2.32 \times 10^{16} \text{ s}^{-1}$  (1<sup>st</sup> order) for fibers.

Table 5. Pre-exponential factors for thermal decomposition of palm leaflet, rachis and fibers

Reaction Order	Conversion (%)							
	10	20	30	40	50	60	70	80
<b>Leaflet</b>								
0th	$1.57 \times 10^0$	$4.48 \times 10^{13}$	$1.12 \times 10^{17}$	$4.70 \times 10^{10}$	$1.24 \times 10^8$	$4.88 \times 10^{10}$	$1.55 \times 10^{22}$	$1.38 \times 10^{25}$
1st	$1.74 \times 10^0$	$5.60 \times 10^{13}$	$1.60 \times 10^{17}$	$7.84 \times 10^{10}$	$2.48 \times 10^8$	$1.22 \times 10^{11}$	$5.18 \times 10^{22}$	$6.91 \times 10^{25}$
<b>Rachis</b>								
0th	$5.49 \times 10^0$	$9.58 \times 10^5$	$2.42 \times 10^8$	$8.00 \times 10^9$	$2.03 \times 10^8$	$4.86 \times 10^6$	$2.43 \times 10^9$	$6.61 \times 10^{26}$
1st	$6.10 \times 10^0$	$1.20 \times 10^6$	$3.45 \times 10^8$	$1.33 \times 10^{10}$	$4.06 \times 10^8$	$1.21 \times 10^7$	$8.10 \times 10^9$	$3.30 \times 10^{27}$
<b>Fibers</b>								
0th	$2.39 \times 10^2$	$8.32 \times 10^4$	$9.65 \times 10^2$	$1.98 \times 10^4$	$7.023 \times 10^4$	$1.86 \times 10^6$	$2.64 \times 10^{14}$	$4.64 \times 10^{15}$
1st	$2.66 \times 10^2$	$1.40 \times 10^5$	$1.38 \times 10^3$	$3.30 \times 10^4$	$1.40 \times 10^5$	$4.66 \times 10^6$	$8.80 \times 10^{14}$	$2.32 \times 10^{16}$

#### 4.0 Conclusion

The differential thermal gravimetric curves of palm leaflet and fibers showed two different weight loss regimes due to thermal decomposition of biopolymers including holocellulose and lignin fractions in the sample, while rachis showed three distinctive weight loss regimes. The average apparent activation energies were; 252 kJ/mol, 200 kJ/mol and 164 kJ/mol, for leaflet, rachis and fibers, respectively and increased with increase in conversion. With future aim of producing high value chemicals from date palm tree, the results of this study are important for understanding the palm biomass characteristics and give an insight on optimum conditions like conversion, decomposition temperature regimes for hemicellulose, cellulose and lignin.

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#### References

1. Agoudjil, B., Benchabane, A., Boudenne, A., Ibos, L. & Fois, M. 2011, "Renewable materials to reduce building heat loss: Characterization of date palm wood", *Energ Buildings*, vol. 43, no. 2, pp. 491-497. <http://doi:10.1016/j.enbuild.2010.10.014>.
2. Saddiq, M., Aleid, S.M. & Adel, A.K. 2013, "Dates: Postharvest science, processing technology and health benefits". (1<sup>st</sup> ed.). Wiley, pp.191.
3. Almi, K., Benchabane, A., Lakel, S. & Kriker, A. 2015, "Potential utilization of date palm wood as composite reinforcement", *Journal of Reinforced Plastics and Composites*, vol. 34, no. 15, pp. 1231-1240. <http://doi:10.1177/0731684415588356>.
4. Annual Book of ASTM Standards. 2013. "Petroleum products, lubricants, and fossil fuels. Petroleum products and lubricants (D): C1234 - D3710", Vol. 05.01, Section 5.
5. Antal, M.J.J. & Varhegyi, G. 1995, "Cellulose Pyrolysis Kinetics: The Current State of Knowledge", *Industrial & Engineering Chemistry Research*, vol. 34, no. 3, pp. 703-717. <http://doi:10.1021/ie00042a001>.
6. Asadullah, M., Adi, A.M., Suhada, N., Malek, N.H., Saringat, M.I. & Azdarpour, A. 2014, "Optimization of palm kernel shell torrefaction to produce energy densified bio-coal", *Energy Conversion and Management*, vol. 88, pp. 1086-1093.
7. Alvarez, V.A. & Vázquez, A. 2004, "Thermal degradation of cellulose derivatives/starch blends and sisal fibre biocomposites", *Polymer Degradation and Stability*, vol. 84, no. 1, pp. 13-21. <http://doi:10.1016/j.polymdegradstab.2003.09.003>.
8. Barneto, A.G., Carmona, J.A. & Conesa, J.A. 2009, "Effects of the Composting and the Heating Rate on Biomass Gasification", *Energy & Fuels*, vol. 23, no. 2, pp. 951-957. <http://doi:10.1021/ef8005806>.
9. Barrevel, W.H. 1993. Date Palm Products in Food and Agriculture Organization of the United Nations Rome, FAO Agricultural Services.
10. Bendhaou, A., Habibi, Y., Kaddami, H. & Dufresne, A. 2009, "Physiochemical characterization of Palm from Phoenix Dactylifera-L, preparation of cellulose whiskers and natural rubber-based nanocomposites", *Journal of Biobased Materials and Bioenergy*, vol.3, pp. 1-10. <http://doi:10.1166/jbmb.2009.1011>.
11. Beyaz, K., Charton, M., Rouilly, A., Vedrenne, E., Vaca-Garcia, C., Benaboura, A. & Thiebaud-Roux, S. 2017, "Synthesis of graft-copolymers from palm cellulose and solketal acrylate and their

- characterization", *Industrial Crops and Products*, vol. 97, pp. 32-40.  
<http://doi:10.1016/j.indcrop.2016.12.001>.
12. Briones, R., Serrano, L., Younes, R.B., Mondragon, I. & Labidi, J. 2011, "Polyol production by chemical modification of date seeds", *Industrial Crops & Products*, vol. 34, no. 1, pp. 1035-1040.  
<http://doi:10.1016/j.indcrop.2011.03.012>.
  13. Caballero, J.A., Conesa, J.A., Font, R. & Marcilla, A. 1997, "Pyrolysis kinetics of almond shells and olive stones considering their organic fractions", *Journal of Analytical and Applied Pyrolysis*, vol. 42, no. 2, pp. 159-175.  
[http://doi:10.1016/S0165-2370\(97\)00015-6](http://doi:10.1016/S0165-2370(97)00015-6).
  14. Carrier, M., Loppinet-Serani, A., Denux, D., Lasnier, J., Ham-Pichavant, F., Cansell, F. & Aymonier, C. 2011, "Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass", *Biomass and Bioenergy*, vol. 35, no. 1, pp. 298-307.  
<http://doi:10.1016/j.biombioe.2010.08.067>.
  15. Chuntanapum, A., Yong, T.L., Miyake, S. & Matsumura, Y. 2008, "Behavior of 5-HMF in Subcritical and Supercritical Water", *Industrial & Engineering Chemistry Research*, vol. 47, no. 9, pp. 2956-2962.  
<http://doi:10.1021/ie0715658>.
  16. Cozzani, V., Lucchesi, A., Stoppato, G. & Maschio, G. 1997, "A new method to determine the composition of biomass by thermogravimetric analysis", *The Canadian Journal of Chemical Engineering*, vol. 75, no. 1, pp. 127-133.  
<http://doi:10.1002/cjce.5450750120>.
  17. Dias, A.S., Pillinger, M. & Valente, A.A. 2005, "Dehydration of xylose into furfural over micro-mesoporous sulfonic acid catalysts", *Journal of Catalysis*, vol. 229, no. 2, pp. 414-423.  
<http://doi:10.1016/j.jcat.2004.11.016>.
  18. Dias, A.S., Lima, S., Pillinger, M. & Valente, A.A. 2006, "Acidic cesium salts of 12-tungstophosphoric acid as catalysts for the dehydration of xylose into furfural", *Carbohydrate Research*, vol. 341, no. 18, pp. 2946-2953.  
<http://doi:10.1016/j.carres.2006.10.013>.
  19. El may, Y., Jeguirim, M., Dorge, S., Trouvé, G. & Said, R. 2012, "Study on the thermal behavior of different date palm residues: Characterization and devolatilization kinetics under inert and oxidative atmospheres", *Energy*, vol. 44, no. 1, pp. 702-709.  
<http://doi.org/10.1016/j.energy.2012.05.022>.
  20. Friedman, H.L. 1963, "Kinetics of thermal degradation of char-forming plastics from Thermogravimetry. Application to a phenolic plastic". *Journal of Polymer Science*, vol. 6 no. 1, 183-195.
  21. Hossain, M.A., Jewaratnam, J. & Ganesan, P., 2016, "Prospect of hydrogen production from oil palm biomass by thermochemical process – A review". *International Journal Hydrogen Energy*. 41(38), 16637-16655.  
<http://doi:10.1016/j.ijhydene.2016.07.104>.
  22. Jain, S. M. & Priyadarshan, P.M., 2009; 2008. *Breeding plantation tree crops: Tropical species*, (1<sup>st</sup> ed.) Springer New York, (pp. 290).
  23. Karimi, K., Emtiazi, G. & Taherzadeh, M.J. 2006, "Ethanol production from dilute-acid pretreated rice straw by simultaneous saccharification and fermentation with *Mucor indicus*, *Rhizopus oryzae*, and *Saccharomyces cerevisiae*", *Enzyme and Microbial Technology*, vol. 40, no. 1, pp. 138-144.  
<http://doi:10.1016/j.enzmictec.2005.10.046>

24. Khiari, R., Mhenni, M.F., Belgacem, M.N. & Mauret, E. 2010;2009;, "Chemical composition and pulping of date palm rachis and Posidonia oceanica – A comparison with other wood and non-wood fibre sources", *Bioresource Technology*, vol. 101, no. 2, pp. 775-780.  
<http://doi:10.1016/j.biortech.2009.08.079>.
25. Kim, S. & Agblevor, F.A. 2007, "Pyrolysis characteristics and kinetics of chicken litter". *Waste Management*. (Oxford). Vol. 27, no.1, pp. 135-140.  
<http://doi:10.1016/j.wasman.2006.01.012>.
26. Kim, S., Ly, H.V., Choi, G., Kim, J. & Woo, H.C. 2012, "Pyrolysis characteristics and kinetics of the alga *Saccharina japonica*", *Bioresource technology*, vol. 123, pp. 445-451.  
<http://doi:10.1016/j.biortech.2012.07.097>.
27. Liou, T., Chang, F. & Lo, J. 1997, "Pyrolysis Kinetics of Acid-Leached Rice Husk", *Industrial & Engineering Chemistry Research*, vol. 36, no. 3, pp. 568-573.  
<http://doi:10.1021/ie9604536>.
28. Ly, H.V., Kim, J. & Kim, S. 2013, "Pyrolysis characteristics and kinetics of palm fiber in a closed reactor", *Renewable Energy*, vol. 54, pp. 91-95.  
<http://doi:10.1016/j.renene.2012.08.053>.
29. Ly, H.V., Kim, S., Kim, J., Choi, J.H. & Woo, H.C. 2015, "Effect of acid washing on pyrolysis of *Cladophora socialis* alga in microtubing reactor", *Energy Conversion and Management*, vol. 106, pp. 260-267.  
<http://doi:10.1016/j.enconman.2015.09.041>.
30. Maiti, S., Purakayastha, S. & Ghosh, B. 2007, "Thermal characterization of mustard straw and stalk in nitrogen at different heating rates", *Fuel*, vol. 86 no.10, pp. 1513-1518.  
[doi:10.1016/j.fuel.2006.11.016](http://doi:10.1016/j.fuel.2006.11.016)
31. Mallaki, M. & Fatehi, R. 2014, "Design of a biomass power plant for burning date palm waste to cogenerate electricity and distilled water", *Renew Energy*, vol. 63, pp. 286-291.  
<http://doi:10.1016/j.renene.2013.09.036>.
31. Mohamed, A.R., Lee, K.T., Noor, N.M. & Zainudin, N.F. 2005, "Oil Palm Ash/Ca(OH)<sub>2</sub>/CaSO<sub>4</sub> Absorbent for Flue Gas Desulfurization", *Chemical Engineering & Technology*, vol. 28, no. 8, pp. 939-945.  
<http://doi:10.1002/ceat.200407106>.
32. Müller-Hagedorn, M., Bockhorn, H., Krebs, L. & Müller, U. 2003, "A comparative kinetic study on the pyrolysis of three different wood species", *Journal of Analytical and Applied Pyrolysis*, vol. 68, pp. 231-249.  
[http://doi:10.1016/S0165-2370\(03\)00065-2](http://doi:10.1016/S0165-2370(03)00065-2).
33. Nakhshiniev, B., Gonzales, H.B. & Yoshikawa, K. 2012, "Hydrothermal Treatment of Date Palm Lignocellulose Residue for Organic Fertilizer Conversion: Effect on Cell Wall and Aerobic Degradation Rate", *Compost Science & Utilization*, vol. 20, no. 4, pp. 245-253.  
<http://doi:10.1080/1065657X.2012.10737055>.
34. Obernberger, I. & Thek, G. 2004. Physical characterization and chemical composition of densified biomass fuels with regard to their combustion behaviour. *Biomass & Bioenergy*, vol. 27 no. 6, pp. 653-669.  
<http://doi:10.1016/j.biombioe.2003.07.006>.
35. Riansa-ngawong, W. & Prasertsan, P. 2011, "Optimization of furfural production from hemicellulose extracted from delignified palm pressed fiber using a two-stage process", *Carbohydrate Research*, vol. 346, no. 1, pp. 103-110.  
<http://doi:10.1016/j.carres.2010.10.009>.
36. Saadaoui, N., Rouilly, A., Fares, K. & Rigal, L. 2013, "Characterization of date palm lignocellulosic by-products and self-bonded composite materials obtained thereof", *Materials and Design*, vol. 50, pp. 302-

308.  
<http://doi:10.1016/j.matdes.2013.03.011>.
37. Sait, H.H., Hussain, A., Salema, A.A. & Ani, F.N. 2012, "Pyrolysis and combustion kinetics of date palm biomass using thermogravimetric analysis", *Bioresource technology*, vol. 118, pp. 382-389.  
<http://doi:10.1016/j.biortech.2012.04.081>.
38. Sbiai, A., Kaddami, H., Fleury, E., Maazouz, A., Erchiqui, F., Koubaa, A., Soucy, J. & Dufresne, A. 2008, "Effect of the Fiber Size on the Physicochemical and Mechanical Properties of Composites of Epoxy and Date Palm Tree Fibers", *Macromolecular Materials and Engineering*, vol. 293, no. 8, pp. 684-691.  
<http://doi:10.1002/mame.200800087>.
39. Shinoj, S., Visvanathan, R., Panigrahi, S. & Kochubabu, M. 2011, "Oil palm fiber (OPF) and its composites: A review", *Industrial Crops & Products*, vol. 33, no. 1, pp. 7-22.  
<http://doi:10.1016/j.indcrop.2010.09.009>.
40. Sumathi, S., Chai, S.P. & Mohamed, A.R. 2008, "Utilization of oil palm as a source of renewable energy in Malaysia", *Renewable and Sustainable Energy Reviews*, vol. 12, no. 9, pp. 2404-2421.  
<http://doi:10.1016/j.rser.2007.06.006>.
41. Jian Ping, T., Md Jahim, J., Harun, S., Ta Yeong, W., Monash University Malaysia & Universiti Kebangsaan Malaysia 2017, "Overview of the Potential of Bio-Succinic Acid Production from Oil Palm Fronds", *Journal of Physical Science*, vol. 28, no. Suppl. 1, pp. 53-72.  
<http://doi:10.21315/jps2017.28.s1.4>.
42. Vamvuka, D., Kakaras, E., Kastanaki, E. & Grammelis, P. 2003. "Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite", *Fuel*. Vol. 82 no. 15, pp. 1949-1960.  
[http://doi:10.1016/S0016-2361\(03\)00153-4](http://doi:10.1016/S0016-2361(03)00153-4).
43. Yin, C.Y., Kadir, Sharifah Aishah Syed Abdul, Lim, Y.P., Syed-Ariffin, S.N. & Zamzuri, Z. 2008, "An investigation into physicochemical characteristics of ash produced from combustion of oil palm biomass waste in a boiler" *Fuel Processing Technology*, vol.89 no.7, pp. 693-696.  
<http://doi:10.1016/j.fuproc.2007.12.012>
44. Yong, T.L.K., Muhamad, N. & Yosuf, N.N.M. 2016, "Furfural production from oil palm biomass using biomass derived supercritical ethanol solvent and formic acid catalyst", *Procedia Engineering*. Vol. 148, pp. 392-400.  
<http://doi.org/10.1016/j.proeng.2016.06.495>.
45. Zainudin, N.F., Lee, K.T., Kamaruddin, A.H., Bhatia, S. & Mohamed, A.R. 2005, "Study of adsorbent prepared from oil palm ash (OPA) for flue gas desulfurization", *Separation and Purification Technology*, vol. 45, no. 1, pp. 50-60.  
<http://doi:10.1016/j.seppur.2005.02.008>.
46. Spoor, W. 2001, "Zohary D, Hopf M. 2000. Domestication of plants in the Old World. 3rd edn. 316pp. New York: Oxford University Press. L19.95 (softback)", *Annals of Botany*, vol. 88, no. 4, pp. 666.

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