CHEMICAL ENGINEERING TRANSACTIONS

VOL. 45, 2015

A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216 DOI: 10.3303/CET1545222

Non-Isothermal Kinetic Analysis of Oil Palm Empty Fruit Bunch Pellets by Thermogravimetric Analysis

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The pyrolysis kinetics of oil palm empty fruit bunch (OPEFB) pellets was examined under non-isothermal conditions in a thermogravimetric (TG) analyser. Thermal analysis was carried out from 30 °C to 1,000 °C using three different heating rates 5, 10, 20 °C min^{-1} under nitrogen gas (N_2). The TG-DTG curves showed that the pyrolysis process occurred in three steps; drying, active pyrolysis and passive pyrolysis signifying the removal of moisture, holocellulose and lignin. The pyrolysis kinetic parameters; activation energy, *Ea*, and frequency factor *A*, were deduced from the Flynn-Wall-Ozawa (FWO) model. The average *Ea* and *A* values from α = 0.10 - 0.60 were 160.20 kJ/mol and 1.38 x 10^{24} min^{-1}. The highest *Ea* (231.42 kJ/mol) and *A* (8.27 x 10^{24} min^{-1}) occurred at α = 0.30 indicating this is the slowest or rate determining step (RDS) during thermal degradation of OPEFB pellets. The average *Ea* for OPEFB pellets was comparably lower than cornstalk (206.40 kJ/mol), sawdust (232.60 kJ/mol) and oak (236.20 kJ/mol). The kinetic compensation or isokinetic effect was also observed during thermal decomposition of the OPEFB pellets. Hence, the results indicate OPEFB pellets can be utilized as a potential feedstock for pyrolysis.

1. Introduction

The large scale cultivation of oil palm (*Elaeis guineensis*) in Malaysia generates enormous quantities of biomass waste such as empty fruit bunch (EFB). Consequently, the inefficiency of current conversion technologies for oil palm waste (OPW) has created socioeconomic, environmental and technological challenges in Malaysia. Therefore, the valorization of OPW into fine chemicals, power generation and clean energy fuels will address the challenges of OPW accumulation in the oil palm industry. Furthermore, the utilization of biomass can potentially address the problems of price volatility, dwindling reserves and environmental pollution associated with fossil fuels (Johari et al., 2015).

Conversely, biomass is mainly available as high moisture, inhomogeneous sized and low energy density fuels which require pre-treatment and conditioning before utilization (Kuparinen et al., 2014). The most widely used biomass pre-treatment techniques include drying, pelletization (Nyakuma et al., 2014a) and torrefaction (Basu, 2010). These techniques can improve the feedstock supply chain (Eranki et al., 2011), thermochemical properties (Nyakuma et al., 2014c) and potential applications of OPW (Kelly-Yong et al., 2007) in thermal bioenergy conversion systems (BCS). Consequently, research groups in Malaysia are currently investigating efficient conversion techniques for valorising OPW via torrefaction (Uemura et al., 2011), gasification (Lahijani and Zainal, 2014) for clean energy applications (Aziz et al., 2015).

The transition from fossil fuels to clean bioenergy fuels requires fundamental knowledge of thermal behaviour and decomposition kinetics of biomass (Munir et al., 2009). This is vital for the feasibility, design and scaling up biomass thermal conversion equipment (Ma et al., 2012). Furthermore, the kinetics of biomass decomposition can be useful in optimizing the yield and composition of desired products during thermochemical conversion (Islam et al., 2015). Consequently, the mathematical models developed by Flynn-Wall (Flynn and Wall, 1966) and Ozawa (Ozawa, 1965) along with analytical techniques such as

Please cite this article as: Nyakuma B.B., Ahmad A., Johari A., Tuan Abdullah T.A., Oladokun O., Aminu D.Y., 2015, Non-isothermal kinetic analysis of oil palm empty fruit bunch pellets by thermogravimetric analysis, Chemical Engineering Transactions, 45, 1327-1332 DOI:10.3303/CET1545222

thermogravimetric analysis (TGA) have been successfully applied to investigate the decomposition kinetics of biomass (Mortari et al., 2014).
To the best of the authors' knowledge, comprehensive studies on the effects of pelletization on the thermal degradation behaviour and decomposition kinetics of OPW is lacking in literature. This study is aimed at investigating the thermal degradation behaviour of oil palm empty fruit bunches (OPEFB) pellets under non-isothermal conditions using thermogravimetric analyser (TGA). Consequently, the decomposition kinetics of the OPEFB pellets during pyrolytic TG analysis is presented using the Flynn-Wall-Ozawa (FWO) kinetic model.

2. Experimental

2.1 Ultimate and Proximate Analysis

The oil palm empty fruit bunches (OPEFB) pellets was supplied by an oil palm mill in Johor, Malaysia. The OPEFB pellets were subsequently pulverised and sifted to obtain 125 µm sized particles. The elemental composition and proximate analysis was examined in as received (ar) basis using standard ASTM techniques, as presented in Table 1. A detailed characterization of the thermochemical fuel properties of OPEFB pellets in presented in our previous study (Nyakuma et al., 2014b).

Table 1: Ultimate and Proximate analysis of OPEFB pellets

C	H	N	S	O	M	VM	FC	A	HHV
45.14	6.05	0.54	0.20	48.08	8.11	72.1	14.91	4.89	17.57

C-Carbon, *H*-Hydrogen, *N*-Nitrogen, *S*-Sulphur, *O*-Oxygen, *M*-Moisture, *VM*-Volatile matter, *FC*-Fixed carbon, *A-Ash, HHV*-Higher heating value in MJ/kg.

2.2 Thermal analysis

Thermal analysis of OPEFB was carried out in a thermogravimetric (TG) analyser (Netzsch™ 209 F3) under nitrogen flow rate of 50 mL min^{-1}. During each run, the temperature program was set to heat the sample from 30 ºC to 1,000 ºC using three heating rates, β = 5, 10, 20 ºC min^{-1}. Subsequently, the FWO model was applied to determine decomposition kinetic parameters; activation energy, *Ea,* and frequency factor, *A* at different conversions, α, during TG analysis. For thermally degrading biomass, the rate of solid state decomposition can be expressed as;

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \quad (1)$$

Where $f(\alpha)$ is the reaction model, and k(T) - temperature dependent rate constant given by;

$$k(T) = \mathrm{A} \exp\left(-\frac{Ea}{RT}\right) \quad (2)$$

Where *A* is the frequency factor, *Ea* - activation energy, *R* - universal gas constant, and *T* - absolute temperature. Relating Eqs(1) and (2) yields the expression for temperature *T*, dependence on conversion, α,

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{Ea}{RT}\right) f(\alpha) \quad (3)$$

By taking into account the effect of heating rate, β, the integral conversion function, $g(\alpha)$ can be deduced;

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T} \exp\left(-\frac{Ea}{RT}\right) dT \quad (4)$$

The expression in Eq(4) is the fundamental equation for analysing the decomposition kinetic parameters of thermal biomass conversion. In this study, the model free isoconversional Flynn-Wall-Ozawa method, derived from Doyle's approximation (Doyle, 1965), was selected to analyse decomposition kinetics of OPEFB pellets. It can be expressed as;

$$\ln(\beta)=\ln\left(\frac{AEa}{Rg(\alpha)}\right)-5.331-1.052\left(\frac{Ea}{RT}\right) \quad (5)$$

Hence, from the plot of *In*(*β*) against (1/T) at different heating rates, the activation energy can be deduced from the slope $-E_a/R$ where the value of *R* is 8.314 J/mol K and frequency factor by In[AR/E_a)].

3. Results and Discussion

3.1 Thermal analysis

The TG and DTG curves for OPEFB pellets are presented in Figures 1 and 2. The plots display the reverse *S*-curves typically observed for thermal degradation of biomass during TG analysis. In addition, the plots showed that increase in heating rate from 5 – 20 °C min^{-1} led to a shift in the TG-DTG curves to higher temperatures signifying the temperature dependency of the pyrolytic thermal decomposition process (Slopiecka et al., 2012). The temperature-heating rate effect can be aptly examined from the characteristic decomposition profiles presented in Table 2.

Table 2: Characteristic temperatures for OPEFB pellet decomposition at different heating rates

Heating Rate (°C/min)	Reaction Time (min)	Peak Temperature (°C)	Residual Weight (%)
5	194.00	308.30	11.03
10	97.00	316.70	15.29
20	48.50	329.60	22.02

From Table 2, it is evident that varying heating rate resulted in a corresponding increase in peak decomposition temperature and residual weight of OPEFB pellets. This is reportedly due a heating transfer limitation which ensures that the thermal energy required for complete pyrolytic decomposition decreases at higher heating rates (Slopiecka et al., 2012). This eventually results in an increase in peak temperatures and residual mass as reported for OPEFB pellets in Table 2.

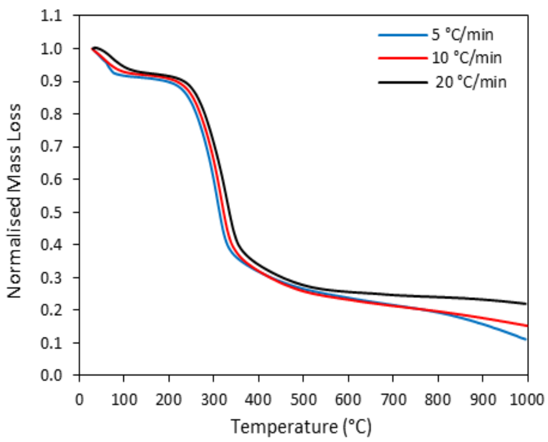

Figure 1: TG curves of Oil Palm Empty Fruit Bunch (OPEFB) pellets.

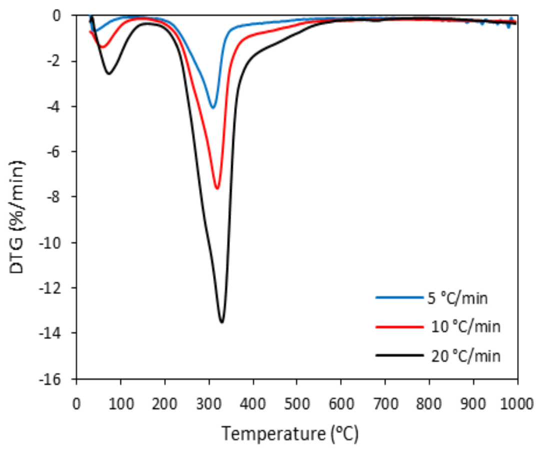

Figure 2: DTG curves of Oil Palm Empty Fruit Bunch (OPEFB) pellets

From Figures 1 and 2, the pyrolytic decomposition of the OPEFB pellets clearly occurred in 3 distinct stages; drying (50 - 200 °C), active pyrolysis (200 – 500 °C) and passive pyrolysis (500 – 1,000 °C). The drying state is characterised by the removal of surface moisture water (Açıkalın, 2011) and low molecular weight volatiles (Çepelioğullar and Pütün, 2014). The active pyrolysis stage is characterized by significant mass loss due to the degradation of the biomass components hemicellulose and cellulose. The passive pyrolysis stage is categorised by slow mass loss rate attributed to lignin degradation (Souza et al., 2009) as denoted by the "tailing" observed above 500 °C in Figure 2.

3.2 Kinetic Analysis

The linear regression plots of *In β* vs *1/T* for conversions *α* = 0.10 – 0.60 for OPEFB pellets are presented in Figure 3. The slope is given by -1.052 *Ea/R* while frequency factor *A* was deduced from the intercept of the plots using the relation *In (AR/Ea)* based on the assumption 2RT << *Ea* (Damartzis et al., 2011). Furthermore, the conversions α < 0.1 and α > 0.8 have been excluded due to the low correlation values (Damartzis et al., 2011).

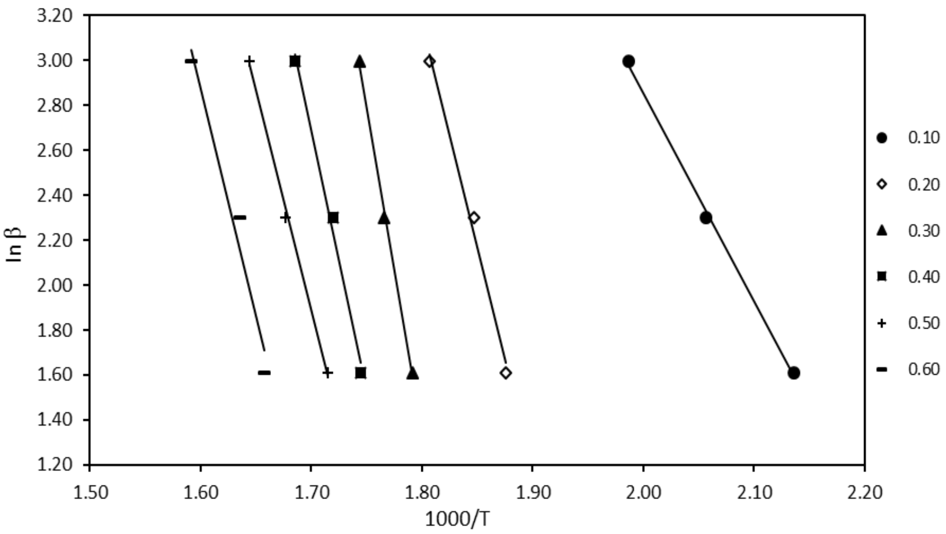

Figure 3: Kinetic plot for OPEFB pellets using the Flynn-Wall-Ozawa (FWO) model

The kinetic plots observed for conversions *α = 0.2 to 0.6* in Figure 3 indicate that the OPEFB decomposition mechanism is characterized by parallel reactions occurring simultaneously. Furthermore, the kinetic parameters and the mechanism of conversion is significantly influenced by complex reactions, typified by the fluctuating *Ea* and *A* values (Ceylan and Topçu, 2014). The slope and intercept of the plots were used to calculate kinetic parameters for OPEFB pellets decomposition for conversions *α = 0.1 - 0.6* as presented in Table 3.

Table 3: Calculated kinetic parameters for OPEFB pellets

Conversion (α)	R^2	E (kJ/mol)	A (min^{-1})
0.10	0.9985	73.42	1.80×10^{10}
0.20	0.9899	159.10	2.50×10^{18}
0.30	0.9975	231.42	8.27×10^{24}
0.40	0.9898	183.37	4.39×10^{19}
0.50	0.9986	154.56	3.35×10^{16}
0.60	0.9638	159.37	3.50×10^{16}
Average	**0.9897**	**160.21**	**1.38×10^{24}**

The activation energy, *Ea* increased from 73.42 to 231.42 kJ/mol while and frequency factor, *A* was from 1.80×10^{10} to 8.27×10^{24} min^{-1} with average correlation $R^2 = 0.99$. Comparatively, the average *Ea* for EFB pellets (160.21 kJ/mol) is lower than cornstalk (206.40 kJ/mol), sawdust (232.60 kJ/mol) and oak tree (236.20 kJ/mol) in literature (Sun et al., 2012). Since activation energy is the minimum energy requirement for reactants before the start of a chemical reaction, high *Ea* values will result in slower reactions. Therefore, the lower *Ea* values of OPEFB pellets emphasizes its suitability as a feedstock for pyrolysis.

3.3 Kinetic Compensation Effect (KCE)

The interdependency of the kinetic parameters *Ea* and *A* are presented in Figure 4. This linear relationship between the kinetic parameters is termed the kinetic compensation effect (KCE) (Slopiecka et al., 2012) or the isokinetic effect (Açıkalın, 2011).

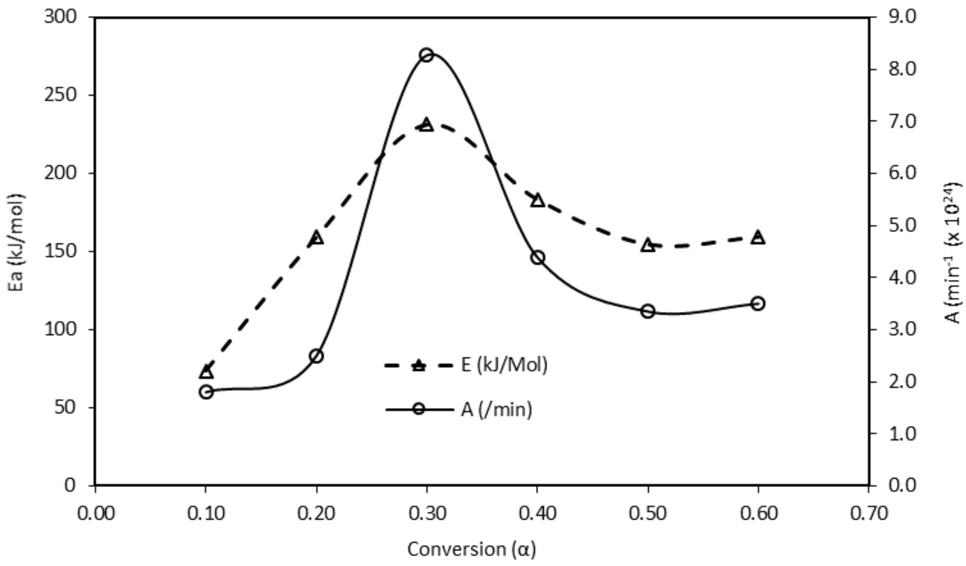

Figure 4: Interdependency of apparent activation energy Ea and Frequency factor A for OPEFB pellets.

From Figure 4, the highest Ea and A values during kinetic analysis were observed at α = 0.30 between α = 0.20 – 0.40. The activation energy at α = 0.30 was 231.42 kJ/mol which is significantly higher than the average apparent activation energy (Ea = 160.20 kJ/mol) of the entire OPEFB pellets pyrolysis process. This indicates that reaction is slowest at this stage and requires a high energy of activation and collision between the reacting particles to proceed to completion. Therefore, this can be denoted as the rate determining step (RDS) as also evidenced by the significant mass loss observed during thermal degradation.

4. Conclusions

The pyrolysis kinetics of OPEFB pellets pyrolysis was investigated under non-isothermal conditions using a TG analyser. The TG/DTG (mass loss) curves indicated that pyrolysis occurred in three stages; drying, active pyrolysis and passive pyrolysis. The Flynn-Wall-Ozawa (FWO) model was applied to the TG/DTG data to deduce the kinetic parameters, activation energy, *Ea*, and frequency factor *A*. The average *Ea* and *A* values were 160.20 kJ/mol and 1.38 x 10^{24} min^{-1}. Furthermore, kinetic analysis also indicated the effect of kinetic compensation during thermal decomposition of the OPEFB pellets. In addition, the average *Ea* value of the OPEFB pellets was lower than other biomass waste such as cornstalk, sawdust, and oak tree reported which confirms that OPEFB pellets is a potentially suitable feedstock for biomass pyrolysis.

Acknowledgment

The authors acknowledge the Ministry of Education (MOE) Malaysia for the Long Research Grant Scheme (LRGS) VOT: 4L817. The authors are grateful to S. L. Wong, and Muhamad Faizal B. A. Halim of Universiti Teknologi MARA, Shah Alam for the TG measurements.

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