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Characteristics and combustion kinetics of fuel pellets composed of waste of polyethylene terephthalate and biomass

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ABSTRACT

BACKGROUND AND OBJECTIVES: The needs of fuel pellets from varied feed stocks have opened up opportunities and challenges for pellets production from non-woody biomass. Wastes of plastic recycling and wood sawing contained a high potential for energy source and suited for pelletizing as a solid fuel.

METHODS: The characteristics and combustion kinetics of fuel pellets made using a mixture of waste of polyethylene terephthalate and biomass (Tectona grandis Linn.f) with a polyethylene terephthalate to biomass ratio of 9:1. The investigation covered physico-chemical properties and their functional group analysis, heavy metal concentration and ionic leachability testing, and ash analysis. In this context, thermogravimetric analysis was used in an atmosphere of oxygen gas, over a temperature range of 50-800 °C and at different heating rates. The work ends with discussion of the kinetics study via three comparative evaluations and the feasibility of fuel pellets for energy utilization.

FINDINGS: Pelletizing with this ratio (9:1) was present the durability of PET/biomass pellets, a uniform dimension, ease handling, storage, and transportation common as woody pellets. Some technical challenges such as low moisture content and high volatile matter content were feedstock dependent. The major characteristics were a combination of those from both the constituent materials. Functional groups of the pellets were contributed by terephthalate and lignocellulose. The addition of a small amount of biomass in pellets could improve their thermal decomposition behavior. The properties of the polyethylene terephthalate/biomass pellets indicated that were fit for combustion with a high heating value equal to 19.20 MJ/kg. Heavy metals and ionic contaminants were below the maximum limits of the standards because of the cleanliness of the raw materials. However, the minor effects of earth materials and a caustic soda detergent were resulted in the alteration of residue chemicals. The pellets had lower ignition, devolatilization, and burnout temperatures than the original polyethylene terephthalate waste; likewise, the peak and burnout temperatures shifted to a lower zone. The activation energy values obtained using the Kissinger-Akahira-Sunose, Ozawa-Flynn-Wall, and Starink models were similar and in the range 142–146 kJ/mol.

CONCLUSION: These findings may provide crucial information on fuel pellets from blended polyethylene terephthalate/biomass to assist the design and operation of a co-combustion system with traditional solid fuels. Such modifications of fuel pellets suggest the possibility of operating in large-scale furnace applications and can further be upgraded to other fuels production via modern bioenergy conversion processes.

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INTRODUCTION

The use of plastics has increased tremendously around the world due to their compatible properties in diversified applications, as well as being relatively cheap and safe. Post-consumption plastic is regarded as a major waste source and creates unhealthy conditions for humans and the environment (Patnaik et al., 2020). The ever-rising amount of plastic waste has tended to increase polyethylene terephthalate (PET) waste. PET usage has rapidly grown in daily life applications such as bottling carbonated soft drinks, beverages, and other liquids and as food containers, microwave trays, and food packaging films. Furthermore, it is appropriate for lightweight, large-capacity, and shatter-resistant containers which are mainly found in the shipping industry (Sinha et al., 2010). Used PET bottles can be recycled using a mechanical recycling process that uses shredding and crushing to convert a bottle into flakes (Jabłońska et al., 2019). In this process, purification and decontamination of the PET-flake are important methods followed by washing (with a detergent) and water soaking, centrifuging, drying, and separating foreign plastics. PET-flake from these processes can be utilized as raw-PET for producing goods with both up- and down-cycling processes (Tolinski, 2011). Nevertheless, secondary waste from a mechanical recycling plant occurs as the process releases undesired materials such as dust, sludge, debris, tiny pieces, and microplastics, as mentioned waste of PET. These amount to 3-5% by weight (%wt) of the PET bottle in a mechanical recycling plant and it is feasible to recover energy and importantly reduce the amount of waste landfill (Beata et al., 2019; Surenderan et al., 2018). Biomass is considered one of the most important renewable sources and is produced in large amounts in industry, agriculture, and forestry (Becidan et al., 2007). It can be directly used or used cooperatively with coal and other solid fuels (Ahn et al., 2014; Basu et al., 2011; Nussbaumer, 2003; Sajdak et al., 2019). Teak sawdust (Tectona grandis Linn.f) provides as a waste of wood industry in the sub-regional area of northern Thailand. It is used as a fuel for firing in pottery furnaces and biomass power plants. Furthermore, it is used as a mixture material for mushroom and vegetable plantation. Pelletizing is one process for handling powder-like materials such as dust, sludge, debris, tiny pieces, and microplastic as well as biomass and sawdust to become fuel pellets. Moreover, it has been widely used for mass and energy densification to overcome the disadvantages associated with raw material use (Mostafa et al., 2019). To avoid the resource wastage and environment contamination, fuel pellets production is proposed to utilize the waste of PET and biomass. Currently, waste of PET and teak sawdust for alternative use is mainly received from local factories. Efforts are being made to understand as the study novelty in the co-densification of the mixtures of dusty PET waste and sawdust invite new challenges to pelletization process. In addition, the detailed studies of fuel pellets from varied feedstocks with different morphology and characteristics are opened up opportunities and challenges (Pradhan et al., 2018). Thus, the co-densification of waste of PET and teak sawdust can be discussed. The use of this type of fuel in co-firing processes reduces greenhouse gas emission and cheaper than traditional fuels (coal, lignite) and sometimes get income by a surcharge (Jabłońska et al., 2019). Previous works, the pyrolysis-gasification of biomass/PET feedstock has been extensively studied by numerous researchers (Abnisa and Wan Daud, 2014; Bu et al., 2018; Madadian et al., 2017; Narobe et al., 2014; Robinson et al., 2016). They reported that the composition and fraction of the feedstock have an important influence on the distribution, composition, and characteristics of the gas, liquid, and solids (Block et al., 2019; Çepelioğullar and Pütün, 2013). Chattopadhyay et al. (2009), reported a significant interaction or synergistic effect between plastics and biomass (paper) under pyrolysis in a thermogravimetric analyzer (TGA). Paper-biomass started to decompose at a lower temperature (below 100 °C) than plastics and rapidly degraded at 350 °C. At higher temperature, PET started with an initial degradation temperature of 200 °C followed by a curve of rapid degradation at around 420-490 °C and a small amount at around 500-550 °C. Since the chemicals in plastic easily break up at higher temperatures, increased mass loss is observed more rapidly at a high temperature. Plastics/biomass composites with a mixed plastics (HDPE, PP, PET) to biomass ratio of 9:1 had the best performance with a slightly decreased mass loss during thermal degradation of 5% at a lower temperature and significantly decreased mass loss of over 95% at 500 °C. This may be due to the higher ratio of plastic in the mixture contains lower moisture, ash, and fixed...
carbon contents than for a low ratio of plastics in fuel pellets (Martín-Gullón et al., 2001). Energy required for the pyrolysis of multicomponent mixtures of waste PET and solid biomass increased with increase in amount of plastic content in the mixture due to the pyrolysis of PET plastic needs more energy than wood (Wang et al., 2021). Combustion of multicomponent mixtures acquired lower the activation energy than pyrolysis, therefore the leads of a minimum biomass supplied as part of plastic wastes instead of a minimum plastic waste supplied as part of biomass needs to be examined further. It is noticed that the study in fraction of these materials (PET/biomass) has not fully explored. The approach has to account for the behavior of PET/biomass during combustion. TGA is a worldwide method to analysis thermal behavior of materials such as food, feedstock, chemical, soil, fertilizer, plastic, advance polymers, biomass, solid fuels such as coal, lignite, shale oil, and so on. TGA is one of the most extensive practices for the preliminary prediction of thermal behavior and kinetics for complex solid fuels (Govindan et al., 2018; Yuan et al., 2017). In TGA, the thermal decomposition of the sample under a selective environment is analyzed by determining its mass loss during an increased temperature duration (Chandrasekaran et al., 2017; Xie et al., 2019). The mass loss is used to determine kinetic parameters including the activation energy, pre-exponential factor, and reaction mechanism. Two common approaches applied for kinetic analysis are the model-fitting and model-free (iso-conversional) methods. The analysis is accurate and convenient for iso-conversional methods compared to model-fitting methods (Bu et al., 2018). Only few data on heating rates assuming negligible mass transfer are required to estimate the activation energy in terms of the degree of conversion (Vyazovkin and Wight, 1999; Xu and Chen, 2013). Many iso-conversional methods, such as the Friedman, Ozawa-Flynn-Wall (OFW), Kissinger-Akahira-Sunose (KAS), and Starink methods have been used for the kinetic analysis of oxidative and non-oxidative processes in various types of solid fuels, including coal and biomass (Chen et al., 2017; Sharara and Sadaka, 2014; Słopiecka et al., 2012). There is a need for research into the utilization of waste of PET by pelletizing in combination with local biomass that could be applied in process of waste to energy. It is a new study pathway revealed with the novel materials, techniques of analysis, and evaluation. The important properties and crucial data of characteristics of fuel pellets from blended PET/biomass with a view towards energy recovery in the combustion process are also considered. Moreover, this study aims to determine their functional group, heavy metals and ionic contaminants, and residue composition as well as evaluation of the kinetic parameters by iso-conversinoal methods (OFW, KAS, and Starink methods). It is expected that the knowledge of the characteristics and combustion behavior of the PET/biomass pellets and in particular the precise estimation of kinetics, will provide essential guidance for further work. This study has been carried out in Phitsanulok province, Thailand in 2019.

**MATERIALS AND METHODS**

**Raw materials and pelletizing**

The waste of PET was sourced from a bulk of waste plastics at a PET bottle recycling plant in Surin province, Thailand. The similar case of mechanical recycling processes for used PET bottles was demonstrated by Jabłońska et al. (2019). The sample of PET waste contained different sizes of PET plastic from <0.5 to 1.5 mm (sieve size no. 14-35). Biomass (teak sawdust; Tectona grandis Linn.f) was sourced from a saw mill in Phrae province, Thailand. Both the PET waste and biomass were dried before pellet production. The fuel pellets of PET/biomass was produced using a flat-die pelletizing machine. Prior to pelletizing, the machine was warmed using a mixture of PET/biomass as a pre-pelleting material. Then, the mixture of PET and biomass (9:1, w/w) was fed at a continuous rate of 1 kg/min. About 10%wt of water was added during the process to prevent materials from sticking. Pellets were approximately 1.0 cm in diameter and 2.4 cm in length, as shown in Fig. 1. Then, pellets were dried in an air oven at 65 °C for 12 hours.

**Proximate, ultimate, and calorific value tests**

The samples of PET waste, biomass, and PET/biomass pellets were analyzed to determine their physical and chemical properties with three replications. The moisture content (MC) was measured by weighting mass before and after heat in a hot-air oven at 105 °C for 24 hours. Volatile matter (VM) of sample was measured by weighting mass before and after the covered sample-containing crucible in
Characteristics and combustion kinetics of PET/biomass pellets

A muffle furnace at 900±10 °C for 4 minutes (CEN/TS 15148). The sample in uncovered crucible was heated at 550±10 °C for 2 hours to determine the ash content (CEN/TS 14775). The fixed carbon (FC) was found by subtraction; FC = 100 - (MC + VM + ash). The carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents of samples were determined using a TrueSpec Micro (Leco, CHNS628) and the oxygen (O) content was calculated based on dry ash-free basis by using the formula; O = 100 - (C + H + N + S + ash), more details found as Samaksaman et al. (2021). In addition, the high heating value (HHV) was carried out based on analysis of the calorific value using a bomb calorimeter (Leco, AC-500) in an atmosphere of oxygen.

Fourier transform infrared spectrometry (FTIR)

Four materials and PET/biomass pellets were tested for the determination of the functional groups of polyethylene terephthalate (polyester group) and biomass components (lignocellulose group) using FTIR technique (Perkin Elmer, Spectrum GX). The IR spectra were recorded at wavenumbers in the range 4,000 to 400/cm at a resolution of 1/cm. The data were interpreted using the Perkin Elmer Spectrum version 10.5.2 software.

Heavy metal and ionic leachability tests

The PET waste and biomass may become contaminated with heavy metals and minerals during the process of mechanical recycling and sawing. These metals may cause scratching and corrosion of machinery. Heavy metals concentration such as copper (Cu), zinc (Zn), chromium (Cr), cadmium (Cd), and lead (Pb) were investigated. The procedure was detailed in a previous work of Samaksaman et al. (2015). Samples of PET waste, biomass, and PET/biomass pellets were digested using an acidic solution (a mixture of hydrochloric and nitric acids), followed by dilution with deionized (DI) water and filtration. Atomic absorption spectrometry (GBC, Avanta PM) was used in the subsequent analysis. The standardized curves with coefficient of determination (R²) values of 0.95-0.99 were used to evaluate heavy metal concentrations. The leachability test was used to determine the concentration of ionic leachates from the samples. The test applies quantity analysis of elements for seven anions leachate (AnL): fluoride (F), chloride (Cl), nitrite (NO₂⁻), bromide (Br), nitrate (NO₃⁻), phosphate (PO₄³⁻), and sulfate (SO₄²⁻); and for six cations leachate (CaL): lithium (Li⁺), sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺), and calcium (Ca²⁺). One gram of each sample

Fig. 1: A flat-die pelletizing machine and the PET/biomass pellets
was placed in a centrifuge tube and mixed with 10 ml DI water. A shaking incubator (JSR, Jssi-300C) was used for extraction at 250 rpm at room temperature for 12 hours. Then the sample was filtered twice using a paper filter before passing through a nylon filter. Prior to measurement, dilution of the sample (1:100 v/v) with ≥18 (mΩ) DI water was carefully conducted in a clean room. The sample solution was analyzed for anions and cations using ion chromatography (Dionex DXS500). All experiments were done three replications.

**Ash composition analysis**

X-ray fluorescence (XRF) spectroscopy is a rapid method used to determine the composition in solid samples like ash and residue. It is a non-destructive technique and suitable for ash samples from the combustion test. The ash samples were the as-receive samples from the combustion of raw materials and pellets within a muffle furnace at 815 °C for 2 hours (Xing et al., 2016). The test was employed using an energy dispersive XRF (EDXRF, Horiba XGT-5200 X-ray Analytical Microscope) with Rh X-ray tube, 1.2 mm of XGT diameter, and 30 kV of X-ray tube voltage.

**Thermogravimetric analysis**

A simultaneous thermal analyzer (Mettler-Toledo, TGA-DSC II) was used to measure the thermal decomposition of samples. Thermogravimetric analysis and derivative thermogravimetry (DTG) were used to analyze samples of PET waste, biomass, and PET/biomass pellets. Raw materials were analyzed in an atmosphere of oxygen, over a temperature range of 50-800 °C at a heating rate of 15 °C/min. The PET/biomass pellets were analyzed under the same conditions as the raw materials but various heating rates of 5, 10, 15, and 20 °C/min.

**Kinetic analysis**

The combustion of carbonaceous material is considered in terms of a gas-solid heterogeneous reaction. The conversion (X) of PET waste, biomass, and pellets during the combustion process can be defined using Eq. 1.

\[
X = \frac{m_0 - m_t}{m_0 - m_f}
\]  

(1)

Where, \(m_0\), \(m_t\), and \(m_f\) are the initial sample mass, the sample mass at time \(t\), and the sample mass left after ending process, respectively. The combustion rate of the materials can be represented using Eq. 2.

\[
\frac{dX}{dt} = k(T) f(X)
\]  

(2)

Where, \(k\) is the combustion rate constant and \(f(x)\) is the reaction model expressing the dependence of the combustion rate. The combustion rate constant \(k\) is temperature-dependent and generally is described using the Arrhenius formula using Eq. 3 (Mishra et al., 2019).

\[
k = A e^{-E_a/RT}
\]  

(3)

Where, \(E_a\) is the activation energy (kJ/mol), \(A\) is the pre-exponential factor (s\(^-1\)), \(T\) is the absolute temperature (K), and \(R\) is the universal gas constant, 8.314 kJ/(kmol·K). A heterogeneous function of the uniform kinetic reaction of the first order \(n = 1\), \(f(x)\) can be written using Eq. 4.

\[
f(X) = \left(1 - X\right)
\]  

(4)

Thus, the rate constant can be expanded using Eq. 5.

\[
\frac{dX}{dt} = A e^{-E_a/RT} (1 - X)
\]  

(5)

In non-isothermal analysis, the heating rate varies with the reaction time and temperature at a constant heating rate, \(\frac{dT}{dt} = \beta\) that can be rewritten as Eq. 6.

\[
\frac{dX}{dT} = \frac{A}{\beta} e^{-E_a/RT} (1 - X)
\]  

(6)

The integral form of \(f(X)\) can be represented as \(g(X)\) by integrating Eq. (6) with respect to temperature as shown in Eqs. 7 and 8.

\[
g(X) = \int_0^x \frac{dX}{f(X)} = \frac{A}{\beta} \int_0^t e^{-E_a/RT} dt
\]  

(7)

\[
g(X) = \frac{AE}{\beta R} \int_0^t u^{-\beta} e^{-u} du = \frac{AE}{\beta R} p(X)
\]  

(8)

**Kissinger-Akahira-Sunose method**

The Kissinger-Akahira-Sunose (KAS) method (Akahira and Sunose, 1971) is an iso-conversional method that uses an approximation of \(p(X) = x^2 e^{-x}\) in Eq. (8) to determine \(E_a\) as shown in Eq. 9.
\[
\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AE_a}{Rg(X)} \right) - \frac{E_a}{RT} \tag{9}
\]

Plotting \( \ln \left( \frac{\beta}{T^2} \right) \) versus \( 1/T \) will obtain the slope and intercept that can be used to estimate \( E_a \) and \( A \), respectively.

**Ozawa-Flynn-Wall method**

The Ozawa-Flynn-Wall (OFW) method is a model-free method applying Doyle’s approximation in Eq. (8) to evaluate the activation energy (Tran et al., 2014) as shown in Eq. 10.

\[
\ln(\beta) = \ln \left( \frac{AE_a}{Rg(X)} \right) - 5.3305 - 1.052 \left( \frac{E_a}{RT} \right) \tag{10}
\]

\( E_a \) was determined using the least square regression line as the slope of \( 1.052E_a/R \) by plotting the graph between \( \ln(\beta) \) on the y-axis versus \( 1/T \) on the x-axis.

**Starink method**

The Starink method is a model-free method like the KAS and OFW methods; however, the value it produces for \( E_a \) is more accurate than from using the other two methods (Gai et al., 2013). The Starink equation is shown in Eq. 11.

\[
\ln \left( \frac{\beta}{T^{1.8}} \right) = C_s - 1.0037 \left( \frac{E_a}{RT} \right) \tag{11}
\]

Plotting a linear graph of \( \ln \left( \frac{\beta}{T^{1.8}} \right) \) and \( 1/T \) enables the values of \( E_a \) and \( A \) to be determined from the slope and intercept, respectively.

**Thermodynamic analysis**

Thermodynamic parameters can be presented by the change in the enthalpy (\( \Delta H \)), Gibbs free energy (\( \Delta G \)), and entropy (\( \Delta S \)) (Manatura, 2019). In brief, \( \Delta H \) represents an endothermic or exothermic reaction which is the nature of the reaction process. \( \Delta G \) indicates the energy related to a chemical reaction that can be used to do work and \( \Delta S \) measures the irreversibility of the system. The parameters can be calculated using Eqs. 12-14.

\[
\Delta H = E_a - RT \tag{12}
\]

\[
\Delta G = E_a + RT_p \ln \left( \frac{K_p T_p^{1.8}}{hA} \right) \tag{13}
\]

\[
\Delta S = \frac{\Delta H - \Delta G}{T_p} \tag{14}
\]

Where, \( K_p \), \( h \), and \( T_p \) are the Boltzmann constant = 1.381 \times 10^{-23} \text{ J/K}, Plank constant = 6.626 \times 10^{-34} \text{ J.s} \) and peak temperature, respectively.

**RESULTS AND DISCUSSION**

**Properties and fuel characteristics**

Table 1 shows that the proximate and ultimate analysis for entire PET waste, biomass, and PET/biomass pellet samples. The PET waste had lower moisture and ash content compared to the biomass. The PET waste contained large amounts of volatile matter due to the nature of the plastic material (Luo et al., 2018; Zhao et al., 2016). The PET/biomass pellets also contained a large amount of volatile matter (83.19%). However, it had higher ash content (4.62%) and fixed carbon (6.83%) than the biomass. These changes in the physical properties of the pellets were due to the mixing ratio and the pelletizing process. Consequently, the HHV of pellets was 19.20 MJ/kg via the calorimetric test and was slightly different from the HHV of pellets via calculation (Huang and Lo, 2020). Mass and energy densification by pelletizing could overcome the disadvantages of PET waste and biomass. The H/C and O/C atomic ratios of PET waste, biomass, and pellet samples were in the range of 0.08–0.13 and 0.85–1.47, respectively. The H/C value for the PET waste was different compared to the biomass and was linked to the H/C value of the PET/biomass pellets. The PET/biomass pellets had a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis (%wt)</th>
<th>Ultimate analysis (%wt)</th>
<th>H/C</th>
<th>O/C</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MC</td>
<td>VM</td>
<td>FC</td>
<td>Ash</td>
<td>C</td>
</tr>
<tr>
<td>PET</td>
<td>5.09</td>
<td>87.80</td>
<td>5.02</td>
<td>2.09</td>
<td>38.41</td>
</tr>
<tr>
<td>Biomass</td>
<td>7.78</td>
<td>78.33</td>
<td>8.26</td>
<td>5.63</td>
<td>47.58</td>
</tr>
<tr>
<td>Pellets</td>
<td>5.36</td>
<td>83.19</td>
<td>6.83</td>
<td>4.62</td>
<td>39.33</td>
</tr>
</tbody>
</table>

ND: not detected
higher H/C value mainly due to the PET composition. The percentage of N showed similar results in the range 0.06-0.08% for the raw materials, while the percentage of S was untraceable in all samples. Previous works reported that C and H contents in PET samples were higher compared to the current study (Luo et al., 2018; Surenderan et al., 2018; Zhao et al., 2016). The N and S content was substantially low. Low emissions of oxides of nitrogen (NOₓ) and sulfurdioxide (SO₂) could be expected when this PET/biomass pellet was used as fuel in the combustion or co-combustion processes (Edo et al., 2016). The current results from the proximate and ultimate analysis suggested that the purity of the PET waste was an important factor in determining their characteristics. Compared to PET waste from bottles, the pure-PET had less contaminants and decay materials from the mechanical process, it would be clearly resulted as a previous work by Jabłońska et al. (2019). In the pelletizing of PET waste and biomass into a fuel pellet, the PET plastic played a key role in the compaction and made the pellets harden, as seen in Fig. 1. In conclusion for this sub-section, the PET/biomass pellets could be used as alternative sources and in combination with solid fuels in the same manner as refuse-derived fuel (RDF) and solid recovered fuel (SRF).

**FTIR results**

The FTIR technique allowed the identification of the functional groups present in the polyethylene terephthalate (polyester group) and biomass components (lignocellulose group). Fig. 2a-c illustrates the IR spectra of samples of PET waste, biomass, and PET/biomass pellets. The identified vibrational groups are summarized in the Table 2. The bands were in agreement with previous works (Chen et al., 2013; Lopes et al., 2018; Manatura, 2020; Pereira et al., 2017; Taleb et al., 2020). The IR spectrum of PET waste (Fig. 2a) contained bands at 2,916/cm (C-H, stretch), 1,714/cm (C=O, stretch), and 1,338-1,408/cm (C-O, stretch). The main observation at 1,247/cm and 1,125/cm affirmed the terephthalate group (OOCC₆H₄-COO). The same results for the PET functional groups were suggested by previous researchers (Chen et al., 2013; Pereira et al., 2017). In addition, the IR bands of the PET waste at around 1,090, 950-1,016, 796, and 439/cm, represented groups of Si-O asymmetric, Si-O(H) asymmetric, Si-O symmetric, and Si-O-Si bending, respectively (Capeletti and Zimnoch, 2016; Pereira et al., 2017). These results were due to the characteristics of soil and sand that remained in the PET waste from the mechanical recycling process of the PET bottles. The IR spectrum of the biomass sample in Fig. 2b shows
Characteristics and combustion kinetics of PET/biomass pellets

A band at 3,324/cm (O-H group) due to the water content in the biomass sample. In addition, there were bands at 2,898/cm (C-H stretch), 1,734/cm (C=O, stretch), 1,593/cm (C=C, aromatic skeleton vibration), 1,442/cm (C-H, CH$_2$, stretch, and CH$_3$, systematic), 1,231/cm (C-C, C-O, and C=O, stretch), 1,026/cm (C-O, stretch), and 559/cm (C-H, bend). Similar results for the functional groups of lignocellulosic materials have been reported using FTIR in teak hardwood, coffee grounds, and sugarcane bagasse (Lopes et al., 2018; Manatura, 2020; Taleb et al., 2020). The PET/biomass pellets characterization interpreted the mixture between PET waste and biomass as seen in Fig. 2c. While functional groups were contributed by both raw materials, the mixture was mainly characterized by the functional groups from the PET waste at around 1,252-1,239/cm, represented groups of terephthalate. Even though the biomass made up a small proportion of the pellets, some biomass characteristics were evident in the band at 1,578/cm that showed vibration of the aromatic skeleton with stretching (C=C) of lignin and at 1,022/cm representing C-O stretching of the ester methyl group of lignin. However, silica group occurred bands at 1,016, 723, and 459/cm in the sample of PET/biomass pellets due to the contamination was resulted from earth materials as found in the sample of PET waste.

Heavy metal concentration and ionic leachability

Table 3 summarizes the results of heavy metal concentration and ionic contaminants of the raw materials and PET/biomass pellets. The concentrations of Pb, Zn, Cr, and Cu in all tests of raw material samples were below regulatory levels and none of the tests yielded evidence of Cd. These results confirmed that the heavy metals (Cd~Cu<Pb<Cr<Zn) content in PET/biomass pellets were below the limits set by some European countries (Finland, Italy, France and the Netherlands) for alternative solid fuels such as RDF and SRF (Zhao et al., 2016). In addition, the contaminant leaching of AnL and CaL was also investigated and reported in Table 4. The PET waste had a high content of chloride (Cl$^-$) of around 3.99 ppm and the other six tested anions were recorded in the range from non-detectable to 0.33 ppm, while for the cations, sodium (Na$^+$) was the highest (28.35 ppm). The biomass sample had a substantially amount of the phosphate (PO$_4^{3-}$) anion at 58.58 ppm with lesser amounts of the other three cations-potassium (K$^+$) at 28.57 ppm, sodium (Na$^+$) at 16.21 ppm, and magnesium (Mg$^{2+}$) at 7.42 ppm. The experimental results showed that pellets characterization regarding ionic leachability was based on the combined properties of the PET waste and biomass. The major ionic elements in

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Table 2: Characteristics bands of the PET waste, biomass, and pellets obtained by FTIR

<table>
<thead>
<tr>
<th>Wavenumber (1/cm)</th>
<th>Characteristics bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Biomass</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2,916</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>2,898</td>
</tr>
<tr>
<td>-</td>
<td>1,734</td>
</tr>
<tr>
<td>1,714</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>1,578</td>
</tr>
<tr>
<td>-</td>
<td>1,442</td>
</tr>
<tr>
<td>1,338-1,408</td>
<td>-</td>
</tr>
<tr>
<td>1,247 &amp; 1,125</td>
<td>-</td>
</tr>
<tr>
<td>1,090</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>1,026</td>
</tr>
<tr>
<td>950-1,016</td>
<td>-</td>
</tr>
<tr>
<td>796</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>559</td>
</tr>
<tr>
<td>439</td>
<td>-</td>
</tr>
</tbody>
</table>

---
the pellets were not higher than in the original biomass for \( \text{PO}_4^{3-}, \text{Cl}^-, \text{F}, \text{SO}_4^{2-}, \text{K}^+, \text{Mg}^{2+}, \) and \( \text{Ca}^{2+} \) and furthermore, were not higher than in the PET waste for \( \text{Cl}^- \) and \( \text{Na}^+ \). The high sodium (\( \text{Na}^+ \)) cation level in the PET waste and the pellets might have been affected by the caustic soda (\( \text{NaOH} \)) detergent used during the cleaning step in the mechanical recycling process for the PET bottles.

### Ash composition

The ash composition analysis obtained by EDXRF technique showed in Table 5. The ashes from combustion of biomass, PET, and PET/biomass pellets would consist of the most common oxides which formed during the sintering process (Lu et al., 2015). Silicon oxide (\( \text{SiO}_2 \)), iron (III) oxide (\( \text{Fe}_2\text{O}_3 \)), calcium oxide (\( \text{CaO} \)), magnesium oxide (\( \text{MgO} \)), and aluminium oxide (\( \text{Al}_2\text{O}_3 \)) were the major components of all ash samples. The content of \( \text{SiO}_2 \) in biomass ash was 48.88%wt or more suggested by Xing et al. (2016) for the raw materials of biomass, which was much lower than PET (78.24%wt) and pellets (80.68%wt). While the lower \( \text{SiO}_2 \) (10.32%wt) composition of waste from PET bottles washing has been reported by Jabłońska et al. (2019). \( \text{SiO}_2 \) composition occurred in the samples of waste PET and PET/biomass pellets due to the contamination was mainly resulted from earth materials. The biomass ash had a substantially amount of phosphorus (V) oxide (\( \text{P}_2\text{O}_5 \)) and potassium oxide (\( \text{K}_2\text{O} \)) were 6.14% and 4.23%, respectively. Chromium (III) oxide (\( \text{Cr}_2\text{O}_3 \)), copper oxide (\( \text{CuO} \)), zinc oxide (\( \text{ZnO} \)), titanium dioxide (\( \text{TiO}_2 \)) were found in the ash of pellets sample. These metal-oxides fractions in the ash were supposed the effect of aggregation of metal elements with oxygen during combustion process (Samaksaman et al., 2015). The appearance of metal elements such as \( \text{CrO}, \text{CuO}, \text{ZnO}, \text{TiO}_2 \) might be released during the process of PET-bottle grinding and PET/biomass pelletizing. Sulfur trioxide (\( \text{SO}_3 \)) was also found in the low value. Trace metals such as manganese (IV) oxide (\( \text{MnO}_2 \)), strontium oxide (\( \text{SrO} \)), zirconium dioxide (\( \text{ZrO}_2 \)), and tantalum (V) oxide were not detected.

### Table 3: The results of heavy metal concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Cu (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limits</td>
<td>200</td>
<td>500</td>
<td>5</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>PET</td>
<td>ND</td>
<td>3.5</td>
<td>ND</td>
<td>9.4</td>
<td>5.0</td>
</tr>
<tr>
<td>Biomass</td>
<td>ND</td>
<td>0.7</td>
<td>ND</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>Pellets</td>
<td>0.8</td>
<td>7.4</td>
<td>ND</td>
<td>5.2</td>
<td>ND</td>
</tr>
</tbody>
</table>

* The limits set by European countries for the RDF and SRF.

ND: not detected

### Table 4: The results of anionic and cationic leachability

<table>
<thead>
<tr>
<th>Sample</th>
<th>F (ppm)</th>
<th>Cl (ppm)</th>
<th>NO(_3) (ppm)</th>
<th>Br (ppm)</th>
<th>NO(_2) (ppm)</th>
<th>PO(_4^{3-}) (ppm)</th>
<th>SO(_4^{2-}) (ppm)</th>
<th>U(^+) (ppm)</th>
<th>Na(^+) (ppm)</th>
<th>NH(_4^+) (ppm)</th>
<th>K(^+) (ppm)</th>
<th>Mg(^{2+}) (ppm)</th>
<th>Ca(^{2+}) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0.06</td>
<td>3.99</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.33</td>
<td>0.33</td>
<td>ND</td>
<td>28.35</td>
<td>ND</td>
<td>0.55</td>
<td>1.52</td>
<td>1.82</td>
</tr>
<tr>
<td>Biomass</td>
<td>0.32</td>
<td>4.61</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>58.58</td>
<td>1.75</td>
<td>ND</td>
<td>16.21</td>
<td>ND</td>
<td>28.57</td>
<td>7.42</td>
<td>3.88</td>
</tr>
<tr>
<td>Pellets</td>
<td>0.06</td>
<td>3.25</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>16.96</td>
<td>0.62</td>
<td>ND</td>
<td>20.88</td>
<td>ND</td>
<td>10.70</td>
<td>2.71</td>
<td>2.03</td>
</tr>
</tbody>
</table>

AnL: Anions leachate; CaL: Cations leachate; ND: not detected

### Table 5: Composition of the different ash samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO (%)</th>
<th>Al(_2)O(_3) (%)</th>
<th>SiO(_2) (%)</th>
<th>P(_2)O(_5) (%)</th>
<th>SO(_3) (%)</th>
<th>K(_2)O (%)</th>
<th>CaO (%)</th>
<th>TiO(_2) (%)</th>
<th>Cr(_2)O(_3) (%)</th>
<th>MnO(_2) (%)</th>
<th>Fe(_2)O(_3) (%)</th>
<th>CuO (%)</th>
<th>ZnO (%)</th>
<th>SrO (%)</th>
<th>ZrO(_2) (%)</th>
<th>TaO(_5) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>3.29</td>
<td>4.23</td>
<td>78.24</td>
<td>0.15</td>
<td>0.27</td>
<td>0.75</td>
<td>3.93</td>
<td>0.95</td>
<td>0.08</td>
<td>0.10</td>
<td>7.88</td>
<td>0.05</td>
<td>0.04</td>
<td>ND</td>
<td>0.03</td>
<td>ND</td>
</tr>
<tr>
<td>Biomass</td>
<td>9.21</td>
<td>10.02</td>
<td>48.88</td>
<td>6.14</td>
<td>0.64</td>
<td>4.23</td>
<td>16.08</td>
<td>0.49</td>
<td>0.06</td>
<td>0.08</td>
<td>4.11</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Pellets</td>
<td>2.86</td>
<td>2.63</td>
<td>80.68</td>
<td>1.27</td>
<td>0.13</td>
<td>0.65</td>
<td>3.80</td>
<td>0.53</td>
<td>0.45</td>
<td>ND</td>
<td>6.94</td>
<td>0.03</td>
<td>0.03</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND: not detected
Fig. 3: (a) TGA and (b) DTG for combustion of waste of PET (PET), biomass (Biomass), and pellets (PET/biomass) at 15 °C/min

Fig. 4: (a) TGA and (b) DTG for combustion of pellets at 5-20 °C/min
(Ta₂O₅) were untraceable in the ash of pellets sample. It is proven that the ash characterization of pellets exhibited unique characters based on the combined properties of the PET waste and biomass. Overall, the results of properties and fuel characteristics, FTIR, heavy metal concentration and ionic leachability, and ash composition made the PET/biomass pellets useful in a co-firing process with traditional solid fuels. Moreover, the PET/biomass pellets can further be upgraded to other fuels production via modern bioenergy conversion processes.

**TGA and DTG results**

The combustion characteristics of PET waste and the raw biomass at 15 °C/min are shown in the TG and DTG curves in Fig. 3. Both waste of PET and biomass are different in chemical structure, but the tests could be compared because used the same condition of oxygen atmosphere and a heating rate. The reaction temperature varied in the range 100 to 800 °C. It was clear that the biomass characteristics differed noticeably compared to those of the PET. For the biomass, below 150 °C represented removing vapor and light volatile matter (Ahmad et al., 2017). The mass loss of about 5.80% was represented as the water content in biomass (Fig. 3a). The clear mass loss of the biomass commenced from 190 up to 500 °C. Two clear peaks were observed during combustion with maximum mass loss rates of 0.0027 s⁻¹ at 317 °C and 0.0014 s⁻¹ at 437 °C, respectively. The first and second peaks were caused by the release of volatile matter in the temperature range from 148 to 372 °C and combustion of the remaining char, respectively (Ahn et al., 2014). For all samples of the PET waste and PET/biomass pellets, no obvious mass loss was detected below 266 °C. However, a small peak was observed with 0.0003 s⁻¹ at 325 °C for the mixed PET with biomass related to the level of higher volatiles in the biomass. The distinct mass loss and rate of mass loss of the PET waste and the pellets started at 278 °C and finished at around 458 °C. Two peaks were observed in Fig. 3b, with the first peak being for PET waste and pellets that were very similar to each other with a maximum mass loss rate of 0.0034 s⁻¹ at 419 °C. The second peak had the same peak temperature (Tₚ) at 454 °C with the mass loss rate for pellets of 0.0026 s⁻¹ and for PET waste of 0.0020 s⁻¹, respectively. It was clear that the biomass blending supported reactivity of the process. In addition, the experimental results affirmed that the decomposition of material with complex structure depended on the loss of chemical bonding and properties of materials. The combustion properties of the PET waste, biomass, and pellets are listed in Table 6. The ignition temperature (Tᵢg) and peak temperature (Tₚ) of PET were consistent with Das and Tiwari (2019). The results indicated that a low content (10%wt) of biomass mixed with PET improved Tᵢg by lowering it. There were no obvious changes in other properties such as the burnout temperature (Tₑ), higher reactivity (Rₑavg), and maximum derivative thermogravimetric value (DTGmax). The effects of the heating rate (5, 10, 15 and 20 °C/min) on mass loss and the rate of mass loss in terms of combustion temperature are shown in Fig. 4. The mass loss and rate of mass loss curves

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tᵢg (°C)</th>
<th>Tₑ (°C)</th>
<th>Tₚ (°C)</th>
<th>DTGmax (1/s)</th>
<th>Rₑavg (1/(s·K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>390</td>
<td>475</td>
<td>419</td>
<td>-0.0034</td>
<td>-4.92E-06</td>
</tr>
<tr>
<td>Biomass</td>
<td>278</td>
<td>458</td>
<td>317</td>
<td>-0.0027</td>
<td>-4.56E-06</td>
</tr>
<tr>
<td>Pellets</td>
<td>380</td>
<td>471</td>
<td>420</td>
<td>-0.0035</td>
<td>-4.99E-06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hearing rate (°C/min)</th>
<th>Tᵢg (°C)</th>
<th>Tₑ (°C)</th>
<th>Tₚ (°C)</th>
<th>DTGmax (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>360</td>
<td>460</td>
<td>398</td>
<td>-0.0012</td>
</tr>
<tr>
<td>10</td>
<td>378</td>
<td>460</td>
<td>411</td>
<td>-0.0021</td>
</tr>
<tr>
<td>15</td>
<td>380</td>
<td>471</td>
<td>420</td>
<td>-0.0035</td>
</tr>
<tr>
<td>20</td>
<td>398</td>
<td>499</td>
<td>426</td>
<td>-0.0053</td>
</tr>
</tbody>
</table>
K. Manatura and U. Samaksaman

were parallel and similar. A higher heating rate required a larger temperature range for complete combustion because there was not sufficient time for the biomass to combust (Manatura et al., 2018). Table 7 shows the combustion characteristics of pellets for the four heating rates. With an increased heating rate, the values of \( T_{\text{ig}} \), \( T_b \), and \( T_p \) increased as did DTG \( \text{max} \), indicating that the lower heating rate produced more effective combustion than the higher heating rate (Lu and Chen, 2015).

**Kinetic analysis**

The iso-conversional KAS, OFW and Starink methods from Eq. (9)-(11) were used to determine the kinetic factors \( (E_a \text{ and } A) \) in this study. The typical linear regression lines of the KAS, OFW, and Starink methods fitted with conversion (X) in the range 0.2 to 0.8 are shown in Fig. 5. The estimates of \( E_a \) and A from the models were very close in value, as shown in Table 8. The quality of linear fitting is shown by \( R^2 \), with the values being mostly higher than 0.96 which implied the simulations had a good fit with the experimental data. Fig. 6 illustrates the variation of \( E_a \) in terms of X. The kinetic factors \( E_a \) and A showed similar trends by increasing first for X values of 0.2 to 0.7, then decreasing at 0.8. The minimum and maximum \( E_a \) values were at X values of 0.2 and 0.7, respectively. It was noticed that a rapid increase in \( E_a \) occurred between X values in the range 0.6-0.7 because almost all the volatile matter was expelled from the char residue. Moreover, \( E_a \) rapidly dropped for X values in the range 0.7-0.8 due to the sudden char combustion at the higher temperature in the oxygenated atmosphere (Das and Tiwari, 2019). The average \( E_a \) value for pellets was in the range 142 to 146 kJ/mol for all prediction models, with these values in accordance with previous work of Das and Tiwari (2019), as was the average value of A represented in the range \( 6.70 \times 10^{12} \) to \( 1.83 \times 10^{15} \) min\(^{-1} \).

**Thermodynamic parameters**

To design a high performance macro-scale combustor requires not only choosing suitable bio-fuels and kinetic parameters but also requires

---

**Table 7**

<table>
<thead>
<tr>
<th>Heating Rate</th>
<th>( T_{\text{ig}} ) (°C)</th>
<th>( T_b ) (°C)</th>
<th>( T_p ) (°C)</th>
<th>DTG ( \text{max} ) (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>200</td>
<td>230</td>
<td>250</td>
<td>12</td>
</tr>
<tr>
<td>Medium</td>
<td>220</td>
<td>260</td>
<td>280</td>
<td>15</td>
</tr>
<tr>
<td>High</td>
<td>240</td>
<td>290</td>
<td>310</td>
<td>18</td>
</tr>
</tbody>
</table>

---

**Fig. 5:** Linear regression lines; (a) KAS, (b) OFW, and (c) Starink at various conversions (X)

**Fig. 6:** \( E_a \) vs X for the KAS, OFW, and Starink

---
investigating the thermodynamic parameters (Xu and Chen, 2013). Thermodynamic factors such as A, ΔH, ΔG, and ΔS evaluated using the OFW method under the TGA conditions of a heating rate at 15 °C/min, are shown in Table 9. The A value increased from 7.63×10⁴ to 1.30×10¹¹ for X values in the range from 0.2 to 0.7, respectively, and then decreased to 5.25×10⁹ at an X value of 0.8. The lowest and highest values of A were 7.63×10⁴ and 1.30×10¹¹ at X values of 0.2 and 0.7, respectively. The higher values of A were due to elevated numbers of molecular collisions so more heat was generated which was related to the values of Eₐ (Fong et al., 2019). On the other hand, the lowest A indicated a restriction in particle rotation of the activated complex compared to the initial reagent, indicating a large surface reaction (Zhang et al., 2016). ΔH is the deviation of energy between the reagent and the activated complex depending on the activation energy (Xu and Chen, 2013). ΔH increased from 88.73 to 167.41 kJ/mol and decreased to 149.48 kJ/mol with an average of 136.61 kJ/mol during the conversion. It was noticed that the deviation between Eₐ and ΔH was very low (about 10 kJ/mol) which implied that this reaction was simple to achieve product formation (Ahmad et al., 2017). Positive values of ΔH represent an endothermic reaction which requires an external heat source to break and form new chemical bonds. The ΔG value refers to the amount of available energy for the formation of activated complexes (Laougé and Merdun, 2020). It was quite steady for X values from 0.2 to 0.8 with an average ΔG of 201.79 kJ/mol which was consistent with Das and Tiwari (2019). This indicated that the combustion of the mixed PET waste with biomass consumed more energy compared to chicken manure (163.37-165.39 kJ/mol) (Yuan et al., 2017). The high ΔG value showed that the PET/biomass pellets were an optimal choice for converting the PET waste and biomass to energy.

### Table 8: Thermokinetic factors of pellets for three models

<table>
<thead>
<tr>
<th>X (−)</th>
<th>KAS</th>
<th>OFW</th>
<th>Starink</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eₐ (kJ/mol)</td>
<td>A (min⁻¹)</td>
<td>R²</td>
</tr>
<tr>
<td>0.2</td>
<td>94.31</td>
<td>2.76E+07</td>
<td>0.92</td>
</tr>
<tr>
<td>0.3</td>
<td>126.15</td>
<td>1.07E+10</td>
<td>0.96</td>
</tr>
<tr>
<td>0.4</td>
<td>140.41</td>
<td>1.53E+11</td>
<td>0.97</td>
</tr>
<tr>
<td>0.5</td>
<td>148.37</td>
<td>6.66E+11</td>
<td>0.98</td>
</tr>
<tr>
<td>0.6</td>
<td>158.46</td>
<td>3.83E+12</td>
<td>0.99</td>
</tr>
<tr>
<td>0.7</td>
<td>173.42</td>
<td>4.06E+13</td>
<td>1.00</td>
</tr>
<tr>
<td>0.8</td>
<td>155.58</td>
<td>1.62E+12</td>
<td>0.99</td>
</tr>
<tr>
<td>Avg.</td>
<td>142.38</td>
<td>6.70E+12</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 9: Thermodynamic analysis of pellets at 15 °C/min

<table>
<thead>
<tr>
<th>X (−)</th>
<th>A (s⁻¹)</th>
<th>ΔH (kJ/mol)</th>
<th>ΔG (kJ/mol)</th>
<th>ΔS (J/mol⋅K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>7.63E+04</td>
<td>88.73</td>
<td>204.07</td>
<td>-166.50</td>
</tr>
<tr>
<td>0.3</td>
<td>2.57E+07</td>
<td>120.45</td>
<td>202.40</td>
<td>-118.29</td>
</tr>
<tr>
<td>0.4</td>
<td>3.40E+08</td>
<td>135.09</td>
<td>201.78</td>
<td>-96.27</td>
</tr>
<tr>
<td>0.5</td>
<td>1.43E+09</td>
<td>142.55</td>
<td>201.46</td>
<td>-85.05</td>
</tr>
<tr>
<td>0.6</td>
<td>8.82E+09</td>
<td>152.56</td>
<td>201.08</td>
<td>-70.04</td>
</tr>
<tr>
<td>0.7</td>
<td>1.30E+11</td>
<td>167.41</td>
<td>200.56</td>
<td>-47.85</td>
</tr>
<tr>
<td>0.8</td>
<td>5.25E+09</td>
<td>149.48</td>
<td>201.19</td>
<td>-74.64</td>
</tr>
<tr>
<td>Avg.</td>
<td>2.08E+10</td>
<td>136.61</td>
<td>201.79</td>
<td>-94.09</td>
</tr>
</tbody>
</table>
a system and shows how near of far the state of the sample is from its own thermodynamic equilibrium. Entropy also shows the degree of arrangement of the carbon layers in samples (Xu and Chen, 2013). Positive values indicate a high affinity of the sorbent and negative values indicate that the adsorption process is mainly driven by $\Delta S$. In the current study, the $\Delta S$ values were negative regardless of the model and process used. The higher values of $\Delta S$ occurred between $X$ values of 0.2 and 0.3 (-166.50 and -118.29 J/(mol.K)), respectively. It was observed that the trend for $\Delta S$ was opposite that of $E_a$, $\Delta H$, and $\Delta G$.

CONCLUSION

Increase in fuel pellets demand coupled with rising environmental issues of the secondary waste from the plastic recycling system have attracted researcher to explore. Fuel pellets production by pelleting is an efficient method for manipulating waste of PET from a mechanical recycling plant and local biomass like teak sawdust. It is a useful tool to manage the waste of PET and biomass in terms of dusty forms (macro-, meso-, micro-, and nano-sizes) and plays a role on reduce the loads of plastic waste pollution that releases into the soil, public water, as well as air emissions. Notice, the reduction of loads of plastic waste dumps into landfills and to prevent the improper disposal of plastic waste are considered. In further, it can adapt into a concept of waste to energy following by converting to fuel pellets and using with industrial furnaces i.e. using as substituent fuels in cement kiln, boiler, power plant, incinerator, and so on. Pelletizing was employed to convert waste of PET and biomass into a potential solid fuel with the fit ratio of 9:1 (PET:biomass). This ratio gives the durability of PET/biomass pellets, a uniform dimension, ease handling, storage, and transportation common as woody pellets. Some technical challenges such as low moisture content and high volatile matter content were feedstock dependent. The PET/biomass pellets had characteristics and physico-chemical properties that were a combination of those of the PET waste and biomass. A high heating value of the PET/biomass pellets (HHV = 19.20 MJ/kg) was obtained from the results of pelletizing the complex solid fuels. The HHV value was slightly decreased by adding biomass. The complex structure of ethylene terephthalate and lignocellulose was clearly identified by FTIR technique. Heavy metals (Cd~Cu<Pb<Cr<Zn) and ionic (7 AnLs and 6 CaLs) contaminants had lower concentration than the limitation of the regulations. The results of ash composition affirmed that the ash of PET/biomass pellets was a non-hazardous residue which was unique characters based on feedstock. Therefore, the PET/biomass pellets can be used without harms of the environment and health impacts. Earth materials (SiO$_2$ composition) and a detergent (Na$^+$ element of caustic soda) from step PET flake cleaning had a slightly effect on the alteration of residue chemicals. However, biomass supplied as part of PET plastic waste improve combustion kinetics such as $T_{ig}$, $T_b$, $R_{avg}$, and $DTG_{max}$. Lower ignition temperature, burnout temperature, reactivity, and $DTG_{max}$ were affected by the blended biomass in the PET/biomass pellets that could be attributed to the combined effect of terephthalate and lignocellulose groups present in the pellet matrix. Subsequently, the combustion characteristics and kinetics of PET/biomass pellet samples were examined via the iso-conversional methods of KAS, OFW, and Starink. The results exhibited similar trends and values for the activation energy ($E_a$) of 142.38, 146.34, and 143.01 kJ/mol, respectively, with the values of conversion ranged from 0.2 to 0.8. The thermodynamic factors of $\Delta H$, $\Delta G$, and $\Delta S$ were 136.61 kJ/mol, 201.79 kJ/mol, and -94.09 J/(mol.K), respectively. These findings may provide comprehensive knowledge to assist the design and operation of a combustion system for adding PET/biomass pellets in a co-firing process with traditional solid fuels. Moreover, PET/biomass pellets can further be upgraded to other fuels production via modern bioenergy conversion processes.

AUTHOR CONTRIBUTIONS

K. Manatura performed the literature review, writing original draft, conceptualization, methodology, investigation, data analysis, visualization, and manuscript edition. U. Samaksaman performed the literature review, experimental design, analyzed and interpreted the data, research summary and recommendation, and manuscript edition.

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**ABBREVIATIONS**

- %: Percentage
- % wt: Weight percentage
- °C: Degrees celsius
- °C/min: Heating rate (degree of temperature per time)
- ΔG: Gibbs free energy
- ΔH: Enthalpy
- ΔS: Entropy
- A: The pre-exponential factor
- Al₂O₃: Aluminium oxide
- AnL: Anions leachate
- β: The heating rate varies with the reaction time and temperature at a constant heating rate
- Br: Bromide
- cm: Centimeter
- 1/cm: The unit of wavenumber of IR spectrum
- C: Carbon
- CaL: Cations leachate
- CaO: Calcium oxide
- Ca²⁺: Calcium
- Cd: Cadmium
- Cl: Chloride
- Cr: Chromium
- Cr₂O₃: Chromium (III) oxide
- Cu: Copper
- CuO: Copper oxide
- CEN/TS 14775: Method for the determination of ash content
- DI water: The deionized water
- DTG: Derivative thermogravimetry
- DTG max: Maximum derivative thermogravimetric value (1/s)
- Eₐ: The activation energy (kJ/mol)
- Eq.: Equation
- EDXRF: Energy dispersive X-ray fluorescence spectroscopy
- f(x): The reaction model expressing the dependence of the combustion rate
- F⁻: Fluoride
- FC: Fixed carbon
- Fe₂O₃: Iron (III) oxide
- FTIR: Fourier transform infrared spectrometry
- g(X): The integral form of f(X)
- h: Plank constant 6.626 × 10⁻³⁴ (J.s)
- H: Hydrogen
- HDPE: High density polyethylene
- HHV: High heating value
- H/C: Hydrogen to carbon atomic ratio
- IR: Infrared radiation
- k: The combustion rate constant
- kg/min: Kilogram per minute
- kV: Kilovoltage
- K: Degrees Kelvin
- K⁺: Potassium
- K₈: The Boltzmann constant 1.381 × 10⁻²³ (J/K)
- KAS: The Kissinger-Akahira-Sunose method
- K₂O: Potassium oxide
- Li⁺: Lithium
- mg/kg: Milligram per kilogram
- ml: Milliliter
- mm: Millimeter
- mΩ: Milliohm
- min⁻¹: The unit of A interm of minute (pre-exponential factor)
- m₀: The initial sample mass
The sample mass left after ending process

The sample mass at time \( t \)

Moisture content

Megajoules per kilogram

Manganese (IV) oxide

Nitrogen

Sodium

Sodium hydroxide (caustic soda)

Ammonium

Oxides of nitrogen

Nitrite

Nitrate

Oxygen

The Ozawa-Flynn-Wall method

Oxygen to carbon atomic ratio

Part per million

Lead

Polyethylene terephthalate

The mixture of PET and biomass

Phosphate

Polypropylene

Phosphorus(V) oxide

The universal gas constant 8.314 (kJ/(kmol·K))

The coefficient of determination value

Higher reactivity

Refuse derived fuel

Rhodium X-ray tube

The unit of \( A \) intern of second (pre-exponential factor)

Sulfur

Silicon oxide

Sulfur dioxide

Sulfur trioxide

Sulfate

Strontium oxide

Solid recovered fuel

The Starink method

The absolute temperature (K)

Tantalum (V) oxide

Titanium dioxide

Burnout temperature

Ignition temperature

Peak temperature

Thermogravimetric analysis

The volume ratio

Volatile matter

The conversion of samples

The X-ray fluorescence spectroscopy

The X-ray irradiation diameter

Zinc

Zinc oxide

Zirconium dioxide


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