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New composites based on low-density polyethylene and rice husk: Elemental and thermal characteristics

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ABSTRACT

We developed new composites by combining the solid waste from Low-Density Polyethylene in the form of plastic bag (PB) and biomass from rice husk (RH), in the form of (RH)ₓ(PB)₁₋ₓ (x = (1, 0.9, 0.7, 0.5)), as alternative fuels for electrical energy sources, and for providing the best solution to reduce environmental pollution. Elemental compositions were obtained by using proximate analysis, ultimate analysis, and X-ray fluorescence spectroscopy, and the thermal characteristics were obtained from thermogravimetric analysis. The compositions of carbon and hydrogen from the ultimate analysis show significant increases of 20-30% with increasing PB in the composite. The activation energy for RH is 101.22 kJ/mol; for x = 0.9 and 0.7, this increases by 4 and 6 magnitude, respectively, and for x = 0.5, shows remarkable increase to 165.30 kJ/mol. The range of temperature of about 480-660°C is required for combustion of the composites (RH)ₓ(PB)₁₋ₓ (x = (1, 0.9, 0.7, 0.5)) to perform the complete combustion process and produce high energy. In addition, the calorific value was determined by using bomb calorimetry, and shows value for RH of 13.44 MJ/kg, which increases about 30-40% with increasing PB content, indicating that PB has a strong effect of increasing the energy realized to generate electricity.

Keywords: Elemental composition, Low-density polyethylene, Plastic bags, Rice husk, Thermal characteristics

1. Introduction

Clean and efficient utilization of biomass as a source of alternative energy is of major concern, and is essential for generating electricity, especially in developing countries. Indonesia as a developing country is still lacking in electrical energy supply, with electrification of around 76.56% [1]. About 23.5% of rural communities have not yet used electrical energy, due to the inability of power plants to meet the increasing power needs of the society and industry every year. More than half of the electricity suppliers in Indonesia generate their electricity from coal [2]. Coal production in Indonesia is quite large, at around 2.751×10⁶ tons in 2010 [3]. However, continuous mining and combustion of coal as fuel damages the natural environment. On the other hand, Indonesia has abundant potential biomass resources that are environmentally friendly. The potential of rice husk (RH) in 2012 was around 1.381×10⁷ tons, equivalent to the electrical energy potential of around 53.702 GWh, the third largest in the world after China and India [4, 5]. Nonetheless, this potential has not been exploited, and few have reported it as a source of energy [6]; it has only been used as a catalyst [7, 8], or wasted, causing environmental pollution. In Indonesia, large amounts of biomass fuels are consumed for cooking, and some biomass of low density, such as RH, is used for heating. The burning of biomass fuel is one of the most important sources of emission of CO and volatile organic matter, which not only cause severe indoor air pollution, but also contribute to regional, global, and climate forcing. Replacing traditional fuel methods with cleaner techniques are challenges in several countries, including Indonesia. Several alternative options that are expected to result in lower emission pollution than traditional burning include pellets and catalyst. However, some studies reported the preparation of RH as pellets or catalyst to be time-consuming and energy intensive, due to low-density biomass, generally performed under high temperature (400-800°C), and long reaction time (up to 15 h) [9-11].
RH is also a widely accepted alternative energy source, due to its high carbon and oxygen composition, which is fundamental for searching sources of energy [12, 13]. Direct combustion in a grate bed combustor can minimize harmful exhaust gasses by using an exhaust emission control device, which is a technique that uses RH as fuel for power plants to generate electricity in Thailand [12], and India [13]. Generating electricity from biomass provides significant benefits to the environment, since it produces clean energy [14].

In addition to the electrical energy shortage, Indonesia also has problems in handling municipal solid waste (MSW), particularly low-density polyethylene (LDPE) type plastic bags (PB). The average household solid waste generated in Jakarta and another big city in Indonesia is 2,416.2 kg per household per year, with PB (14%) being the second largest, and increases every year by about 2-5% [15, 16]. PB at landfills may take tens to hundreds of years to be completely decomposed, and subsequently, those particles could contaminate the soil and water of the surrounding area [17]. In fact, PB has a calorific value (CV) of about 41.5 MJ/kg [18]. PB combustion in the grate can minimize harmful exhaust gasses [19-21], and PB is also used as fuel for power plants to generate electric power of about 8.9 MW in Malaysia [21-25].

Based on the fuel needed for generating electricity, and the potential of solid waste and biomass, in this study, we developed new composites by combinations of solid waste and biomass. Potentials of solid waste and biomass, in this study, we developed composites (RH) \( x \) (PB) \( 1-x \) (x = (1, 0.9, 0.7, 0.5)) as alternative new composites by combinations of solid waste and biomass. The samples in this study are composites (RH) \( x \) (PB) \( 1-x \) (x = (1, 0.9, 0.7, 0.5)) samples, with a mass test of about 5.5-5.8 mg.

2. Materials and Methods

2.1. Materials Preparation

The samples in this study are composites (RH) \( x \) (PB) \( 1-x \) (x = (1, 0.9, 0.7, 0.5)) from RH and PB as alternative energy sources. We chose PB type LDPE identified by the logo triangle figure in the middle of the LDPE sign, which is usually used for shower curtains, packaging, films, and clamshell. After being sun-dried, RH and PB were cut and ground to reduce size using a mill. Raw materials were sieved to obtain uniformity of size of between 0.125 and 0.3 mm (for details, see [4, 22]). The physical mixing of samples was performed by weighting each raw sample to obtain uniform and homogeneous composites. The samples were mixed by using an exhaust emission control device to minimize harmful exhaust gasses [19-21], and PB is also used as fuel for power plants to generate electric power of about 8.9 MW in Malaysia [21-25].

2.2. Proximate Analysis, Ultimate Analysis, and Calorific Value

The chemical compositions of composites (RH) \( x \) (PB) \( 1-x \) (x = (1, 0.9, 0.7, 0.5)) were determined from the proximate analysis, ultimate analysis, and XRF spectroscopy. The proximate and ultimate analyses were conducted based on the Standard Methods ASTM D 3172 - D 3174, ASTM D 4239, ASTM D 5373, and ISO 565. Meanwhile, the CV was carried out by using bomb calorimeter according to the Standard Methods ASTM D.5865 (for details, see [26, 27]).

2.3. Oxidative and Kinetic Study

The oxidative study of the (RH) \( x \) (PB) \( 1-x \) (x = (1, 0.9, 0.7, 0.5)) was conducted to determine the characteristics of the kinetic parameter based on the some previous studies [28-32], by using thermal gravimetric analysis (TGA) and differential thermal gravimetric (DTG). The oxidative reaction was carried out from temperature 30 to 800°C for about 82 min, at a heating rate of about 10°C/min, and flow rate of air of about 50 mL/min. The Mettler test was performed on the (RH) \( x \) (PB) \( 1-x \) (x = (1, 0.9, 0.7, 0.5)) samples, with a mass test of about 5.5-5.8 mg. The characteristics of (RH) \( x \) (PB) \( 1-x \) (x = (1, 0.9, 0.7, 0.5)) from TGA and DTG were analyzed by using Sma4Win software. A two-stage reaction kinetic scheme has been proposed for the thermal degradation (TD) of composites under an oxidative atmosphere [31], representing the DTG curves:

First stage: \( \text{A (solid)} \rightarrow \text{B (char)} + \text{C1 (gas)} \) (1)

Second stage: \( \text{B (char)} \rightarrow \text{C2 (gas)} + \text{D (ash)} \) (2)

The kinetic parameters were calculated from the linear regression curve with the correlation factors (above 0.90), based on the Arrhenius law. The activation energy (Ea) that occurs at every TD process [33-35] was determined by using the following equations:

\[
k = Ae^{-\frac{Ea}{RT}}
\]

where, \( k \) is the reaction rate, \( Ea \) is the activation energy for the reaction (J/mol), \( A \) is the pre-exponential factor (1/min), \( R \) is the universal gas constant (8.314 JK mol), and \( T \) is the absolute temperature (K). The equation can be written in logarithmic form:

\[
\ln k = \ln A - \left( \frac{Ea}{RT} \right) \ln e
\]

where, \( \ln e = 1 \)

\[
\ln k = -\frac{Ea}{R} \times \frac{1}{T} + \ln A
\]

Based on previous studies [33, 36, 37], the Eq. (5) was obtained:

\[
\ln k = -\ln \left[ \frac{1}{T^2} \right]^{(1-\alpha)} \text{ and } \ln A = \ln \frac{AR}{\beta E}
\]

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Thus, Eq. (5) can be written as:

\[
\ln \left( \frac{1 - \alpha}{T^2} \right) = \frac{E_a}{R} \times \frac{1}{T} + \ln \left( \frac{AR}{\beta E} \right)
\]

(6)

where, \( \beta \) is the heating rate (K/min). The mass loss fraction \( \alpha \) (mg) for every stage of the thermal degradation is defined as:

\[
\alpha = \frac{M_i - M_f}{M_i - M_f}
\]

(7)

where, \( M_i \) is the initial mass of the sample at the beginning reaction (mg), \( M_a \) is the actual mass of the sample (mg), and \( M_f \) is the final mass, or the mass after oxidation of the sample (mg). The \( E_a \) may then be extracted from a plot of \( \ln k \) vs. \( 1/T \), which should be linear. Eq. (5) can be analogous to the equation of a straight line, which is often symbolized by the linear regression equation \( y = mx + b \). Thus, the \( -\ln \left( \frac{1 - \alpha}{T^2} \right) \) is the y-axis, \( \frac{1}{T} \) is the x-axis, and \( b = \ln \left( \frac{AR}{\beta E} \right) \) is the intercept of the line with the y-axis, with \( m = \frac{E_a}{R} \) as slope. The \( E_a \) is obtained for every step of degradation (mass loss) [33, 37, 38].

### 3. Results and Discussion

Table 1 shows the results of the proximate and ultimate analyses of \( (RH)_x(PB)_{1-x} \) (\( x = (1, 0.9, 0.7, 0.5) \)). For RH, it shows good agreement with previous results [38] for elemental composition (fixed carbon (FC), volatile matter (VM), ash (A) content, carbon (C), hydrogen (H), and oxygen (O)), with differences <10%. We also compared the results with several reported in previous studies [39-42] for the value of moisture content (MC), VM, FC, nitrogen (N), sulphur (S), O, H, and A, where the values were similar. This shows that the parameters of the test results and methodology used in this study show good accuracy, with acceptable values. The most important elements for energy application, which must be of high content, are C, FC, H, and MC, but other elements should be low. PB shows high C and H, and low A, MC, N, O, and S; while RH shows high FC and MC. By mixture of RH and PB to form composites, a good characteristic element can be obtained for the release of energy. Table 1 shows that composites \( (RH)_x(PB)_{1-x} \) reveal homogeneous samples; all elemental composition is increased gradually with increasing PB content for an element with higher content in PB, and vice versa.

For C, H, and O, we have compared with the results of predictive equation by using data from proximate analysis as input.
parameter, proposed by [43] in the form: C = -35.9972 + 0.010 + 0.33, while the predictive proposed by Thomas Klasson [44] shows reasonable agreement for RH with differences of about 10%, and increases by about 0.5% with increasing PB content in composites. For H, good agreement is shown between the ultimate analysis data and the predictive equation from [44], only for RH, and from [43] only for 30%PB and 50%PB, compared with the ultimate analysis data. For O, the content shows a big difference of about 30-40% between the ultimate analysis data with predictive from [43], and good agreement only for 30% PB with the predictive from [44]. These results indicated that the existing predictive equations from [43] and [44] show good accuracy in results compared with the ultimate analysis data only for several compositions in composites RH and PB.

Table 1 shows that we compared the CV determined by bomb calorimetry in this study with the predictive model developed by Majumder et al. [45] in the form: CV (MJ/kg) = -0.034 - 0.11M + 0.33VM + 0.35FC. RH shows CV of about 13.44 MJ/kg, which is very good agreement with [40] of about 13.30 MJ/kg, and [41] of about 13.50 MJ/kg; and PB shows CV of about 41.21 MJ/kg in this study, which is also comparable with the previous studies [46-48]. For composites, the CV was increased by about 30% with increasing PB content in composites. The differences between predictive equations with the result in this study for 30 and 50% PB in composites are about 10%, but become high for pure RH and PB. This indicated that the predictive CV from [43] is valid for high PB content in composites, and shows good agreement with ethanol (30 MJ/kg) and methanol (23 MJ/kg) as acceptable fuels [49].

For composites (RH)_(x)(PB)_(1-x) (x = (0.9, 0.7, 0.5)), the CV increased with increasing amount of PB to RH from 17.85 MJ/kg for x = 0.9. 23.97 MJ/kg for x = 0.7, to 28.93 MJ/kg for x = 0.5.

Moreover, increasing the CV showed a positive correlation with C, H, and VM of the fuel. In contrast, the addition of PB lowered the percentage of O, S, N, FC, MC, and A. The physical properties of the fuel depend on the content of CV, MC, and AC that influence the energy production. The amount of MC in the fuel affected the CV and A of the combustion products [35]. One would expect the fuel mixture to have a maximum CV and minimum A. The energy and power that can be generated depend on the CV content in the composites for fuel.

The addition of PB to RH can improve the quality of fuel, such as increasing CV, C, H, and VM, and decreasing FC, MC, S, N, O, and A. The increasing content of C and H means a greater contribution to the energy released [35]. However, the percentage of O decrease in the fuel means increasing the content of C and H, as well as increasing CV of the fuel, but O is required in the process of fuel combustion. The high CV can increase energy production; thus, composites in this study become attractive as an energy source. Small amounts of N will reduce NOx emissions in the air, while small amounts of S can reduce pollution and corrosion. High amounts of VM and A and low MC are important characteristics required in the process of energy production. The high amount of A is affected by the reduction of energy production, and an increase of handling cost for the disposal process [50]. High MC will aggravate the chemical properties of the fuel, hence complicating the process of energy production. The increasing amount of PB in composites resulting in decrease in the amount of N and S indicated the formation of NOx and SOx, decreased; these are both hazardous gasses, and very harmful to the environment [51-53]. Thus, the addition of PB into RH to form composites will increase energy production, and also decrease the amount of MC, A, NOx, and SOx.

Table 2 shows the elemental composition by using XRF spectroscopy after heating the composites at the temperature of 105°C for several hours. The main elements for ash from RH are Si and K of about 73.61 and 14.31%, respectively, which are similar to those reported in Refs. [26, 27], and those for ash from PB are Ca and Ti of about 75.61 and 12.93%, respectively, which are similar values to those reported in [54]. The composites show Si and K as the main elements of ash from RH decrease
with increasing the amount of PB, and similarly, the elements of ash from PB are increased with increasing the amount of RH.

TGA and DTG curves show that there is a difference between the oxidation process of \((RH)_{1}(PB)_{1-x}\) \((x = (1, 0.9, 0.7, 0.5))\), as shown in Fig. 1. The TGA and DTG curves of \((RH)_{1}(PB)_{1-x}\) \((x = (1, 0.9, 0.7, 0.5))\) show the dehydration process (DP) with degradation temperature (DT) from 40 to 100°C and mass loss (ML) from 2.3 to 5.2%, as moisture evaporation indicated the dehydration processes. The TD of composites is of two stages for \(x \geq 0.7\), and of three stages for \(x = 0.5\). TD in the first zone (TDZ1) is in the range of temperature 240-360°C with ML in the range 40.4-43.7%, while TDZ2 is in the range of temperature of 370-490°C, with ML in the range 25.4-32.6%. Furthermore, TDZ3 is in the range of temperature 600-670°C, with ML of about 2.8%. The total ML during the degradation of \((RH)_{1}(PB)_{1-x}\) \((x = (1, 0.9, 0.7, 0.5))\) is in the range 71.6-79%, and generated A approximately in the range 21-28.4%. This shows that the addition of PB to RH influences the thermal characteristics of composites by enlarging the energy production and reducing the A residues. Table 3 shows the parameters of kinetic study for the oxidative environment of \((RH)_{1}(PB)_{1-x}\) \((x = (1, 0.9, 0.7, 0.5))\).

Fig. 2 shows the \(E_a\) that occurred in the TDZ1 of the \((RH)_{1}(PB)_{1-x}\) \((x = (1, 0.9, 0.7, 0.5))\). The activation energy for the TDZ1 of RH of 56.49 kJ/mol was obtained on the basis of the linear regression: \(y_1 = 6.794x + 1.902\), with \(R^2 = 0.915\) for DT in the

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**Table 3. Parameters of the Kinetic Study for the Oxidative Environment of Composites (RH)\(_{1}\)(PB)\(_{1-x}\) (x = 1, 0.9, 0.7, 0.5) for Thermal Degradation Zone (TDZ1, TDZ2, TDZ3) Based on Fig. 1**

<table>
<thead>
<tr>
<th>Materials</th>
<th>MS (mg)</th>
<th>DP</th>
<th>TDZ1</th>
<th>TDZ2</th>
<th>TDZ3</th>
<th>(E_aT) (kJ/mol)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH</td>
<td>5.8</td>
<td>5.2</td>
<td>50-100</td>
<td>41</td>
<td>240-360</td>
<td>25.4</td>
<td>370-480</td>
</tr>
<tr>
<td>10%PB</td>
<td>5.5</td>
<td>4.4</td>
<td>50-100</td>
<td>43.7</td>
<td>240-360</td>
<td>25.8</td>
<td>370-490</td>
</tr>
<tr>
<td>30%PB</td>
<td>5.6</td>
<td>2.3</td>
<td>50-100</td>
<td>42.4</td>
<td>250-380</td>
<td>27.9</td>
<td>390-490</td>
</tr>
<tr>
<td>50%PB</td>
<td>5.5</td>
<td>3.2</td>
<td>50-100</td>
<td>40.4</td>
<td>250-380</td>
<td>32.6</td>
<td>390-460</td>
</tr>
</tbody>
</table>

---

![Fig. 1. TGA and DTG spectra for the temperature range 30-800°C with a heating rate of 10°C/min and flow rate of air of about 50 mL/min from composites (RH)\(_{x}\)(PB)\(_{1-x}\), for (a) x = 1, (b) x = 0.9 , (c) x = 0.7, and (d) x = 0.5.](image-url)
range 240-360°C (Fig. 2(a)). The $E_a$ of 10%PB of 55.55 kJ/mol was based on the equation: $y_1 = 6.681x + 2.340$ with $R^2 = 0.978$ for DT in the range 240-380°C (Fig. 2(b)). For 30%PB, the $E_a$ is 64.63 kJ/mol, based on the equation: $y_1 = 7.774x + 0.721$ with $R^2 = 0.959$ for DT in the range 250-380°C (Fig. 2(c)). Furthermore, the $E_a$ of 50%PB is 54.42 kJ/mol based on the equation: $y_1 = 6.546x + 3.005$ with $R^2 = 0.979$ for DT in the range 250-380°C (Fig. 2(d)). By the same method, Table 4 shows the equation and $E_a$ for the TD process in the second (TDZ2) and the third zones (TDZ3) obtained by linear regression.

Table 4 clearly shows that the amount of PB in composites is important in increasing the $E_a$ value. The higher contents of PB in composites are the higher values of $E_a$. The oxidative process of the TD processes for RH was perfect after reaching a temperature of about 480°C, and increased to 490°C for 10 and 30%PB. For 50%PB, the TD process was perfect after reaching

![Fig. 2. The first degradation (TDZ1) stage of the oxidative process to determine activation energy ($E_a$) and $R^2$ values from the linear regression of $-\ln [\ln (1 - \alpha)/T^2]$ vs. $1/T$ for composites (RH)x(PB)1-x, for (a) $x = 1$, (b) $x = 0.9$, (c) $x = 0.7$, and (d) $x = 0.5$.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>DT (°C)</th>
<th>Linear regression of Arrhenius law</th>
<th>($R^2$)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH</td>
<td>240-360</td>
<td>$y_1 = 6.794x + 1.902$</td>
<td>0.915</td>
<td>56.49</td>
</tr>
<tr>
<td></td>
<td>370-480</td>
<td>$y_2 = 5.380x + 4.792$</td>
<td>0.916</td>
<td>-</td>
</tr>
<tr>
<td>10%PB</td>
<td>240-380</td>
<td>$y_1 = 6.681x + 2.340$</td>
<td>0.978</td>
<td>55.55</td>
</tr>
<tr>
<td></td>
<td>390-490</td>
<td>$y_2 = 5.831x + 4.216$</td>
<td>0.961</td>
<td>48.48</td>
</tr>
<tr>
<td>30%PB</td>
<td>250-380</td>
<td>$y_1 = 7.774x + 0.721$</td>
<td>0.959</td>
<td>64.63</td>
</tr>
<tr>
<td></td>
<td>390-490</td>
<td>$y_2 = 5.571x + 4.627$</td>
<td>0.971</td>
<td>46.32</td>
</tr>
<tr>
<td></td>
<td>250-380</td>
<td>$y_3 = 6.546x + 3.005$</td>
<td>0.979</td>
<td>54.42</td>
</tr>
<tr>
<td></td>
<td>390-460</td>
<td>$y_3 = 6.444x + 3.637$</td>
<td>0.915</td>
<td>53.58</td>
</tr>
<tr>
<td>50%PB</td>
<td>390-460</td>
<td>$y_3 = 6.892x + 4.695$</td>
<td>0.924</td>
<td>57.30</td>
</tr>
<tr>
<td></td>
<td>600-660</td>
<td></td>
<td></td>
<td>165.3</td>
</tr>
</tbody>
</table>
a temperature of about 660°C, and from temperature in the range 600-800°C, there was no TD or ML. This shows that the composites (RH)\textsubscript{x}(PB)\textsubscript{1-x} (x = 1, 0.9, 0.7, 0.5) combustion as fuel requires a temperature range of about 480-660°C to perform the complete combustion process to produce high energy.

4. Conclusions

New composites (RH)\textsubscript{x}(PB)\textsubscript{1-x} (x = 1, 0.9, 0.7, 0.5) have been obtained, and show gradually increased elemental composition with increasing PB content for an element with higher content in PB, and decrease with increasing PB for lower content in PB, indicating a homogeneous composite sample. The CV determined by bomb calorimetry shows about 13.44 MJ/kg for RH, and about 41.21 MJ/kg for PB, indicating a homogeneous composite sample. The CV decreased by about 30% with increasing PB content in composites, and about 13.44 MJ/kg for RH is 101.22 kJ/mol, which increases by (4 and 6) magnitude for x = (0.9 and 0.7), respectively, and increases remarkably to 165.30 kJ/mol for x = 0.5. The thermal characteristics, calorific value, and elemental analysis show the activation energy, calorific content, carbon, and hydrogen content, respectively, were strongly affected by the PB content, which contributed to increasing the realized energy.

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