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To cite this article: Muhammad Anshar *et al* 2018 *IOP Conf. Ser.: Earth Environ. Sci.* **105** 012034

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Pyrolysis characteristic of rice husk with plastic bag as fuel for power generation by using a thermogravimetric analysis

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Abstract. Determination of the characteristics of rice husk (RH) with plastic bag (PB) mixture as a source of energy is carried out in pyrolysis study. Test characteristics of RH with PB mixture is performed by using a thermogravimetric analysis at temperatures from 30 - 800°C, heating rate of 10°C/min, and nitrogen flow rate of 50 ml/min. The dehydration process occurs at temperatures from 40 - 100°C, while for thermal degradation at temperatures from 200 - 340°C, 400-500°C, and 580 - 670°C. Activation energy and calorific value of RH with PB mixture increase significantly with the addition of 10%, 30%, and 50% PB in RH. It is concluded that pyrolysis characteristic of RH with PB mixture is better as fuel for power generation if compared with its original state.

1. Introduction

Fossil fuel consumption in Indonesia recorded a high value of approximately 95% in 2011. The use of oil is the largest portion of the total energy i.e. reaching up to 49.5%, where as coal and gas were in the proportion of 26% and 20.4%, respectively. Continuous utilization of fossil energy sources particularly oil, natural gas and coal will result in an expected deflection of these resources approximately 23, 55, and 83 years from the year 2011, respectively. The same time, electrification ratio in Indonesia was recorded at 72.95%, which meant that there were still 27.05% of households that did not receive electricity, especially in remote areas [1]. These conditions prompt optimization on renewable energy consumption in order to meet the needs for electrical energy, which also implies that the availability of electrical energy in Indonesia is still lacking. Base on previous studies result [2-3] show Indonesia has a great potential of rice husk (RH) is about 13.81×10^6 tons in 2013 with an energy potential of approximately 53,702 GWh. the CV of RH about 13.44 MJ/kg is within the range of 13 - 16 MJ/kg [4]. Meanwhile, the potential of plastic solid waste (PSW) of about 693 tons with energy potential of 28,752,528 MJ, equivalent to 1,065 tons of coal or 593 ton of oil. PSW, specially plastic bags (PB) has great energy with a calorific value (CV) of about 41.2 MJ/kg. This value is within the range of 39.03 – 41.5 MJ/kg [5]. Pyrolysis methods have received much

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attention because these methods have the potential in reducing the volume of waste, recovery of various chemicals and as replacement for fossil fuels [6].

2. Materials and methods

2.1. Materials

The sample of PB was dried in an oven at a temperature of 105°C for 1 hour and 7 hours for RH, as from previous studies [7-9]. The PB and RH mixture was sieved to obtain homogeneous sizes within the range of 0.125 - 0.3 mm to allow for an even mix, as in previous studies [10]. The sample was mixed with the following mass ratios of RH to PB: 90% RH: 10% PB (R₉P₁), 70% RH: 30% PB (R₇P₃) and 50% RH: 50% PB (R₅P₅).

2.2. Proximate and ultimate analysis

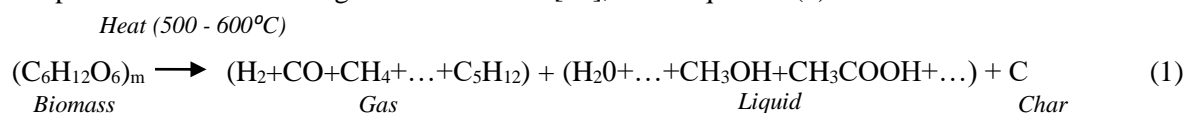
Testing characteristics of the sample is done with proximate and ultimate analysis base on previous studies [9]. The CV was obtained by using a bomb calorimeter, model IKA C 2000, according to DIN 51900 methods. The proximate analysis was done according to standard methods i.e. ASTM D3175, ASTM D 3172, ASTM D3173 and ASTM D3174. The ultimate analysis of the samples was done according to standard methods, i.e. ASTM D 4239, ASTM D 3176, and ASTM D 5373 as in previous studies [11-12].

2.3. Thermogravimetric analysis

Thermogravimetric analysis was conducted using the TGA/SDTA851, Mettler Toledo to analyze pyrolysis studies. The heating rates were controlled at 10°C/min from 30 - 800°C. The pyrolysis process used nitrogen flow rate of 50 ml/min as previous studies [9, 13-15]. The dehydration process and thermal degradation on pyrolysis process were analyzed using TGA and DTG curves with the *Sma4Win software*.

2.4. Kinetics study

Kinetic study on pyrolysis process was done to investigate firstly the dehydration process (DP) from 40 - 100°C, thermal degradation (TD) of hemicelluloses from 200 - 260°C and followed by cellulose from 240 - 340°C and finally lignin from 280 - 500°C. The pyrolysis reaction is complete as the temperature reaches the range of 500 - 600°C [16], as in equation (1):



The degradation of hemicelluloses, cellulose and lignin in RH were approximately 30 - 35%, 21 - 31%, and 4 - 19%, respectively [16-17]. The kinetics of the degradation reactions are largely described by the first-order Arrhenius law. Activation energy (E_a) that occurs at every TD process can be obtained from the linear regression equation of the Arrhenius law [9-10, 14-15] as shown in the following equation:

$$k = A e^{(-E_a/RT)} \quad (2)$$

where; E_a is the activation energy for the reaction (J/mol), A is the pre-exponential factor (min⁻¹), R is the gas constant (8.314 J/K mol), T is the absolute temperature (K). The equation can be written in logarithmic form:

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right) \ln e, \text{ where } \ln e = 1 \quad (3)$$

$$\ln k = -\frac{Ea}{R} \times \frac{1}{T} + \ln A \quad (4)$$

Based on previous studies [9, 13] the following equations are obtained:

$\ln k = -\ln\left[\frac{\ln(1-\alpha)}{T^2}\right]$ and $\ln A = \ln \frac{AR}{\beta E}$. Thus, equation (5) can be written as:

$$-\ln\left[\frac{\ln(1-\alpha)}{T^2}\right] = \frac{E}{R} \times \frac{1}{T} + \ln \frac{AR}{\beta E} \quad (5)$$

where; β is the heating rate (K/min), the mass loss fraction α for every stage of the thermal degradation is defined as:

$$\alpha = \frac{M_i - M_a}{M_i - M_f} \quad (6)$$

where; α is mass loss fraction (mg), M_i is the initial mass of the sample at the beginning of the reaction (mg), M_a is the actual mass of the sample (mg), M_f is the mass after pyrolysis of the sample (mg). The E_a may then be extracted from a plot of $\ln k$ vs. $1/T$, which should be linear. This plot is known as the "Arrhenius plot". It is often symbolized by the linear regression equation: $y = mX + b$.

Thus, the $-\ln\left[\frac{\ln(1-\alpha)}{T^2}\right]$ as y-axis, $\frac{1}{T}$ as x-axis, $m = \frac{E}{R}$ as slope, and $b = \ln \frac{AR}{\beta E}$ as the intercept of the line with y-axis.

3. Results and discussion

3.1. Characteristic of fuels

The results of proximate and ultimate analysis are presented in Table 1, which shows the characteristic parameters of the fuel. The CV of RH is 13.44 MJ/kg; the addition of PB 10%, 30% and 50% into RH increases the CV of R₉P₁, R₇P₃, and R₅P₅ to approximately 17.85 MJ/kg, 23.97 MJ/kg and 28.93 MJ/kg, respectively. Meanwhile, VM, C and H increases with the amount of percentage of PB into RH. In contrast, the percentage of O, S, N, FC, MC, and ash decreased with the increase of PB percentage. The addition of PB into RH can improve the quality of fuel as such CV and VM increase whereas MC, S, N and ash decrease. Small amounts of N will reduce NO_x emissions into the air while small amounts of S can reduce or minimize pollution and corrosion.

Table 1. Test result on calorific value, proximate and ultimate analysis of RH and PB.

Parameters	Unit	RH	R ₉ P ₁	R ₇ P ₃	R ₅ P ₅	PB
Calorific value (CV)	(MJ/kg)	13.44	17.85	23.97	28.93	41.21
Proximate Analysis						
a. Fixed carbon (FC)	(%)	14.81	13.62	10.89	8.00	0.72
b. Volatile matter (VM)	(%)	55.62	58.65	65.21	72.39	89.04
c. Moisture content (MC)	(%)	10.46	9.68	7.53	5.26	0.22
d. Ash	(%)	19.11	18.05	16.37	14.35	10.02
Ultimate Analysis						
a. Carbon (C)	(%)	37.48	40.21	47.00	53.60	67.49
b. Hydrogen (H)	(%)	5.08	5.82	7.10	8.61	10.25
c. Oxygen (O)	(%)	37.81	35.45	29.13	23.08	11.92
d. Nitrogen (N)	(%)	0.43	0.38	0.31	0.28	0.26
e. Sulfur (S)	(%)	0.09	0.09	0.09	0.08	0.06
f. Ash	(%)	19.11	18.05	16.37	14.35	10.02

3.2. Thermal degradation of pyrolysis

The pyrolysis result of RH, PB, R₉P₁, R₇P₃, and R₅P₅ can be seen the TGA curve, which was obtained using the *Sma4Win* software as shown in Fig. 1. The pyrolysis process for RH occurs at temperatures from 40°C - 100°C for dehydration process (DP) and 250°C - 390°C for (TD process), whereas PB occurs at a temperature range from 380°C - 500°C and 620°C - 680°C without the DP because PB is a non-polar material. Meanwhile, for the pyrolysis process of R₉P₁, R₇P₃, and R₅P₅, the TD occurs at temperatures from 40°C - 100°C, 250°C - 390°C, 400°C - 510°C, and 580°C - 680°C.

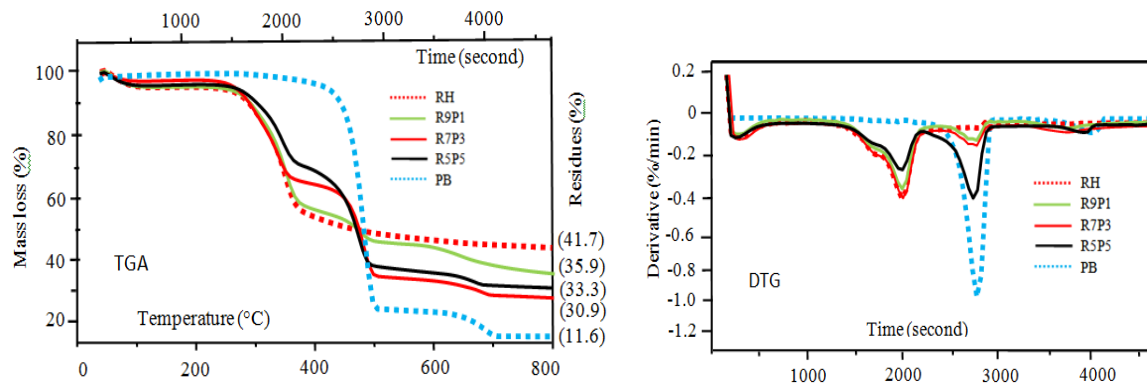


Figure 1. TGA and DTG curve of RH, R₉P₁, R₇P₃, R₅P₅, and PB for pyrolysis at heating rate of 10°C/min, temperatures range of 30°C - 800°C, and nitrogen flow rate of 50 ml/min.

Table 2 shows the pyrolysis process of RH in DP occurs in the temperature range of 40°C - 100°C with a mass loss (ML) of about 5.5%. The TD process zone 1 (TDZ 1) occurs in the temperature range of 250°C - 390°C with ML of about 52.8%, which is volatile to produce energy. Thus, the remaining mass of the char residue is approximately 41.7%. The pyrolysis process of R₉P₁, R₇P₃, and R₅P₅ in zone 1 showed the TD occurs in the temperature range of 250°C - 390°C with a ML of about 42.5%, 35.8% and 27.6% (respectively), which is volatile to produce energy. This is in contrast to the TDZ 2, where mass loss (energy released) of R₉P₁, R₇P₃, and R₅P₅ becomes greater with the increase in percentage of PB in to RH i.e. about 11.4%, 22% and 31.4%, respectively and occurs in the temperature range from 420°C - 510°C.

Table 2. The parameter results of kinetic study for pyrolysis.

Fuels	SM (mg)	DP		TDZ 1		TDZ 2		TDZ 3		Char residues (%)
		ML (%)	T (°C)	ML (%)	T (°C)	ML (%)	T (°C)	ML (%)	T (°C)	
RH	5.6	5.5	40 - 100	52.8	250 - 380	-	-	-	-	41.7
R ₉ P ₁	5.4	4.8	40 - 100	42.5	250 - 390	11.4	420 - 490	5.2	580 - 680	35.9
R ₇ P ₃	5.5	4.5	40 - 100	35.8	260 - 390	22.0	420 - 510	4.4	600 - 660	33.3
R ₅ P ₅	5.4	4.4	40 - 100	27.6	260 - 370	31.4	400 - 500	5.7	600 - 670	32.9
PB	5.6	-	-	79.7	380 - 500	8.8	620 - 680	-	-	11.6

The TDZ 3 occurs in the temperature from 580°C - 680°C with mass loss of about 5.2%, 4.4%, and 5.7%, respectively. Similarly, the TDZ 3 occurs for R₉P₁, R₇P₃, and R₅P₅ in the temperature range of 580°C - 680°C, 600°C - 660°C, 600°C - 670°C, with mass loss of 5.2%, 4.4%, and 5.7%, respectively. In total, the pyrolysis of R₉P₁, R₇P₃, and R₅P₅ where ML occurs about 64.1%, 66.7%, and 67.1%; therefore, the char residues generated is about 35.9%, 33.3%, 32.9%, respectively. This shows smaller

ash content with the increasing percentage of PB in the fuel. These characteristics indicate that the use of R₉P₁, R₇P₃, and R₅P₅ as fuels requires minimum temperatures of 680°C.

3.3. Kinetic parameters analysis

The linear regression of the Arrhenius equation of pyrolysis for RH, R₉P₁, R₇P₃, R₅P₅, PB at every stage of TD was obtained using Microsoft Excel. Based on the TD occurred at temperatures from 250°C - 390°C was obtained $E_{a1} = 57.01$ kJ/mol based on the linear regression equation: $y_1 = 6857x + 2.144$, $R^2 = 0.99$. The linear regression curve of R₉P₁ is presented in figure 2 (a). By the same method, the linear regression equation and E_a according to Arrhenius can be obtained for R₇P₃ and R₅P₅ as shown in Figs. 2B and 2C. Similarly, the linear regression curve for RH and PB can be obtained by the same method.

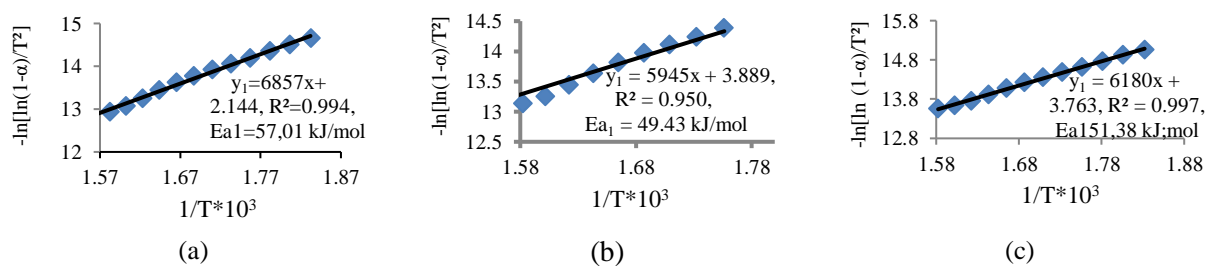


Figure 2. The linear regression curve of (a) R₉P₁, (b) R₇P₃, and (c) R₅P₅ for pyrolysis.

Based on the analysis of kinetic studies, the determination of E_a for each TD was conducted based on the linear regression equation. The value of R^2 shows the relationship between variables x and y . The linear regression equation can be used to determine the value of E_a when $R^2 > 0.9$. The results of PB pyrolysis gave E_a of about 255.5 kJ/mol, which is relatively large if compared with the E_a of RH, which is only 52 kJ/mol. The PB addition of approximately 10%, 30% and 50% into RH improve the E_a of R₉P₁, R₇P₃, and R₅P₅. The linear regression equation, E_a value in pyrolysis process for RH, R₉P₁, R₇P₃, and R₅P₅, PB is presented in table 3.

Table 3. Linear regression of Arrhenius function and activation energy for pyrolysis.

Fuels	TD (°C)	A	Linier regression	(R ²)	Ea (kJ/mol)			
					Ea ₁	Ea ₂	Ea ₃	Total
RH	250 – 380	0.11-0.79	$y_1 = 6934x + 1.763$	0.99	57.7	-	-	57.7
R ₉ P ₁	250 – 390	0.12-0.65	$y_1 = 6857x + 2.144$	0.99	57.1	-	-	-
	420 – 490	0.72-0.85	$y_2 = 1889x + 10.22$	0.91	-	15.7	-	-
	580 - 680	0.80-0.97	$y_3 = 1908x + 10.62$	0.96	-	-	15.9	88.6
R ₇ P ₃	260 – 390	0.14-0.60	$y_1 = 5945x + 3.889$	0.95	49.4	-	-	-
	420 – 510	0.64-0.92	$y_2 = 5194x + 5.728$	0.92	-	43.2	-	-
	600 - 660	0.95-0.98	$y_3 = 1870x + 10.35$	0.93	-	-	15.6	108.2
R ₅ P ₅	260 – 370	0.08-0.4	$y_1 = 6180x + 3.763$	0.99	51.4	-	-	-
	400 – 500	0.50-0.83	$y_2 = 7127x + 3.293$	0.91	-	59.3	-	-
	600 – 670	0.93-0.98	$y_3 = 4695x + 7.394$	0.93	-	-	39.0	149.7
PB	380 – 500	0.01-0.87	$y_1 = 25430x - 20.44$	0.99	211.4	-	-	-
	620 – 680	0.92-0.97	$y_2 = 5296x + 6.935$	0.97	-	44.1	-	255.5

Based on data analysis, the pyrolysis process showed greater content of plastic in the sample, produces a large and increasing the E_a and the residues were getting smaller. This is due to plastic has a CV and VM are large with a small ash residue.

4. Conclusion

Pyrolysis characteristics of RH with PB shows an increase in activation energy, calorific value, volatile matter, and carbon content. On the contrary, ash, nitrogen, sulfur, and moisture show a decrease. The addition of PB into RH increases the activation energy and calorific value of R₉P₁, R₇P₃, and R₅P₅, and reduced char residues, significantly. Pyrolysis results of RH and PB showed improve the thermal characteristics of the RH for improving the performance, resulting in large energy release and lowers the ash residue. Pyrolysis results of RH and PB show feasibility in the implementation as an alternative energy source as fuel in power generation.

5. Acknowledgement

The authors would like also to thank the Ministry of Higher Education of Republic of Indonesia, which has provided funding for research and development in Indonesia.

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