

Thermogravimetric and Kinetic Analysis of Cassava Starch Based Bioplastic

Nanang Eko Wahyuningtiyas^{1,2}, Heru Suryanto^{3*}, Eddy Rudyanto⁴, Sukarni Sukarni⁵, and Poppy Puspitasari⁶

¹ Environmentalist, Samarinda, East Borneo, Indonesia

^{2,3,4,5,6} Department of Mechanical Engineering, Faculty of Engineering, Universitas Negeri Malang
heru.suryanto.ft@um.ac.id

ABSTRACT

Cassava starch based bioplastic for packaging application has great potency because of the various starch-producing plants in Indonesia. Bioplastic can contribute to reduce the dependence on fossil fuels and petroleum that can solve the environmental problem. The purpose of this research is to find out the thermal decomposition and the activation energy of cassava starch based bioplastic. The methods were synthesis bioplastic with cassava starch as main component and glycerol as plasticizer. The thermogravimetry analysis was conducted to obtain the decomposition process mechanism of bioplastic and the heating value of bioplastic was measured using the adiabatic bomb calorimetric. Data analysis was conducted using a fitting model approach with an acikalin method to determine the activation energy. The result of the thermogravimetric analysis showed that bioplastic is gradually decomposed to the moisture, volatile matter, fixed carbon, and ash in four stages mechanism. Totally decomposition of bioplastic was 530°C, then all of bioplastic was become the ash. The activation energy in the early and primary thermal decomposition stages are 1.27 kJ/mol and 22.62 kJ/mol, respectively and heating value of bioplastic is 15.16 MJ/kg.

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Keywords: Activation energy, Bioplastic, Cassava starch, Decomposition, Kinetic analysis, Thermogravimetric

I. Introduction

The synthetic plastic is made of petroleum, coal and natural gas [1]. Plastic waste poses a risk to the human health and the environment [2]. Indonesia is one of the second largest plastic waste donors in the world after China [3]. Waste plastic has become an environmental problem around the world [4] because it takes a long time to be degraded [5][6] and take 50 years to be degraded in nature [7]. Bioplastic can help to reduce the problem of plastic waste, because of easy to make it, abundant and affordable raw materials [8][9][10]. It is categorized to environmental friendly [11] and able to be degraded by the activity of microorganisms by 10 to 20 times faster than the conventional plastic resulting in carbon dioxide, methane, water, biomass, humus and other natural substances from the sources of compounds in plants, such as starch, cellulose, and lignin [5][12][13].

The number of bioplastics produced in a worldwide is less than 200.000 tons per year, a smaller number when compared to 30 million tons of petroleum-based plastic [1]. However, in 2020, the utilization of bioplastic is predicted to reach at least 10%-30% of the global plastics industry [14]. The potential of cassava starch as bioplastic material is great since Indonesia has high cassava production, the third largest in the world [15]. The potential of cassava starch as an environmentally friendly plastic materials is very large because Indonesia is the third largest producer of cassava in the world with cassava products reached 26 million tons in 2014 [16]. The use of fossil fuels will lead to global warming [17][18] because of the fossil-made plastic release about 2900 kg/tons of CO₂ [19]. Imperfect process in the incineration also produces the harmful gases, such as SO₂, CO, NO_x, NO, N₂O, HCl, and HF [20]. Bioplastic offers a solution in reducing the dependence on fossil fuels that have an adverse impact on the sustainable environment [2]. The incineration of bioplastic will produce CO₂ [21], but lower than synthetic plastic because of the raw material (starch) is more environmental friendly. Thus, this paper explores the thermal decomposition of cassava starch based bioplastic using the thermogravimetric and kinetic analysis



II. Material and method

A. Material

The research material was the cassava starch from Malang, East Java, Indonesia. The glycerol in technical grade with concentration of 98% used as the plasticizer, provided by CV. Makmur Sejati, Malang, Indonesia.

B. Synthesis of Bioplastic

The synthesis of bioplastic refers to Wahyuningtyas and Suryanto[6], through the process of mixing the cassava starch with glycerol. The cassava starch 5% (b/v) was mixed with water/aquadest of 98.5 ml, then were stirred on a magnetic stirrer at 900 rpm for 5 min. Next, glycerol at concentrations of 1.5% (v/v), was added to each solution, and then the solutions were re-stirred for 5 min at 900 rpm. The solutions were heated on a magnetic stirrer at 80°C while being stirred with a magnetic stirrer at 900 rpm for 45 min. Each stirred solutions were casted into a mold 88 mm in diameter, then dried in an oven for 24 hours at 70°C, and finally placed at ambient temperature (27-30°C) then kept in a desiccator.

C. Thermogravimetry analysis

The thermogravimetry analysis refers to ASTM E1131 [22]. Thermal decomposition of bioplastic was analyzed using a thermogravimetry (Mettler Toledo TGA/DSC1 simultaneous analyzer). The 10 mg sample was heated from 30°C to 800°C with a heating rate of 10°C/min in the presence of air with a flow rate of 50 mL/min. The thermogravimetric (TG), derivative thermogravimetric (DTG) can identify the thermal decomposition that occurs in bioplastic through the loss of weight.

D. Kinetic Reaction

The kinetic reaction of thermal decomposition of bioplastic can be analyzed using the thermogravimetric method. The kinetic reaction behavior was obtained from the loss of mass towards the temperature. The activation energy (E) of bioplastic was calculated by using the kinetic calculation of Arrhenius method according to Acikalin. The following reaction scheme can illustrate the combustion of biomass:

The fraction of biomass combustion (or conversion) α , is defined as follows:

$$\alpha = \frac{(m_0 - m_t)}{(m_0 - m_f)} \quad (1)$$

Where m_0 , m_t and m_f refer to the initial mass of biomass, the final value of time t and mass m at the end of the combustion, respectively. The degree of combustion, $d\alpha/dt$, is a linear function of constantly determined temperature (k), and reaction model (sample temperature conversion function), $f(\alpha)$:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

Replace the constant rate (k) using the Arrhenius equation, and enter the heating rate ($\beta = dT/dt$) in the non-isothermal case, so that equation 2 will be:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{\left(-\frac{E}{RT}\right)} f(\alpha) \quad (3)$$

Where A is the pre-exponential factor, R is constant gas (8.314 J oK mol⁻¹), E is activation energy, β , and T is a constant temperature. Determine the value of n to derive equation 3, so that equation 4 will be:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} e^{\left(-\frac{E}{RT}\right)} dT \quad (4)$$

Equation 4 is the expression used as the basic model in the calculation method for kinetic analyses of TG data. The activation energy and the pre-exponential factor of each active combustion stage are calculated from the corresponding slope ($-E/R$) and the interception of each final plot ($\ln(A/\beta)$), respectively.

E. Heating value

The heating value of bioplastic was conducted by using IKA type C2000 basic adiabatic bomb calorimetric. The sample about 0.25 g was heated from a temperature of 25°C to 270°C was applied for 15 min with 75% moisture and an oxygen pressure of ± 30 bars. The heating value obtained from the process of the device is J/g unit, by the standard of ASTM D 240. The heating value is calculated by using the measurement of the temperature of the water which increases due to heat. The bioplastic samples were wrapped in paper and burned in the bomb calorimetric. The heating value of the paper wrap without bioplastic was also measured to subtract the heat value of the paper-wrapped bioplastic sample so that the heating value of the bioplastic was obtained from the subtraction. The heating value of solid bioplastic can be determined by using bomb calorimetric.

III. Results and discussion.

A. Thermogravimetry analysis

Thermogravimetric analysis is a method used to study the reaction of thermal decomposition [24] between weight change and temperature [25] which are lost due to the effect of temperature on the material. The result of the thermal analysis is in the form of a curve called a thermogram. Thermal decomposition is a process of changing the form of a sample into a simpler form [26] which is influenced by many factors such as temperature, heating rate, pressure, moisture, residence time, particle size, and material composition [27].

Thermal decomposition involves changes in the weight of the polymer [28]. The thermal decomposition of the polymer refers to an increase in temperature that either has or has not experienced any chemical changes and also serves to find out various chemical mechanisms which experience the underlying structural changes, polymer morphology effect, additive reaction path and filler interaction [29]. The mechanism of the thermal decomposition of starch based bioplastic is shown in Fig. 1.

Stage 1 is the reduction weight caused by the release of moisture or water until 10.7% that occurred at 30°-130°C for 12 min. In this stage, the very light volatile matter compounds also lost [26] and the initial stage of the thermal decomposition process occurs due to evaporation of the water [30].

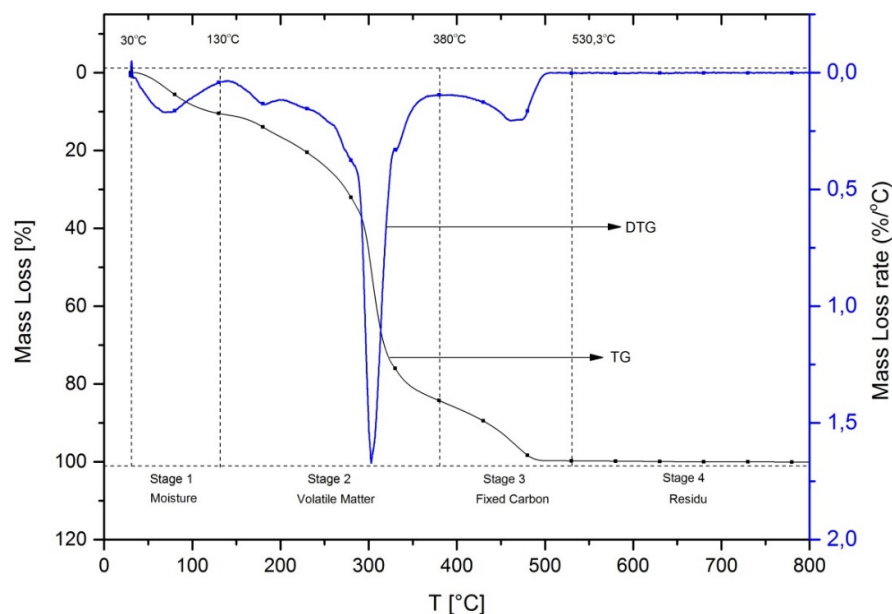


Fig. 1. TG-DTG curve of bioplastic

Stage 2 is the process of releasing volatile matter that occurred at 130°C-380°C for 25 min. This stage is the main thermal decomposition stage because a high level of material lost (69.10% b/b) since cassava starch contains amylose particles which can form carbohydrate lipids: carbon, hydrogen, and oxygen in the volatile cassava starch [31][32]. Cassava starch starts to decompose thermally at the temperature of 300°C [33]. The process of this stage triggers the rapid thermal decomposition with a large mass loss [34] and runs rapidly due to the considerable amount of oxygen.

Stage 3 is the stage after the release of volatile matter in the samples occurred at the temperature of 380°C–530°C for 16 min. The fixed carbon content of bioplastic was relatively low, i.e., 20.17% (b/b). In this stage, the charcoal is flammable as it is surrounded by volatile matter and oxygen diffused on the surface of the charcoal, which burn the charcoal and volatile matter simultaneously. This stage occurs after the release of volatile matter which leaves or forms carbon [35].

Stage 4 is the last stage of the thermal decomposition process in bioplastic that occurred at 530°C-800°C for 23 min. This process does not produce ash, since it has been fully decomposed in the thermal decomposition process shown in the TG-DTG graphic of the low thermal decomposition reaction, since the residue of the charcoal is surrounded by the combustion ash marked by the flat TG graph in Fig. 1, thus indicating the slowly confined mass.

Acikalinmethod

This research used a fitting model approach. The fitting model is a kinetic method which involves a single heating rate [36]. The Acikalin method is used for determining the activation energy in this study. The final equation of the Arrhenius method can be obtained by using the logarithm of Eq. 4 and makes some rearrangement as follows [37]:

$$\ln\left(\frac{d\alpha}{dT}\right) - n \ln(1 - \alpha) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \quad (5)$$

Where:

$$\frac{d\alpha}{dT} = \frac{\alpha_{T_2} - \alpha_{T_1}}{T_2 - T_1} \quad (6)$$

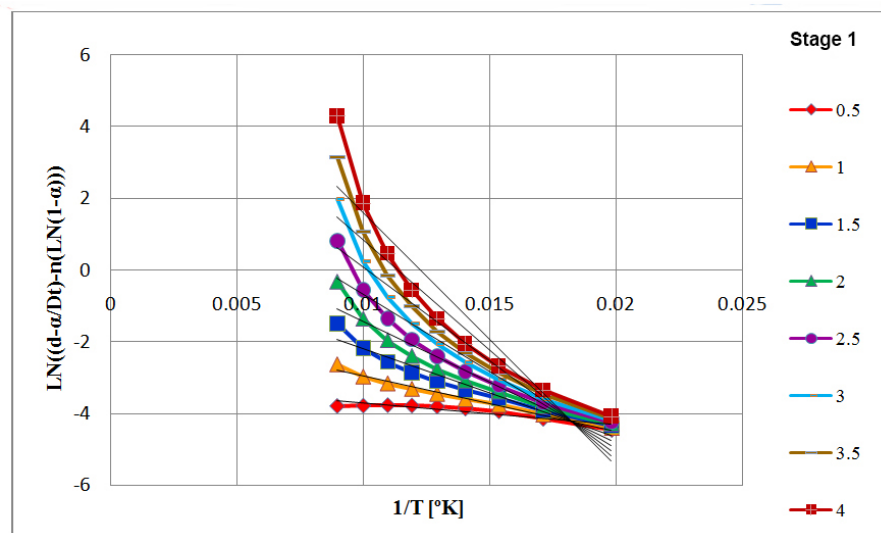


Fig. 2. Curve of stage I plot $\ln(d\alpha/dT) - n \ln(1 - \alpha)$ vs $(1/T)$

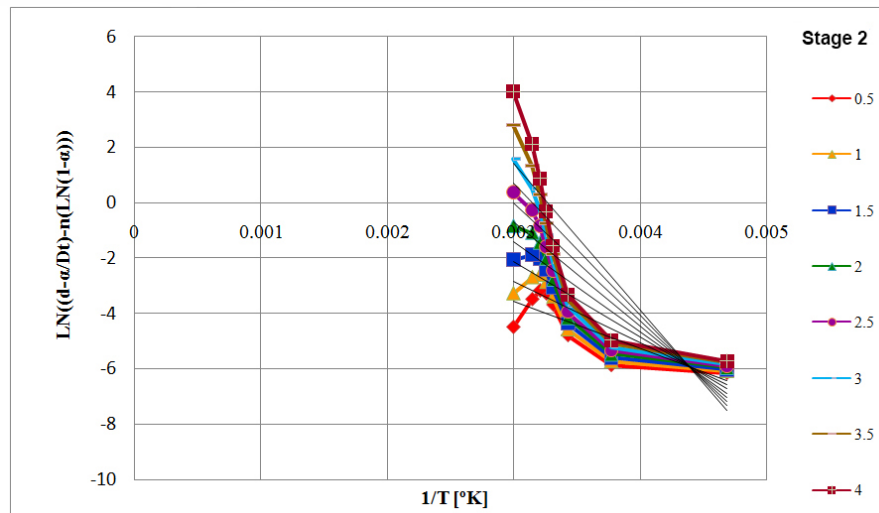
Fig. 3. Curve of stage 2 plot $\ln((d\alpha/dT) - n \ln(1 - \alpha))$ vs $(1/T)$

Table 1. The parameter values in Arrhenius Acikalin formula

Stage	β /oC min-	E/kJ mol-1	R2	N	Plot equation
1	10	1.26954	0.982	1.0	-152.7x - 1.429
2	10	22.62239	0.768	1.5	-2721.x + 6.027

According to Eq. 5, plot $\ln((d\alpha/dT) - n \ln(1 - \alpha))$ vs $(1/T)$ results in a straight line (slope) to determine the value of reaction order (n) (Fig. 3 and Fig. 2). In order to determine the suited n value in the active combustion stage, several n values were selected, the plot was drawn, and the related correlation coefficient (R2) was calculated to generate the R2 curves vs. n.

The highest R2 value ensures the most appropriate n value to determine the curve of all decomposition levels studied from the n value and had the final plot drawn. The activation energy and the pre-exponential factor of each active combustion stage were calculated from the related slope $(-E/R)$ and interceptions $(\ln(A/\beta))$ of each final plot. The results obtained by the Arrhenius method on the final plot are shown in Table 1.

$$E = \text{Slope} \times R \quad (7)$$

Kinetics is a science that discusses the rate and reaction mechanism [38]. According to Arrhenius, activation energy is the minimum energy required to start a chemical reaction (combustion). There are two ways to convert bioplastic into energy (heat), thermochemically and biochemically or biologically [17]. The conversion of bioplastic into thermochemical energy can be performed by pyrolysis, gasification, and combustion [39]. This research used combustion method. The combustion process is the process in which the combustion process occurs due to a reaction of bioplastic and oxygen to convert the solid bioplastic into the energy [38].

The activation energy determination using Flynn-Wall-Ozawa (FWO) method for cassava starch, banana starch, and potato starch was 188.0 kJ/mol, 199.3 kJ/mol, and 203.60 kJ/mol, respectively. The activation energy determination using Coats-Redfern methods for cassava starch, banana starch, and potato starch is 188.3 kJ/mol, 200.2 kJ/mol, and 204.8 kJ/mol, respectively [40]. It shows that the activation energy of cassava starch is low. It possibly caused by the long polymer chains and the increased polymerization, because amylose content [40] can form carbohydrate lipids: carbon, hydrogen, and oxygen in the volatile starch [41][32] in the volatile matter process. The amylose content in cassava starch is higher for 24.3% ([42] than in banana starch for 18.33% and potato starch for 16.88% [43].

The cassava starch has the lowest activation energy compared to banana and potato starch. The higher activation energy will reduce the reaction rate [44] as it will be harder to start the combustion

reaction process. The low activation energy of 1.27 kJ/mol on stage 1 indicates the weak bonds between volatile materials and polymers (bioplastic) [45]. In stage 2, it takes a higher energy of 22.62 kJ/mol and a long time for 25 min to thermally decompose the carbohydrate particles.

Table 3 indicates that the bioplastic is easy to decompose with activation energy of 22.62 kJ/mol. This activation energy is higher than the activation energy of plastic poly-lactic acid (PLA) (11.2 kJ/mol) [46][47] but lower than an inorganic plastic waste such as PE (248.0 kJ/mol), PP (183.8 kJ/mol), PS (172.0 kJ/mol), HDPE (233.2 kJ/mol), LDPE (206.4 kJ/mol), PVC (190 kJ/mol) [48] and the types of coal like brown coal (39.15 kJ/mol), low coal (73.96 kJ/mol) [49], anthracite (40.43 kJ/mol), lignite (28.60 kJ/mol) [50], and bituminous (36.18 kJ/mol) [51]. The higher activation energy value causes the slow and harder to initiate the combustion reaction [44][52].

The heating value

The heating value is the energy released per unit mass of a material or when the material is fully combusted or burned. The heating value obtained using the calorimetric bomb experiment [23]. The heating value of bioplastic is indicated by HHV (Higher Heating Value) [53] and the heating value of materials are listed in the Table 2.

The heating value of a substance is influenced by the composition of the substance contained in the sample [60]. As shown in the thermogravimetric test result (Fig. 1), it shows that almost bioplastic is fully combusted in the volatile matter process that contains a high level of carbohydrates results in the higher heating value or energy contained [61]. The samples with low ash content are perfect specimens because they reduce the exhaust emissions [62].

The heating value test of bioplastic sample is 15.16 MJ/kg (Table 2). The heating value of bioplastic is relative same with the Polyvinyl Chloride (PVC) with HHV of 18.00 MJ/kg [54]. The heating value of bioplastic is also higher than four types of coal: bituminous coal Spanish, lignite coal Germany, anthracite Spanish, and peat Swedish with HHV of 7.55 MJ/kg, 9.00 MJ/kg, 7.97 MJ/kg, and 12.66 MJ/kg, respectively [56]. The heating value of bioplastic is also higher than of food waste, husk, textiles, and paper with HHV of 4.00 MJ/kg, 15.00 MJ/kg [55], 15.02 MJ/kg [63], 15.02 MJ/kg [57], respectively.

Table 2. Heating value from a variety of materials

Sample	Heating value (MJ/kg)	References
Bioplastic cassava starch	15.16	This study
Polyvinyl Chloride (PVC)	18.00	[54]
Polypropylene (PP)	46.40	[54]
Polyethylene (PE)	46.30	[54]
Polystyrene (PS)	41.40	[54]
Food waste	4.00	[55]
Rice husk	15.00	[55]
Textiles	15.02	[56]
Bituminous coal Spanish	7.55	[56]
Lignite coal Germany	9.00	[56]
Anthracite Spanish	7.97	[56]
Peat Swedish	12.66	[56]
Corn stalks	18.48	[57]
Wood	18.42	[58]
Straw	15.61	[59]

IV. Conclusion.

The cassava starch based bioplastic was thermally decomposed in four stages mechanism and, has an activation energy at the initial and main thermal decomposition stages of 1.27 kJ/mol and 22.62 kJ/mol, respectively. Thus, the heating value of bioplastic obtained in the heat test for 15.16 MJ/kg. The bioplastic can be thermally degraded as easy as the synthetic plastic.

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