Thermal Characteristics of Geopolymer from Co-combustion Residuals of Bamboo and Kaolin

A Purbasari¹, T W Samadhi², Y Bindar², and W Wulandari²

¹ Department of Chemical Engineering, Diponegoro University
Jl. Prof. Soedarto, Kampus Tembalang, Semarang 50275, Indonesia
² Chemical Engineering Program, Bandung Institute of Technology
Jl. Ganesha No. 10, Bandung 40132, Indonesia

Email: aprilina.purbasari@che.undip.ac.id

Abstract. Geopolymer, inorganic polymer with Si-O-Al bonds, can be utilized as Portland cement substitute. Resistance to fire or high temperature is one of the characteristics that should be possessed by building materials. In this paper, the behaviour of geopolymer from co-combustion residuals of bamboo and kaolin when exposed to high temperature was studied from thermogravimetric, derivative thermogravimetric, and differential scanning calorimetry analysis. The result showed that geopolymer from co-combustion residuals of bamboo and kaolin underwent dehydration, densification by viscous sintering, and further densification processes with mass loss of 19.5 % after exposure to temperature of 1000 °C.

1. Introduction
Geopolymer is inorganic polymer with Si-O-Al bonds derived from material containing alumino-silicate oxide and solution of alkali hydroxide/silicate as activator at temperature below 100 °C. Empirical formula of geopolymer is Mn(-(SiO₂)z-AlO₂)n.wH₂O, where: M=Na+/K+ cation; z=1,2,3; n=degree of polycondensation. Geopolymer has an amorphous to semi-crystalline three-dimensional structure and can be used as cement, encapsulation of hazardous chemicals or radioactive wastes, heat/fire resistant composites, and other purposes [1]. Geopolymer has potential as cement or construction material with lower carbon footprint. Application of geopolymer as cement also has shown higher compressive strength as well as higher acid and fire resistance compared to Portland cement [2].

Geopolymer can be produced from material containing alumino-silicate oxide, i.e. natural minerals (kaolin, metakaolin) and solid wastes (fly ash, slag) [2]. Biomass ash containing high silica such as bamboo ash can be utilized as raw materials for geopolymer production [3]. Bamboo can be used as an energy source because bamboo contains calorific value that comparable to wood [4]. In this paper, bamboo was combusted with kaolin as additives and produced co-combustion residuals containing high silica and alumina [5] that used as geopolymer raw material.
The behaviour of geopolymer from co-combustion residuals of bamboo and kaolin when exposed to high temperature was studied in this paper from thermogravimetric, derivative thermogravimetric, and differential scanning calorimetry analysis, i.e. based on mass loss and heat flow during thermal decomposition and temperature change in relation to a reference during heating. The results would provide information of physical or chemical change occurring in geopolymer when exposed to high temperature that useful for geopolymer application as Portland cement substitute.

2. Methods
Materials used in this study were bamboo (*Gigantochloa apus*), commercial kaolin powder, commercial potassium hydroxide flakes (purity of 90%), and commercial sodium silicate solution (SiO$_2$=30 %, Na$_2$O=9 %, H$_2$O=61 %). Bamboo was obtained in Semarang, Indonesia; while chemicals were obtained in Bandung, Indonesia. Mixture of bamboo and kaolin with weight ratio of 95:5 was combusted first in fixed bed furnace and then in electric furnace at 550 ºC for 3 hours. Co-combustion residuals of bamboo and kaolin mainly contained SiO$_2$ (50.66 %), Al$_2$O$_3$ (30.98 %), and K$_2$O (11.37 %).

Geopolymer paste was prepared from co-combustion residuals and alkaline activators, i.e. mixture of 10 N potassium hydroxide solution and sodium silicate solution with weight ratio of 1:2. Co-combustion residuals were sieved with 100 mesh standard sieve first and then mixed with alkaline activator and stirred for 6 minutes. The weight ratio of alkaline activator to co-combustion residuals was 1:1:1. The mixture was poured into 5 x 5 x 5 cm cubic mould and cured in mould for 24 hours. After geopolymer paste was removed from the mould, geopolymer paste cured in oven at 60 ºC for 8 hours and then at room temperature for 28 days.

Thermal characteristics of geopolymer paste were examined by thermal analysis instrument, namely LINSEIS STA Platinum Series. Sample testing was conducted at room temperature up to 1000 ºC with a heating rate of 10 ºC/min under air atmosphere condition.

Data of mass loss from thermogravimetric analysis can be used to determine mechanism model of decomposition and kinetic parameters for geopolymer using Coats and Redfern equation [6]:

\[
\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\frac{A}{\beta E_a} - \frac{E_a}{R T}.
\]

where: \(g(\alpha)\)=mechanism model function, \(\alpha\)=mass loss fraction, \(T\)=absolute temperature, \(A\)=frequency factor, \(E_a\)=activation energy, \(\beta\)=heating rate, and \(R\)=gas constant. Solid state rate equations for different mechanism models are shown in table 1 [7]. The plot of (\(\ln(g(\alpha)/T^2)\) versus (1/T) yields linear line. Kinetic parameter, i.e. \(E_a\) (activation energy), can be determined from the slope of the regression equation having the highest R$^2$ value.
### Table 1. Solid state rate equations.

| Mechanism model      | Differential form | Integral form       |
|----------------------|-------------------|---------------------|
| f(α)=(1/k).(dα/dt)   | g(α)=k.t         |                     |

- **Nucleation models**
  - Power law: \(4α^{3/4}\) \(α^{1/4}\)
  - Power law: \(3α^{2/3}\) \(α^{1/3}\)
  - Power law: \(2α^{1/2}\) \(α^{1/2}\)
  - Avrami-Erofeev: \(4(1-α)[−\ln(1−α)]^{3/4}\) \([-\ln(1−α)]^{1/4}\)
  - Avrami-Erofeev: \(3(1-α)[−\ln(1−α)]^{2/3}\) \([-\ln(1−α)]^{1/3}\)
  - Avrami-Erofeev: \(2(1-α)[−\ln(1−α)]^{1/2}\) \([-\ln(1−α)]^{1/2}\)

- **Diffusion models**
  - 1D diffusion: \(1/2α^{-1}\) \(α^2\)
  - Jander diffusion (3D diffusion): \(2(1−α)^{2/3}[1−(1−α)^{1/3}]−1\) \([1−(1−α)^{1/3}]^2\)

- **Order reaction models**
  - Mampel (order 1): \(1−α\) \(-\ln(1−α)\)
  - Order 2: \((1−α)^2\) \((1−α)^{-1}−1\)

- **Geometrical contraction models**
  - Contracting area: \(2(1−α)^{1/2}\) \(1−(1−α)^{1/2}\)
  - Contracting volume: \(3(1−α)^{2/3}\) \(1−(1−α)^{1/3}\)

### 3. Results and Discussion

Geopolymer when exposed to high temperature can undergo dehydration of free water \((100-300 °C)\); dehydroxylation \((250-600 °C)\); densification by viscous sintering \((550-900 °C)\); and crystallization, expansion due to cracking, further densification \(>900 °C)\ [8]. Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric Analysis (DTA) curves of geopolymer paste from co-combustion residuals of bamboo and kaolin are shown in figure 1 and figure 2, respectively.
Geopolymer paste had a mass loss about 19.5 % after heated up to 1000 °C as shown in figure 1. There are three rapid mass loss zones indicated by three downward peaks in figure 2. The first zone having sharp peak (<130 °C) is attributed to water evaporation (dehydration) with mass loss of about 10 %. The second zone (748.2-834.2 °C) and the third zone (852.4-937.5 °C) having small peaks are due to densification by viscous sintering and further densification, respectively. This mass loss is lower than mass loss of geopolymer paste from metakaolin with potassium hydroxide and sodium silicate as activator, i.e. about 30 % when heated up to 800 °C as reported by Kong et al. [9]. Furthermore, mass loss of geopolymer paste is relatively the same as mass loss of aluminate cement paste, i.e. about 20 % after heated up to 1000 °C [10]. Aluminate cement is cement with high alumina content and for high temperature/refractory application [11].
Figure 3. DSC curve of geopolymer paste.

Differential Scanning Calorimetry (DSC) curve of geopolymer paste is shown in figure 3. Upward peaks show exothermic reactions and downward peaks show endothermic reactions. There are three major peaks with endothermic reactions. The first peak centered at 78.2 ºC is the result from dehydration reaction, the second peak centered at 791.4 ºC corresponds to densification by viscous sintering process, and the last peak centered at 889.5 ºC is due to further densification.

Mechanism model and activation energy for each decomposition stage of geopolymer is shown in table 2. All decomposition stages follow first order reaction model. Dehydration process with the lowest activation energy value is the easiest process to occur compared to others. Densification by viscous sintering and further densification require higher temperature and more energy to occur.

| Stage                        | Temperature (ºC) | Mechanism model | R²   | Eₐ (kJ/mol) |
|------------------------------|------------------|-----------------|------|-------------|
| Dehydration                  | 41-122.3         | order 1         | 0.994| 43.59       |
| Densification by viscous sintering | 748.2-834.2    | order 1         | 0.979| 393.48      |
| Further densification         | 852.4-937.5      | order 1         | 0.958| 617.48      |

4. Conclusion
Thermal characteristics of geopolymer from co-combustion residuals of bamboo and kaolin had been studied from thermogravimetric, derivative thermogravimetric, and differential scanning calorimetry analysis. Geopolymer can undergo dehydration at temperature under 130 ºC, densification by viscous sintering at temperature of 748.2-834.2 ºC, and further densification at temperature of 852.4-937.5 ºC. Geopolymer had a mass loss about 19.5 % after heated up to 1000 ºC.
Acknowledgements

The authors are grateful to Laboratory of Mineral and Inorganic Material Technology, Bandung Institute of Technology for providing access to equipment used in this study.

References

[1] Davidovits J 2008 Geopolymer: Chemistry and Applications 2nd ed (Saint-Quentin: Institut Géopolymère)
[2] van Deventer, J S J, Provis, J L and Duxson, P 2012 Miner. Eng. 29 89
[3] Purbasari A, Samadhi T W and Bindar Y 2017 Adv. Sci. Lett. 23(6) 5723
[4] Engler B, Schoenherr S, Zhong Z and Becker G 2012 Int. Journal of Forest Engineering 23(2) 114
[5] Purbasari A, Samadhi T W and Bindar Y 2016 Int. Journal of Renewable Energy Development 5(2) 95
[6] Fischer P E, Jou C S and Gokalgandhi S S 1987 Ind. Eng. Chem. Res. 26(5) 1037
[7] Khawam A and Flanagan D R 2005 Thermochim. Acta. 436 101
[8] van Riessen, A and Rickard, W 2009 Thermal properties of geopolymers Geopolymers: Structure, Processing, Properties and Industrial Applications., ed JL Provis and JSJ van Deventer (Cornwall: Woodhead Publishing Limited and CRC Press LLC) chapter 15 pp 315-342
[9] Kong D L Y, Sanjayan J G and Sagoe-Crentsil K 2007 Cem. Concr. Res. 37 1583
[10] Nithya R, Barathan S, Govindarajan D, Raghu K and Anandhan N 2010 Int. Journal of Chemistry 2(1) 121
[11] Lourenco R R, Angelica R S and Rodrigues J d A 2013 Mat. Res. 16(4) 731