Reaktor, Vol. 14 No. 4, Oktober 2013, Hal. 298-304

ISOTHERMAL PYROLYSIS OF KRAFT PULP MILL SLUDGE

Syamsudin, Herri Susanto*), and Subagjo

Chemical Engineering Department, Industrial Technology Faculty, Institut Teknologi Bandung
Jl. Ganesha 10, Bandung – Indonesia
*)Coresponding author: herri@che.itb.ac.id

Abstract

Kraft pulp mill sludge cake composed of rejected wood fibers and activated sludge microorganisms. With a heating value about 14 MJ/kg (dried basis), this type of biomass had a potential as an alternative energy source. Unfortunately, it had an ash content of 27.6% and a moisture content of 80%. For reducing moisture content with minimum energy consumption, a combination of mechanical dewatering and thermal drying was studied previously. Meanwhile, experiments on isothermal pyrolysis had been carried out for further improvement on ultimate and proximate analysis of solid fuel. Final mass of char obtained from pyrolysis at 500^oC was not significantly different from that of 700^oC, so pyrolysis was considered to be optimum at 500^oC. A char obtained from pyrolysis at temperature of 500^oC had a pore surface area of 77.049 m^2/g (highest among other temperatures). Kinetic of isothermal pyrolysis was well represented with a first order modified volumetric model with a frequency factor of 0.782 1/s and an activation of 34.050 kJ/mol.

Keywords: *first order volumetric model; kinetics of pyrolysis; mechanical dewatering; proximate and ultimate analysis*

Abstrak

PIROLISIS ISOTERMAL LUMPUR KERING PABRIK PULP PROSES KRAFT. *Lumpur pabrik pulp kraft tersusun dari serat terbuang dan mikroorganisme lumpur aktif, Dengan nilai kalor mencapai 14 MJ/kg (dasar kering), lumpur ini seharusnya dapat dimanfaatkan sebagai bahan bakar alternatif. Sayangnya, kadar air lumpur mencapai 80% yang menurunkan nilai kalor. Pengeringan yang efektif dapat dilakukan secara mekanik dan termal. Pengeringan juga dapat dibantu dengan penambahan serbuk batubara pada pengeringan mekanik.Peningkatan sifat bahan selanjutnya telah dilakukan dengan pirolisis untuk mengurangi kadar zat terbang. Hasil arang dari pirolisis pada 500°C tidak jauh berbeda dengan yang 700°C, jadi pirolisis sebaiknya dilakukan pada temperature 500°C saja. Arang hasil pirolisis pada 500°C ini memiliki luas permukaan pori 77,049 m^2/g yang terbaik diantara arang hasil pirolisis pada temperatur lain. Kinetika pirolisis isotermal lumpur dapat dinyatakan dengan model volumetrik termodifikasi order satu dengan faktor frekuensi 0,782 1/detik dan energi akticasi 34,050 kJ/mol.*

Kata kunci: *model volumetrik order satu; kinetika pirolisis isotermal; pengeringan kempa; analisis proksimat dan ultimat.*

INTRODUCTION

Pulp kraft mill is one of industries that consumes great amount of energy. Increasing natural gas price makes pulp industries conserve energy and use alternative renewable energy. One of the potential energy resources in pulp industry is sludge waste. This sludge comes from wastewater treatment. The amount of solid waste that must be treated varies, depending on pulp production and wastewater treatment process. Usually, pulp mill produces about 58 kg sludge/tone pulp (Scott, 1995).

A challenge is to find an innovative and cheap method to treat the sludge with considering environmental issue. Pulp industries have used several methods to treat the sludge. One of them is by sludge dewatering. The dewatered sludge is then burned as fuel, or just incinerated. This method can reduce sludge volume that must be dumped into landfill and recover energy contained in the sludge to fulfill a part of mill's energy demand.

Gasification can produces gaseous fuel, as well as synthesis gas that can be converted further into DME, diesel fuel via Fischer-Tropsch process, and hydrogen gas. Thermodynamics simulation shown that gas fuel from sludge gasification can substitute 18% of natural gas used as fuel in pulp mill's lime kiln

(Syamsudin and Susanto, 2012). Sludge utilization as gasification fuel is based on the fact that sludge has high organic content and high heating value. Unfortunately, sludge cake has a high water content up to 80% (as received). This water content reduces the heating value significantly, and get worse the combustion properties.

Similar to other biomass, sludge cake composes of lignin, cellulose, and hemicellulose. Hemicellulose begin to decompose by heat at 220-315°C with fastest decomposition occured at 270°C. Cellulose is degraded by heat at 315°C, and its maximum decomposition occurs at about 350°C (Yang *et al.*, 2007). Unlike cellulose and hemicellulose with crystalline structures, lignin has amorphous structure and a high thermal stability. Lignin degrades slowly and its degradation temperature can reach 900^{o}C (Yang *et al.*, 2007). Thus, the yield of pyrolysis of sludge cake will depend on the process condition such as: surrounding atmosphere, final temperature, heating rate, pressure, and residence time of volatile matter.

Reducing water content is usually done with thermal drying, but this method is costly. Meanwhile mechanical dewatering has a limit in achieveable water content. Intracellular water in the sludge makes mechanical dewatering more difficult. Special treatment is needed to reduce the effect of intracellular water in dewatering process. An example, sludge mixing with coal powder was investigated and patented to increase the dewatering rate (Qi, 2011). Therefore combination of mechanical dewatering and thermal drying has been considered as a method for getting a dry sludge with minimum energy.

The purpose of this research was to evaluate the effects of: (i) mechanical dewatering on thermal drying; (ii) coal powder addition on dewatering characteristics; (iii) size of sludge briquettes on drying characteristics, and (iv) pyrolysis temperature on char porosity and morphology. The most important research target reported in this paper is the evaluation on the kinetics of isothermal pyrolysis as functions of time and temperature. This data will be very important in designing a pyrolysis process in a gasification unit.

KINETICS MODEL OF ISOTHERMAL PYROLYSIS

Pyrolysis of sludge cake may be expressed as the following lumped reaction:

$$\text{[Sludge Cake]} \xrightarrow{k} \text{[Solid Residue]} + \text{[Volatile Matter]} \quad (1)$$

Under a flowing N_2, the above pyrolysis reaction is considered as irreversible reaction, since the inert gas carries out the volatile matter immediately. Kinetics of pyrolysis may be represented using the following equation (Otero *et al.*, 2008):

$$\frac{d\alpha}{dt} = k\, f(\alpha) \quad (2)$$

Mass loss fraction (α) is defined as:

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (3a)$$

or residual mass ratio :

$$1 - \alpha = \frac{m_o - m_t}{m_o - m_f} = \frac{m_t - m_f}{m_0 - m_f} \quad (3b)$$

with:
t = reaction time
α = mass loss fraction
f(α)=a function of mass loss fraction
m_0 = mass of solid initially
m_t = mass of solid at anytime t
m_f = mass of solid at the end of pyrolysis.

The function of mass loss fraction f(α) may be used to represent a model of reaction hypotheses. Among various proposed models in literature, the first order reaction model, f(α) = (1−α) is the most often used to fits the experimental data satisfactory. Three derivations of this model were used in our study reported in this paper.

First order volumetric model:

$$kt = -\ln(1-\alpha) \quad (4)$$

$$\frac{m_t - m_f}{m_0 - m_f} = e^{-kt} \quad (5)$$

First order volumetric with time lag (θ) model:

$$k(t-\theta) = -\ln(1-\alpha) \quad (6)$$

$$\frac{m_t - m_f}{m_0 - m_f} = e^{k(t-\theta)} \quad (7)$$

First order modified volumetric model, with an exponent to time (β):

$$kt^{\beta} = -\ln(1-\alpha) \quad (8)$$

$$\frac{m_t - m_f}{m_0 - m_f} = e^{-kt^{\beta}} \quad (9)$$

Effect of temperature on reaction rate constant follows to Arrhenius equation:

$$k = A.\, e^{-E/RT} \quad (10)$$

$$\ln k = \ln A - \frac{E}{R.T} \quad (11)$$

with:
A = pre-exponential factor (1/s)
R = universal gas constant (8.314 J/(mol.K))
E = activation energy (J/mol)
T = absolute temperature (K).

Our study dealed with finding out the best with among the above three models and their kinetics parameters.

EXPERIMENTAL SET UP

Sludge cake was obtained from the wastewater treatment plant in a pulp mill in South Sumatera. Sludge cake contained of 55% (v/v) primary sludge and 45% secondary sludge, and a total moisture of 80%-w. Coal powder with a size of 32-60 mesh was used as a filtration aid, and also to get an increase in heating value. The characteristics of the sludge and the coal powder are shown in Table 1.

The scope of our research is shown in Figure 1. Coal powder acts as filtration aid to help dewatering process. The amount of coal powder added to sludge cake were: 0, 5%, 10%, and 20% by weight. Sludge and coal mixture obtained from the mechanical dewatering was in form of wet briquettes. For further evaluation on mass transfer inside the particle, the size of the briquette were varied: (i) loose powder; (ii) briquette with diameter and thickness of 1 cm and 0.5 cm, repectively; and (iii) briquette with diameter and thickness of 1 cm and 1 cm, repectively (Prawiranto *et al*., 2012).

Pyrolysis was carried out under a flowing N_2 with a flowrate of 10 mL/s. Constant temperatures were applied during pyrolysis, i.e.: 300, 350, 400, 500, and 700°C. Oven dried sample was loaded into a stainless steel basket. Sample and basket then was inserted into the preheated furnace upto a specified temperature. The amount of dried sludge cake for pyrolysis experiment was about 10 gram. The mass loss as a function of time was used for kinetic analysis. Characterization of samples included proximate analysis and ultimate analysis. Pore characteristics were analysed with BET method by using Nova 1000 Quantachrome Co, at degassing temperature of 200°C for sludge and 300°C for char.

Table 1. Characteristics of sludge cake and coal powder

No.	Analysis	Sludge Cake	Coal Powder
1.	Proximate (dry basis):		
	Ash	27.60%	2.77%
	Volatile matter	61.00%	48.80%
	Fixed carbon	11.40%	48.44%
2.	Ultimate (dry basis):		
	Carbon	34.54%	70.64%
	Hydrogen	4.29%	4.45%
	Nitrogen	1.18%	0.94%
	Total sulfur	0.36%	0.00%
	Oxygen	32.03%	21.21%
3.	Organic Compound:		
	Cellulose	49.16%	-
	Hemicellulose	6.15%	-
	Lignin	14.15%	-
4.	Heating value (db)	13.25 MJ/kg	27.94 MJ/kg

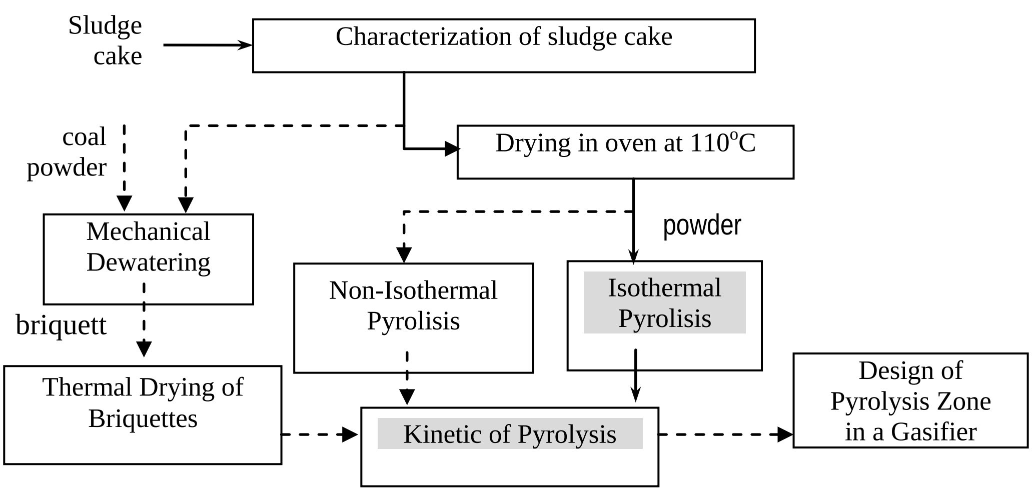


Figure 1. Scope of research on sludge cake gasification

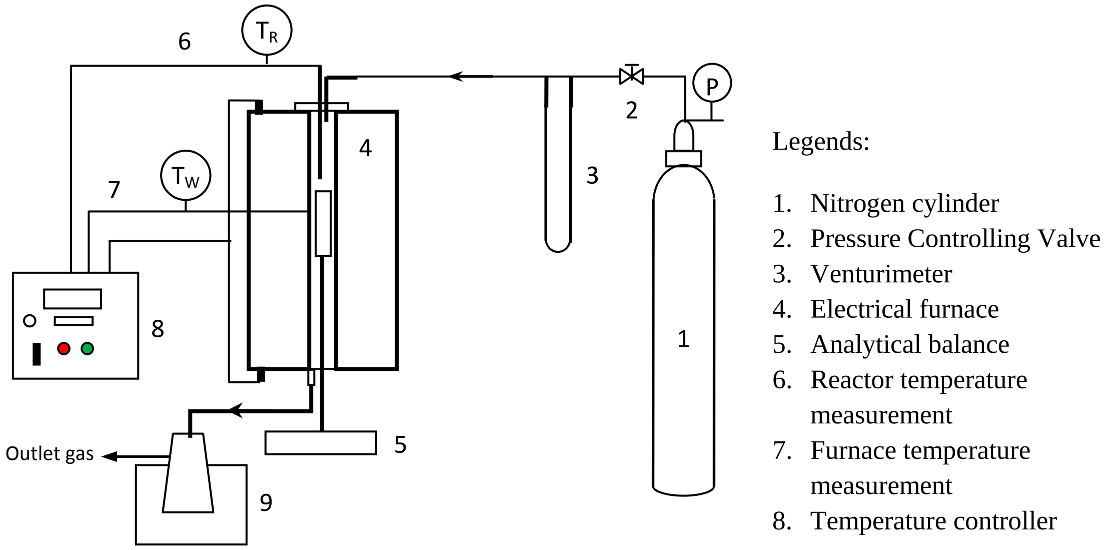
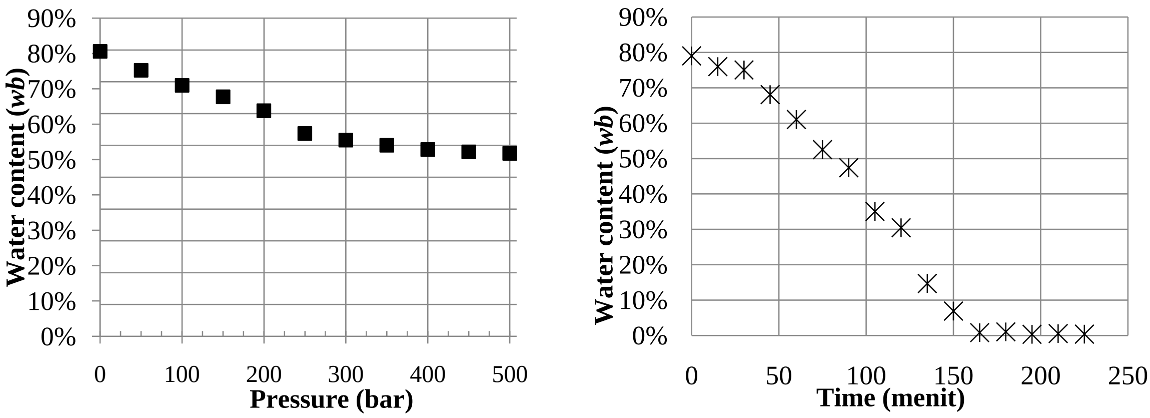


Figure 2. Experimental equipment



(a) Mechanical dewatering (b) Thermal drying at 110°C.

Figure 3. Comparison of mechanical dewatering and thermal drying of sludge cake (Prawiranto *et al*., 2012)

RESULTS AND DISCUSSIONS

Mechanical dewatering could reduced the moisture content from 80% to about 53% depending on pressure applied during compression. A moisture content in dewatered sludge of about 53% was probably the intracellular water, and effect of pressure was not significant above 300 bar.

As expected, the use of coal powder as a filtration aid was found to increase the dewaterability resulted a lower final water content. Mechanical dewatering with a compression of 50 bar could reduce the water content to 72%, but adding coal of 20% could further reduce the water content to 61%. Mechanical dewatering with a compression of 400 bar with the addition of 20% coal could reduce the water content down to 37%. Since the mechanical dewatering resulted a moisture content of 53%. An optimum combination for drying with short time and minimum energy consumption was the mechanical dewatering of 300 bar to get a moisture content of 73% and then thermal drying at 100°C to a desired moisture content (Prawiranto *et al*., 2012).

Effects of pyrolysis temperature on the final mass of char (solid residue) and the rate of mass loss (rate of pyrolysis) were clearly observed (see Figure 4, and note that mass of solid was presented in ash free basis). The higher temperatures, the rates of mass loss were faster. Time lags of mass loss were observed significantly for pyrolysis at 300, 350 and 400°C (time between 1 to 2 minutes, see Figure 4.a). It was also observed less significantly for pyrolysis at 500°C, but not for 700°C. This phenomenon was understandable as particle heating up period when a sample was introduced directly into the desired temperatures (typically happen in a fluidized bed reactor). For pyrolysis at temperature 700°C, heating up of particle would be shorter. In this condition, particle might undergo rapid pyrolysis.

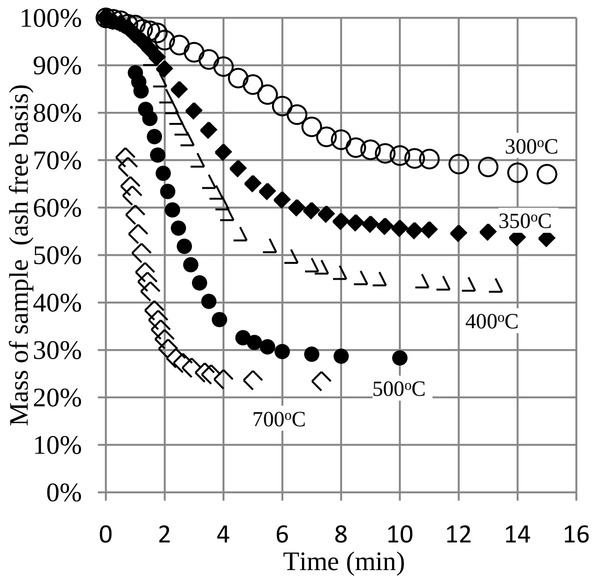
The higher pyrolysis temperature, less char yields were obtained. Exception, final char yields from pyrolysis at 500 and 700°C were more or less the same. Further evaluation on residual mass as a function of time for pyrolysis at 500 and 700°C indicated that these pyrolysis finished after 7 and 5 minutes, respectively. A conclusion might be drawn that pyrolysis at 500°C, thermal degradations of sludge components were completed already: hemicellulose at 225-325°C, cellulose at 325-375°C and lignin at 250-500°C. If the sorrounding atmosphere contained H_2O (residual or intracellular moisture), steam gasification of char probably also took place and contributed to the mass loss (Yip *et al*., 2007).

Evaluation on the kinetic of pyrolysis was based on mass loss ratio (Equation 3a or 3b). Based on this definition, the progress of pyrolysis would start at a mass loss ratio of 1 and terminated at 0 (see Figure 5; derived from Figure 4). The first order modified volumetric model (Equations 8 and 9) seemed to fit the experimental data much better than the other two models (Equations 4 and 5; Equations 6 and 7). Even the first order modified volumetric model could represent the observed time lag better than the first order volumetric with time lag model (Equations 6 and 7).

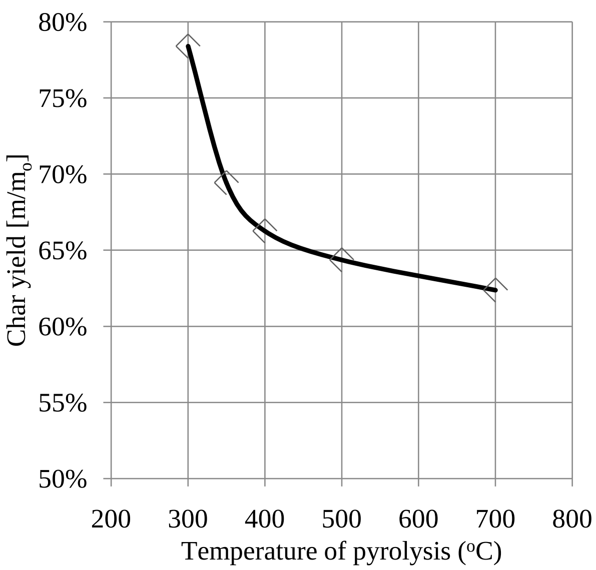
Having experimental data at 300, 350, 400, 500 and 700°C, kinetic parameters of the first order modified volumetric model has been found (see Figure 6): A= 0.782 1/s and E = 34.050 kJ/mol. These value weres different to the value reported by Chao for pyrolysis of sludge from petrochemical wastewater treatment: A = 0.096 1/s and E = 20 kJ/mol (Chao *et al*., 2002).

Since the volatile matters evolved during pyrolysis, the concentration of ash in the solid residue increased (see proximate analysis in Table 2, and also Table 1). Presented in moisture and ash free basis, carbon content of char was very high. Even pyrolysis at a low temperature of 400°C produced char already with a higher carbon content than coal (Table 2). Based on van Krevelen diagram, these mole ratios of H/C and O/C also indicated that chars had a characteristic close to lignite. Unfortunately the ash content in char was too high, because sludge cake from a kraft pulp mill contained much ash mainly natrium salt. With respect to the high ash content, char might gave a problem in gasification.

Although char had a high ash content, it had larger pore surface area and volume than the original sludge cake (see BET measurement in Table 2). Thus the pore properties were still affected by devolatilization of organic compounds instead of the present of ash. Having a large pore surface area and volume, char might had a better reactivity in gasification process.



a. Progress in pyrolysis at various temperature



b. Final char yield as a function of temperature

Figure 4. Char yield as functions of time and temperature

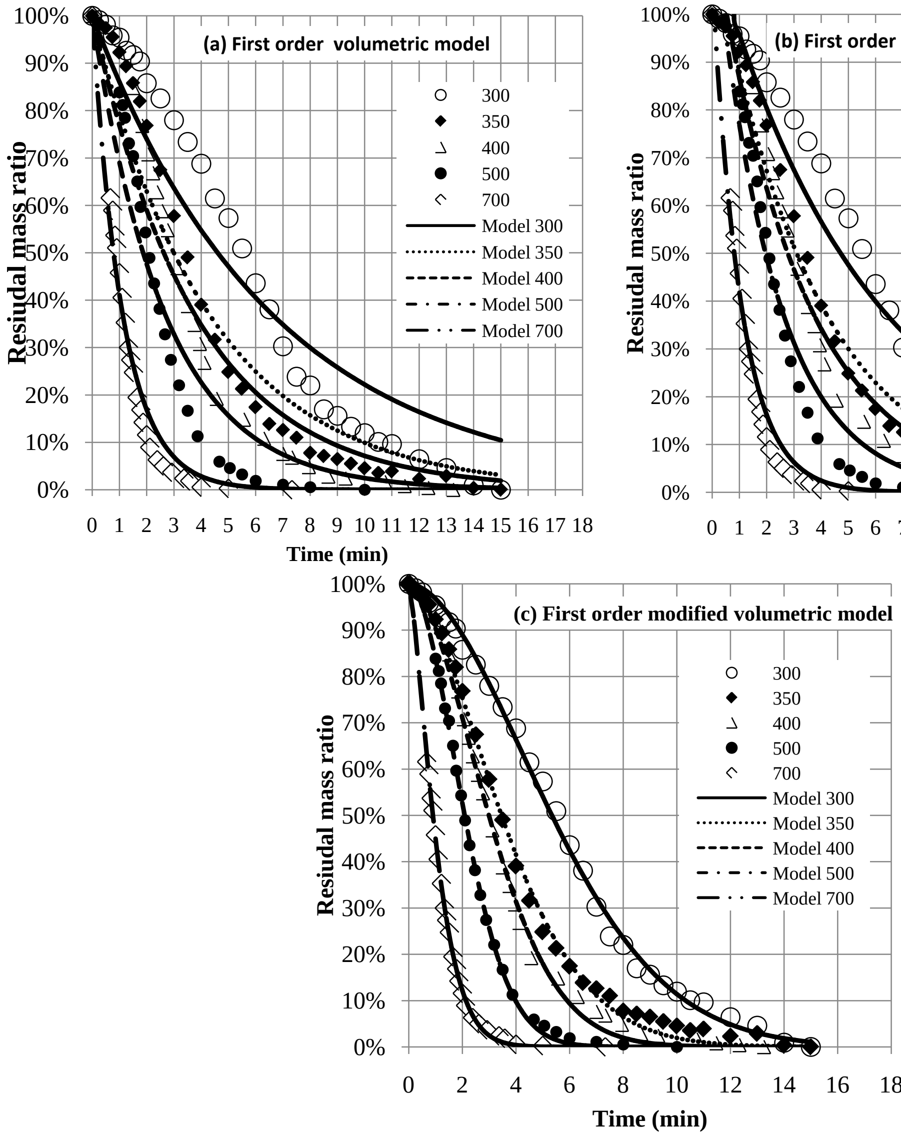


Figure 5. Modelings of kinetic of pyrolysis

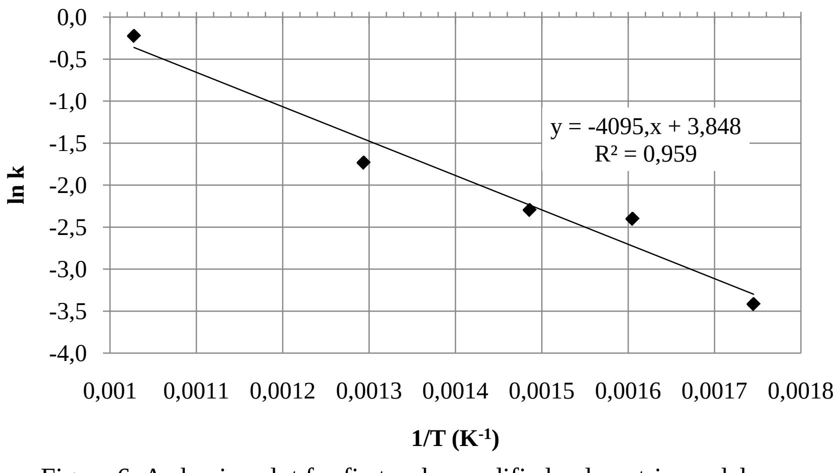


Figure 6. Arrhenius plot for first order modified volumetric model (Equations 6, 7 and 10)

Table 2. Characteristic of sludge and char

No.	Parameter	Dry sludge	Char from pyrolysis at 400ºC	Char from pyrolysis at 500ºC	Char from pyrolysis at 700ºC
1.	Proximate analysis (moisture free basis):				
	a. Ash	33.83%	74.61%	76.96%	81.45%
	b. Volatile matter	55.02%	13.22%	10.15%	5.11%
	c. Fixed carbon	11.15%	12.17%	12.89%	13.44%
2.	Ultimate analysis (moisture and ash free basis):				
	a. Carbon	49.92%	65.95%	76.52%	91.48%
	b. Hydrogen	7.77%	6.48%	6.23%	5.53%
	c. Nitrogen	4.10%	4.07%	4.30%	5.42%
	d. Oxygen	48.32%	34.46%	23.92%	8.08%
	e. Sulfur	0.73%	2.53%	2.96%	3.82%
3.	mol ratio of H/C	0.156	0.098	0.081	0.060
4.	mol ratio of O/C	0.968	0.523	0.313	0.088
5.	HHV (MJ/kg)	21.25	21.25	24.94	26.31
6.	Char yield (percentage to original mass)		66.26%	64.36%	62.38%
7.	Pore characteristic (BET measurement):				
	a. Pore surface area, m^2/g	10.812	59.732	77.049	71.883
	b. Pore volume, cm^3/g	$5.47x10^{-2}$	$13.49x10^{-2}$	$15.22x10^{-2}$	$16.05x10^{-2}$
	c. Pore diameter, Å	202.2	90.3	79.0	89.3

CONCLUSIONS

Mechanical dewatering might be used to reduce the water content in sludge cake down to about 53%. Further decrease in water content must be carried out using thermal drying. Char yield and rate of mass loss during isothermal pyrolysis of oven dried sludge cake were affected by temperature. As expected, a higher temperature of isothermal pyrolysis produced a less char or a larger mass loss, and a higher rate of pyrolysis. Char produced at a higher temperature had a larger pore surface area and volume, for which a better reactivity for gasification might be expected. Kinetic of the isothermal pyrolysis was well modeled with the first order modified volumetric reaction model.

ACKNOWLEDGEMENT

This research is was a part of Syamsudin’s doctoral dissertation funded by *Agency of Assessment of Policy, the Climate and Industry Quality, Indonesian’s Ministry of Industry*. In particular, experimental work presented in this paper was funded by Research and Inovation Fund of ITB 2011. The authors acknowledge the support of Kevin H. Prawiranto and Saefuludin in the experimental work. Contribution of Dr. Mahidin is gratefully mentioned for the arrangement and English correction of this paper.

REFERENCES

Otero, M., Calvo, L.F., Gil, M.V., García, A.I., and Morán, A., (2008), Co-combustion of Different Sewage Sludge and Coal: A Non-Isothermal Thermogravimetric Kinetic Analysis, *Bioresource Technology*, 99(14), pp. 6311-6319.

Prawiranto, K., Syamsudin, and Susanto, H., (2012), Mechanical Dewatering and Thermal Drying Characteristics of Pulp Mill Sludge Cake, *Proceeding of the 19th Regional Symposium on Chemical Engineering (RSCE 2012)*, Denpasar.

Qi, Y., Thapa, K.B., and Hoadley, A.F.A., (2011), Application of Filtration Aids for Improving Sludge Dewatering Properties-A Review, *Chemical Engineering Journal*, 171, pp. 373-384.

Scott, G.M., Abubakr, S., and Smith, A., (1995), Sludge Characteristics and Disposal Alternatives for the Pulp and Paper Industry, in *Proceedings of the 1995 International Environmental Conference*, TAPPI Press, Atlanta, pp. 269-279.

Syamsudin and Susanto, (2012), Study on Alternative Fuels for Lime Kiln in A Kraft Pulp Mill, in *Proceeding on 2012 International Symposium on Resources Efficiency in Pulp and Paper Technology*, Bandung.

Yang, H., Yan, R., Chen, H., Lee, D.H., and Zheng, C., (2007), Characteristics of Hemicelluloses, Cellulose and Lignin Pyrolysis, *Fuel*, 86, pp. 1781-1788.

Yip, K.V., Wu, H., Zang, D., and Coleman, J., (2007), The Effect of Pyrolysis Condition on Collie Coal, *Research Report 72*, Cooperative Research Centre for Coal in Sustainable Development, Australia, http://www.ccsd.biz, accessed on 12th Sepetember 2010.