Torrefaction of high moisture content biomass using fresh dairy manure

（乳牛ふんを用いた高含水率バイオマスの半炭化）

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CHAPTER 1

General Introduction

1.1 Problem identification

Demand to biomass will continue in the coming years for renewable energy to overcome the natural resources and environmental deficit. Bioethanol is widely known bioenergy where this green energy product are mostly generated from crops [1-3]. Crops are reported as predominant biomass feedstock in order to produce bioenergy for transportation, electricity and heat usage [4-6]. For example, the US used corn as the feedstock to replace its 10% gasoline demand with bioethanol for transportation while Brazil use sugarcane [6]. Others such as Europe use sugar beet and wheat while Canada use wheat and corn and China use corn, wheat and cassava for bioethanol sources [6]. Those examples are the first generation (1st generation) biofuel where they are globally accepted to be the best solution for the reduction of fossil fuel depletion, petroleum cost escalation and greenhouse-gas emissions [7]. However, the dubiousness of how green these 1st generation biomass feedstock have been recently growing when Demirbas et al. [4, 8, 9] Youngs & Sommerville. [8,] and Ho et al. [9] find out the crops that planted purposely for biofuel may disrupt land capacity and nutrient supply. At the same time, Stone et al. [10] are concerning of crops-based biofuel may affect depletion in water reservoir. Besides,

increment of food price which is said as a side effect of crops being grown for biofuel production making fuel from 1st generation may not be sustainable solution to the world's energy need anymore [11]. These environmental cost are asking for an alternative biomass and the usage of second generation biofuel (2nd generation) is currently preferred [12]. According to Srirangan et al. [13] second generation feedstock are non-edible and comprise of raw materials derived from lignocellulosic biomass and crop waste residues from various agricultural and forestry processes. Second generation biofuels are widely seen as a sustainable response to the increasing controversy surrounding 1st generation [14], particularly their utilization will reduce direct competition of biofuels with human food and animal feed [15-17]

Livestock manure is categorized into second generation biomass feedstock which is a byproduct of livestock farming. Livestock is crucial because (i) the meat and dairy product are protein sources for human and (ii) the manure provide organic material for human needs [18]. In addition, Scholten et al. [19] expected that global demand for animal product will be double due to the growth of the world population by the year of 2050. This in the same time contributes to the higher amount of livestock waste production. As for now, the United States produces 35 million dry tons of livestock dung annually while the EU-27 produces more than 1500 million fresh tons of livestock effluent a year [20].

Japan on the other hand produces around 97 million tons livestock manure per annum [21]. In other words, livestock manure seems to be sustainable and valuable resource as 2nd generation biofuel since it will always be produce for humankind.

However, certain drawback of livestock manure such as high moisture content sets the limitation of its use. Thus, pretreatment is necessary and torrefaction has emerged as an important step for upgrading biomass. Torrefaction is a mild thermal decomposition treatment to convert biomass into a solid fuel [22]. The conversion process is operated at low temperatures from 200 °C to 300 °C under inert atmospheric conditions [23]. Torrefaction produces a solid fuel product called torrefied biomass [24], bio-char or bio-coal [25]. Other names for torrefaction are slow and mild pyrolysis, high temperature drying, and roasting [26]. In general, the torrefaction process includes heating, drying, post-drying, torrefaction and cooling [27, 28]. During the process, biomass is decomposed, oxygen is removed, and the fibrous structure and tenacity are destroyed [29]. These resultant characteristics give in the advantages of torrefied biomass over the non-torrefied biomass; torrefied biomass is more grindable and hydrophobic, contains high calorific value [30] and easily transported and stored [31].

In general, torrefaction is conducted using dried or very low moisture content of feedstock. Also, inert condition is applied. However, there have been no reports on direct

usage of high moisture content biomass as a feedstock during torrefaction. By using high moisture content biomass, the prediction for whole biomass degradation processes can be improved, beneficial to clarify the mechanism of biomass torrefaction. In addition, a simplified approach by implementing torrefaction in non-inert condition can be adapted for real life scenario that offer low cost benefit.

1.2 Research objectives

This research aims to better understand the torrefaction process, particularly on using high moisture content biomass from fresh dairy manure. Additionally, the research applies limited oxygen condition for bioenergy production. Thus, considering the points above, specific objectives of this research are;

i) To study the capability of high moisture content dairy manure to become a solid product through torrefaction.

ii) To identify the reaction mechanism of high moisture content biomass torrefaction using dairy manure.

1.3 Dissertation organization

Chapter 1 address the problem of the research. Here, the fundamental of this thesis

is established. Brief introduction on livestock manure as feedstock and torrefaction treatment are discussed. The issue is no framework have been dedicated to study the direct usage of high moisture content biomass as a feedstock during torrefaction. Thus, the aims of this thesis is to better understand the torrefaction process, particularly on direct usage of high moisture content biomass from fresh dairy manure and study the reaction mechanism.

Chapter 2 introduces livestock manure and its potential to be a sources of bioenergy through waste-to-energy (WTE) treatment technology. The conversion are two types; (i) thermochemical and (ii) biochemical. However, the highlights of the WTE is on thermochemical, particularly torrefaction process.

Chapter 3 deals with the understanding of torrefaction on high moisture content dairy manure. Here, an industrial rotary kiln combustion type reactor was used. The effects of temperature is observed and the properties of the torrefied manure including mass yield, higher heating value (HHV) and production efficiency are discussed. This chapter has been published as 'Torrefaction of high moisture content biomass in an industrial rotary kiln combustion type reactor' in Journal of the Japanese Society of Agriculture Machinery and Food Engineers.

Chapter 4 highlights the reaction mechanism of high moisture content dairy

manure during torrefaction. At this time, a continuous thermal degradation experiment was conducted using a laboratory oven. The weight loss profile data was collected and treated as a major source to understanding the reaction. Resultant mass profile data confirmed that the torrefaction reaction involved a simultaneous process of drying and degradation. For a comprehensive prediction, we develop a simplified mathematical model for both process based on exponential model. This chapter has been published as 'Thermal treatment of high moisture content biomass using fresh dairy manure' in the Transactions of the ASABE.

Chapter 5 present general conclusion from this study and suggestions for future work.

References

[1] P. Silva Ortiz, S. de Oliveira Jr, Exergy analysis of pretreatment processes of bioethanol production based on sugarcane bagasse. *Energy* **76** (2014) 130-138.

[2] C. A. Cardona, J. A. Quintero, I. C. Paz, Production of bioethanol from sugarcane bagasse: Status and perspectives. *Bioresource Technology* **101** (2010) 4754-4766.

[3] S. Haghighi Mood, A. Hossein Golfeshan, M. Tabatabaei, G. Salehi Jouzani, G. H. Najafi, M. Gholami, M. Ardjmand, Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment. *Renewable and Sustainable Energy Reviews* **27** (2013) 77-93.

[4] D. P. Ho, H. H. Ngo, W. Guo, A mini review on renewable sources for biofuel. *Bioresour Technol* **169** (2014) 742-749.

[5] H. Kopetz, Renewable resources: Build a biomass energy market. *Nature* **494** (2013) 29-31.

[6] Y. Zhang, P. Bi, J. Wang, P. Jiang, X. Wu, H. Xue, J. Liu, X. Zhou, Q. Li, Production of jet and diesel biofuels from renewable lignocellulosic biomass. *Applied Energy* **150** (2015) 128-137.

[7] J. P. W. Scharlemann, W. F. Laurance, How green are biofuels? *Science* **319** (2008) 43-44.

[8] M. Fatih Demirbas, M. Balat, H. Balat, Biowastes-to-biofuels. *Energy Conversion and Management* **52** (2011) 1815-1828.

[9] H. Youngs, C. Somerville, Best practices for biofuels. *Science* **344** (2014) 1095-1096.

[10] K. C. Stone, P. G. Hunt, K. B. Cantrell, K. S. Ro, The potential impacts of biomass feedstock production on water resource availability. *Bioresour Technol* **101** (2010) 2014-2025.

[11] S. Mayfield, P. K. Wong, Forum chemical engineering: Fuel for debate. *Nature* **476** (2011) 402-403.

[12] D. Graham-Rowe, Agriculture: Beyond food versus fuel. *Nature* **474** (2011) S6-S8.

[13] K. Srirangan, L. Akawi, M. Moo-Young, C. P. Chou, Towards sustainable production of clean energy carriers from biomass resources. *Applied Energy* **100** (2012) 172-186.

[14] A. Mohr, S. Raman, Lessons from first generation biofuels and implications for the sustainability appraisal of second generation biofuels. *Energy Policy* **63** (2013) 114-122.

[15] R. E. H. Sims, W. Mabee, J. N. Saddler, M. Taylor, An overview of second generation biofuel technologies. *Bioresource Technology* **101** (2010) 1570-1580.

[16] S. N. Naik, V. V. Goud, P. K. Rout, A. K. Dalai, Production of first and second generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews* **14** (2010) 578-597.

[17] W. Thompson, S. Meyer, Second generation biofuels and food crops: Co-products or competitors? *Global Food Security* **2** (2013) 89-96.

[18] J. Martinez, P. Dabert, S. Barrington, C. Burton, Livestock waste treatment systems for environmental quality, food safety, and sustainability. *Bioresource Technology* **100** (2009) 5527-5536.

[19] M. C. T. Scholten, I. J. M. de Boer, B. Gremmen, C. Lokhorst, Livestock farming with care: Towards sustainable production of animal-source food. *NJAS - Wageningen Journal of Life Sciences* **66** (2013) 3-5.

[20] H. L. Choi, S. I. A. Sudiarto, A. Renggaman, Prediction of livestock manure and mixture higher heating value based on fundamental analysis. *Fuel* **116** (2014) 772-780.

[21] X. Xiao, D. D. Le, L. Li, X. Meng, J. Cao, K. Morishita, T. Takarada, Catalytic steam gasification of biomass in fluidized bed at low temperature: Conversion from livestock manure compost to hydrogen-rich syngas. *Biomass and Bioenergy* **34** (2010) 1505-1512.

[22] B. Acharya, I. Sule, A. Dutta, A review on advances of torrefaction technologies for biomass processing. *Biomass Conversion and Biorefinery* **2** (2012) 349-369.

[23] T. Ogura, Y. Date, M. Masukujane, T. Coetzee, K. Akashi, J. Kikuchi, Improvement of physical, chemical, and biological properties of aridisol from botswana by the incorporation of torrefied biomass. *Scientific Reports* **6** (2016) 28011.

[24] L. J. R. Nunes, J. C. O. Matias, J. P. S. Catalão, A review on torrefied biomass pellets as a sustainable alternative to coal in power generation. *Renewable and Sustainable Energy Reviews* **40** (2014) 153-160.

[25] P. Basu, Chapter 4 - torrefaction. In *Biomass gasification, pyrolysis and torrefaction (second edition)*. (Academic Press, Boston, 2013), pp. 87-145.

[26] D. Ciolkosz, R. Wallace, A review of torrefaction for bioenergy feedstock production. *Biofuels, Bioproducts and Biorefining* **5** (2011) 317-329.

[27] M. J. C. van der Stelt, H. Gerhauser, J. H. A. Kiel, K. J. Ptasinski, Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass and Bioenergy* **35** (2011) 3748-3762.

[28] D. R. Nhuchhen, P. Basu, B. Acharya, A comprehensive review on biomass torrefaction. *International Journal of Renewable Energy & Biofuels* **2014** (2014) 1-56.

[29] A. Pimchuai, A. Dutta, P. Basu, Torrefaction of agriculture residue to enhance combustible properties. *Energy & Fuels* **24** (2010) 4638-4645.

[30] R. H. H. Ibrahim, L. I. Darvell, J. M. Jones, A. Williams, Physicochemical characterisation of torrefied biomass. *Journal of Analytical and Applied Pyrolysis* **103** (2013) 21-30.

[31] Q. Chen, J. Zhou, B. Liu, Q. Mei, Z. Luo, Influence of torrefaction pretreatment on biomass gasification technology. *Chinese Science Bulletin* **56** (2011) 1449-1456.

CHAPTER 2

Literature review

2.1 Livestock manure

2.1.1 Livestock manure and its application

For centuries, animal dung has been widely applied as a natural sources for human used particularly soil fertilizer for crops [1] and fuel for heating and cooking [2]. To cook using animal dung fuel, traditional open stove is normally used and this leads to indoor air pollution and increases the risk for respiratory disorders [3-5]. Study by Deka & Hoque [6] that compare emission of biomass fuel smoke particles (BFSPs) between cow dung stick, mixed biomass, cow-dung stick-mixed biomass and sugarcane bagasse published that cow dung emits the most polluting BFSPs for rural kitchens of South Asia compared to other studied biomass. Before that, study of Kang et al. [4] found the combustion of yak dung cakes for indoor cooking in the nomadic tent in the Tibetan Plateau produces higher concentration of total suspended particles (TSP) with a value of 4.45 mg m^{-3} during the cooking/heating period (17 hours) and average is 3.16 mg m^{-3} for the 24 hours and the TSP concentration is about 63 times higher than WHO air quality guidelines for PM_{10}. In addition, the study also found that indoor air quality of that nomadic tents also enriched with Cd, As and Pb with 3.16µg m^{-3}, 35 µg m^{-3} and 81.39 µg m^{-3} respectively after 24

hours due to the higher TSP concentration compared in the normal yak dung alone. Kang et al.[4] also discussed that direct combustion of animal dung releases highest respirable particles and causes the maximum indoor air pollution. Hence, applying advance technologies in treating livestock dung and transform it from waste to bioenergy is necessary before used and should be encouraged vigorously for human health as well as the environment.

2.1.2 Livestock manure and treatment technology

The capability of advanced technology to transform waste into an energy made livestock manure among one of the potential biofeedstock. The conversion are through two types of treatment; (i) thermochemical such as pyrolysis, gasification and liquefaction and (ii) biochemical which are aerobic and anaerobic digestion [7]. The conversion produce a bioenergy product that can be classified into three form which are neither solid, liquid nor gas [8]. Each form further recognized as biochar for solid, bio-oil for liquid and biogas for gas [9, 10]. Those product can be use in three major area that are for heat and power generation, transportation fuels and chemical feedstocks [11]. Figure 2.1 shows the bioenergy production and its application.

To date, biogas and anaerobic digestion (AD) are the upmost established biofuel product and waste-to-energy (WTE) technology for animal manure [7, 12]. When livestock

manure undergone anaerobic composting, gaseous are released and methane gas is the major emission [13-15]. Methane trapping during biogas production via installation of anaerobic digester made methane gas be seen no longer as an environmental pain but a gain [16-19]. A study by Tsai & Lin [13] reported that previously in Taiwan, biogas produced by livestock manure management was a major source of methane emission but had shown a decrement of 35 % after about 10 years which is 56 Gg methane emitted in 1995 to about 36 Gg in 2007. Through the anaerobic digestion application technology, the trapped methane further contributed $7.2x10^7$ kW-hyear^{-1} to national electricity generation. Furthermore, studies by [20-25] had proved that the anaerobic digestion (AD) may not only ameliorate human health and local environmental issue, but also social and economic aspects. For example, installation of AD digester at Wangma village of Kang Xiling town of rural areas of Qinzhou China, found the biogas that supply using pigs, ducks, geese and poultry manure are enough to meet the need of fuel of daily usage [26]. The residents also reuse the digestate to the rice fields and for vegetable planting. Besides, Sub-Saharan Africa residents also agreed that installation of manure-based biogas digester systems particularly to household is well suited as it improves both soil conditions and household sanitation [1, 27]. On the other hand, in Cambodia, the National Biodigester Programme

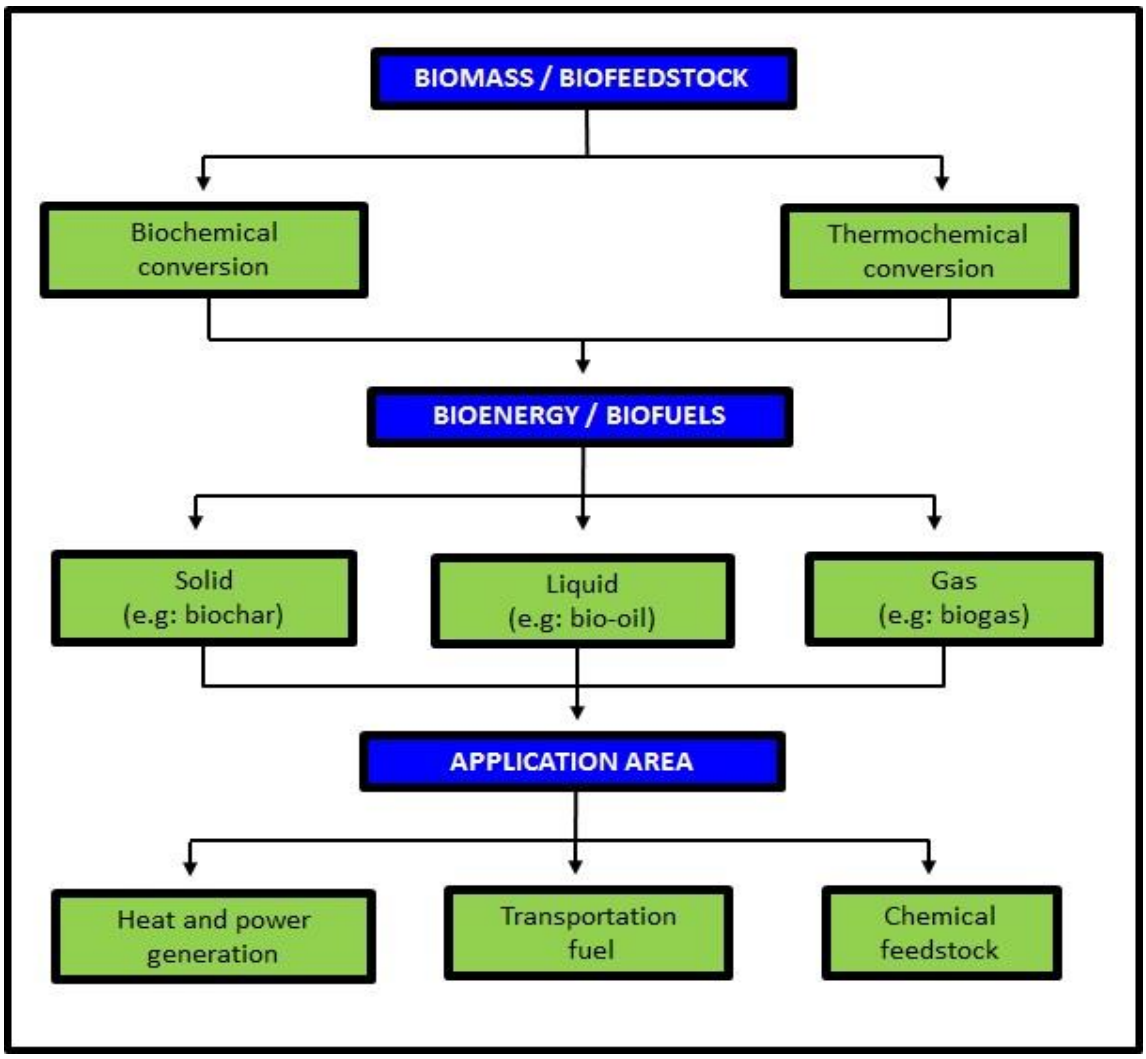

Figure 2.1 – Bioenergy production and its application.

(NBP) reported that the benefit of AD application are include less demand for imported chemical fertilizers, increase in quality of livestock, decrease in deforestation and cumulative greenhouse gas emission, better health in rural population and more development for rural areas through skills, capacity building and employment opportunities [28]. These studies show that the WTE technologies via AD is benefiting in many aspects.

2.2 Thermochemical conversion (TCC)

2.2.1 Introduction

Thermochemical treatment is also a promising technologies of WTE in order to produce biofuel from livestock manure[8, 10, 29, 30]. Even the anaerobic digestion technology is well established and robust, the process is time consuming [31] and may take about days and weeks because of depending on microbial decomposition process. In addition, the treatment need further disposal for the digestate produced from it [11]. In contrast, thermochemical treatment only require treatment period in the span of minutes to hours and most organic matter is fully converted into energy-rich and valuable end products without additional treatment. According to Cantrell et al. [11], thermochemical treatment of animal dung offer several other advantages such as the reactors can be designed to fit the intended usage based on manure type, no fugitive gas emissions generated and nutrient recovery is able to achieve efficiently. As livestock manure is also belong to biomass, it encounter several drawbacks like other biomass do that require TCC for improvement. According to Uemura et al. [32], the untreated biomass has (1) non-homogenous composition, (2) high ash content, (3) lower calorific value, and (4) high cost for transportation and collection. Another important drawbacks of raw biomass is containing high amount of water. High moisture content biomass increases the cost for production

and may interrupt the process efficiency during treatment. In the same time, biomass with high moisture happen to degrade naturally and lead to lower quality and issues on give off a harmful gas emission during storage [33].

Generally, thermochemical conversion (TCC) technology include combustion, gasification, liquefaction, pyrolysis, carbonization and torrefaction [34] and apply high temperature to decompose the biomass into bioenergy [18]. For instance, gasification operates at elevated temperature from 800 to 1000 °C to produce synthesis gas or syngas while pyrolysis is between 300 °C to 650 °C for bio-oil [35] and torrefaction is from 200 to 300 °C for biochar generation [36]. Among all of the TCC, pyrolysis is the most common practice [9, 37, 38] and it is enable to produce all kind of bioenergy form and the product are known as biochar, bio-oil and syngas [10, 39, 40]. The utmost goal of the pyrolysis is maximizing the production of liquid for bio-oil and minimizing the solid char. The motivation thus categorized the process into two; slow and fast and both are conducted under oxygen deficient condition [41]. Slow pyrolysis operate with temperature range from 300-400 °C [42] while fast pyrolysis is 450-650 °C [35]. Besides, pyrolysis often accompanied by torrefaction and carbonization as a pre-treatment or the drying step of TCC technology [43] where both are belong to slow or mild pyrolysis and limit for biochar production only. In an industrial practice, although bio-oil is concerned in fast pyrolysis, the by-products

char or gas is fully reuse particularly for sources of heat or co-firing for electricity in an engine [44] . Since TCC is highly dependent on the temperature and the heating rate [37], and in the same time the biomass have various characteristics such as different chemical composition and moisture content level [39], therefore, it is important to clearly determine at the very beginning TCC process that adapt to the bioenergy of interest.

2.2.2 TCC to produce solid biofuel

In order to have a solid bioenergy, TCC that suite to that are torrefaction, carbonization and slow pyrolysis. Therefore, torrefaction is sometimes confused with the other two TCC. Those account for thermal decomposition of biomass and overlapping to some extent between them are unavoidable. Specifically, carbonization and torrefaction are more alike but the level of temperature during the process make the difference. Torrefaction operated at low temperatures ranges from 200 °C to 300 °C under an inert atmospheric conditions [45] while, carbonization takes place at 300-600 °C with a certain level of oxygen. On the other hand, slow pyrolysis aim mainly to produce solid char that could function as intermediate energy carrier and feedstock for subsequent processing [44] to enhance the production. As an example, Study by Chen et al. [46] showed that gasification from treated char increase the production of gas in comparison to non-treated solid char.

2.2.3 Torrefaction

Torrefaction is a thermal decomposition treatment to divert biomass into a solid fuel. The raw biomass is upgraded through a limited devolatilization and partly decompose to produce various types of volatiles. The final product is solid and may called torrefied biomass [47], bio-char or bio-coal [48]. Other names for torrefaction are slow and mild pyrolysis, high temperature drying as well as roasting [49]. Typical range of temperature for this process is between 200 °C and 300 °C. Other ranges have been suggested; 220-300 °C [50], 225-300 °C [51] and 230-300 °C [52] but not exceed the 300 °C. Torrefaction that above 300 °C would result to an extensive devolatilization [53] rather than limited and it is unpleasant because tar formation may encounter the process due to fast thermal cracking of cellulose between 300-320 °C [48] . Torrefaction above 300 °C also may allowing severe loss of lignin. Thus, these causes will restrict the uniform shape of torrefied biomass.

Torrefaction process includes heating, drying, post-drying, torrefaction and cooling [54, 55]. At that time, biomass is going through; (1) an evaporation at 100 °C, (2) surface water loss at non-reactive drying (100-150 °C), (3) bound water loss at reactive drying (150-200 °C) and (4) limited devolitilization and depolymerization (200-300 °C) On the other hand, Tumuluru et al. [33] describe torrefaction according to three level of

drying; non-reactive, reactive and destructive drying. During those processes; biomass undergo a decomposition process, oxygen removal, and destruction of the fibrous structure and tenacity [52]. These phenomena explained the advantages of torrefied biomass over the non-torrefied biomass where it will more grindable and hydrophobic, contains high calorific value [56], and easily transported and stored [46]. Therefore, torrefaction has improvise the drawbacks of raw biomass as mentioned earlier by Uemura et al.[57].

While the advantages of torrefaction are known, very limited literature for torrefaction from livestock manure were reported. Nevertheless, solid fuel made by other TCC method from manure such as pyrolysis and biochar are available. Ro [58] summed up examples and benefits of manure-based biochar from swine, chicken litter and broiler litter in his report. It is believed that biochar from animal manure contains higher nutrient compared from plant but with various characterisation [59, 60]. For instance, Touray et al. [37] reported goat-manure-derived biochars could be best soil amendment and environmental remediation rather than fossil fuel alternatives due to its porous structure and high mineral-ash content.

2.2.4 Inert condition of torrefaction

Generally, torrefaction is conducted under an inert condition i.e very limited oxygen supply or non-oxidizing environment. This is because the presence of oxygen

potentially increases the spontaneous combustion [61] which inevitably diverts the carbon into flue gas instead of remained in the torrefied biomass. Currently, in the laboratories practice, the use of inert condition require an additional gas of nitrogen to the system for an optimum result. In an industrial perspective, a continuous supply of inert gas attributes to additional cost to the process. An economically viable torrefaction could potentially be achieved if the process could be conducted in air [62] or reuse the flue gas emitted from the system [63] . In the same time, Basu [48] suggests that it is not essential to provide oxygen-free environment in torrefaction. Oxygen with modest amount is acceptable which may bring beneficial effect on the torrefaction process.

Recently, a number of study was conducted on the thermal treatment of biomass under an oxidative condition. In all cases, researchers agree that pretreatment at higher temperature in air resulted low solid and energy yield as the concentration of oxygen increased[32, 62, 64, 65] For example, Uemura et al. [57] carried out torrefaction containing 0, 3 %, 9 % and 15 % of O_2 concentration. They found out that solid and energy yield of torrefied oil palm empty fruit bunches (EFBs) decreased with increasing O_2 concentration. Study of Wang et al.[66] also found out that the energy yield of torrefied sawdust and pellet in oxidative condition were close to the torrefied sawdust in inert condition. The torrefaction was conducted in a fluidized bed reactor with 0 to 6 % of O_2 concentration.

On the other hand, study of Lu et al.[64] on oil palm fiber (OPF) and eucalyptus using inert and oxidative conditions presented that HHV of OPF conducted under air atmosphere decreased with temperature (250 °C to 350 °C). Furthermore, the HHV of torrefied OPF at 350 °C (14.9 MJ/kg) was lower than the raw material (17.1 MJ/kg). For eucalyptus, the highest HHV was at 275 °C (23.3 MJ/kg) and it decreased as temperature increased. In contrast, HHV of OPF and eucalyptus in an inert atmosphere provided quite similar results of biomass as reported in other literature.

Other than oxygen, torrefaction of biomass that carried out together with carbon dioxide environment also has been conducted. The motivation is to optimize the treatment system through reuse of flue gases emitted from the process for increase cost effective. Therefore, the capability of CO_2 gas to function in torrefaction is studied [63]. The torrefaction of oil palm kernel shell (OKS) was conducted with 0, 3 %, 9 %, 12 % and 15 % of CO_2 concentration with nitrogen balance to 100 %. The basis of the gas concentration is according to the percentage of flue gases emission from burners and boilers. They discovered that the energy yield of PKS decreased at increasing CO_2 concentration particularly at 300 °C. However, the energy yield was more than 70 %. Finally, they suggest that, the oxidative torrefaction with carbon dioxide at 220 °C and 250 °C may carried out without a significant problem.

References

[1] N. Z. Lupwayi, M. Girma, I. Haque, Plant nutrient contents of cattle manures from small-scale farms and experimental stations in the ethiopian highlands. *Agriculture, Ecosystems & Environment* **78** (2000) 57-63.

[2] T. V. Ramachandra, G. Kamakshi, B. V. Shruthi, Bioresource status in karnataka. *Renewable and Sustainable Energy Reviews* **8** (2004) 1-47.

[3] K. Lal, U. Mani, R. Pandey, N. Singh, A. K. Singh, D. K. Patel, M. P. Singh, R. C. Murthy, Multiple approaches to evaluate the toxicity of the biomass fuel cow dung (kanda) smoke. *Ecotoxicology and Environmental Safety* **74** (2011) 2126-2132.

[4] S. Kang, C. Li, F. Wang, Q. Zhang, Z. Cong, Total suspended particulate matter and toxic elements indoors during cooking with yak dung. *Atmospheric Environment* **43** (2009) 4243-4246.

[5] T. Saud, R. Gautam, T. K. Mandal, R. Gadi, D. P. Singh, S. K. Sharma, M. Dahiya, M. Saxena, Emission estimates of organic and elemental carbon from household biomass fuel used over the indo-gangetic plain (igp), india. *Atmospheric Environment* **61** (2012) 212-220.

[6] P. Deka, R. R. Hoque, Chemical characterization of biomass fuel smoke particles of rural kitchens of south asia. *Atmospheric Environment* **108** (2015) 125-132.

[7] K. B. Cantrell, T. Ducey, K. S. Ro, P. G. Hunt, Livestock waste-to-bioenergy generation opportunities. *Bioresour Technol* **99** (2008) 7941-7953.

[8] K. P. Shadangi, K. Mohanty, Thermal and catalytic pyrolysis of karanja seed to produce liquid fuel. *Fuel* **115** (2014) 434-442.

[9] A. Demirbas, E. Pehlivan, T. Altun, Potential evolution of turkish agricultural residues as bio-gas, bio-char and bio-oil sources. *International Journal of Hydrogen Energy* **31** (2006) 613-620.

[10] M. Görling, M. Larsson, P. Alvfors, Bio-methane via fast pyrolysis of biomass. *Applied Energy* **112** (2013) 440-447.

[11] K. Cantrell, K. Ro, D. Mahajan, M. Anjom, P. G. Hunt, Role of thermochemical conversion in livestock waste-to-energy treatments: Obstacles and opportunities. *Industrial & Engineering Chemistry Research* **46** (2007) 8918-8927.

[12] M. M. Rahman, J. V. Paatero, A methodological approach for assessing potential of sustainable agricultural residues for electricity generation: South asian perspective. *Biomass and Bioenergy* **47** (2012) 153-163.

[13] W.-T. Tsai, C.-I. Lin, Overview analysis of bioenergy from livestock manure management in taiwan. *Renewable and Sustainable Energy Reviews* **13** (2009) 2682-2688.

[14] M. Saidu, A. Yuzir, M. R. Salim, Salmiati, S. Azman, N. Abdullah, Influence of palm oil mill effluent as inoculum on anaerobic digestion of cattle manure for biogas production. *Bioresource Technology* **141** (2013) 174-176.

[15] N. B. Singh, A. Kumar, S. Rai, Potential production of bioenergy from biomass in an indian

perspective. *Renewable and Sustainable Energy Reviews* **39** (2014) 65-78.

[16] C. T. Thien Thu, P. H. Cuong, L. T. Hang, N. V. Chao, L. X. Anh, N. X. Trach, S. G. Sommer, Manure management practices on biogas and non-biogas pig farms in developing countries – using livestock farms in vietnam as an example. *Journal of Cleaner Production* **27** (2012) 64-71.

[17] J. W. De Vries, C. M. Groenestein, I. J. De Boer, Environmental consequences of processing manure to produce mineral fertilizer and bio-energy. *J Environ Manage* **102** (2012) 173-183.

[18] K. Srirangan, L. Akawi, M. Moo-Young, C. P. Chou, Towards sustainable production of clean energy carriers from biomass resources. *Applied Energy* **100** (2012) 172-186.

[19] P. K. Halder, N. Paul, M. R. A. Beg, Assessment of biomass energy resources and related technologies practice in bangladesh. *Renewable and Sustainable Energy Reviews* **39** (2014) 444-460.

[20] K. C. Surendra, D. Takara, A. G. Hashimoto, S. K. Khanal, Biogas as a sustainable energy source for developing countries: Opportunities and challenges. *Renewable and Sustainable Energy Reviews* **31** (2014) 846-859.

[21] H. Insam, M. Gómez-Brandón, J. Ascher, Manure-based biogas fermentation residues – friend or foe of soil fertility? *Soil Biology and Biochemistry* **84** (2015) 1-14.

[22] T. Bond, M. R. Templeton, History and future of domestic biogas plants in the developing world. *Energy for Sustainable Development* **15** (2011) 347-354.

[23] P. C. Ghimire, Snv supported domestic biogas programmes in asia and africa. *Renewable Energy* **49** (2013) 90-94.

[24] Y. Feng, Y. Guo, G. Yang, X. Qin, Z. Song, Household biogas development in rural china: On policy support and other macro sustainable conditions. *Renewable and Sustainable Energy Reviews* **16** (2012) 5617-5624.

[25] Y. Chen, G. Yang, S. Sweeney, Y. Feng, Household biogas use in rural china: A study of opportunities and constraints. *Renewable and Sustainable Energy Reviews* **14** (2010) 545-549.

[26] Z. Xiao-zhu, O. U. She-liang, H. Chun-lan, Problems and solutions based on comprehensive utilization of biogas. *Energy Procedia* **5** (2011) 42-47.

[27] M. Landi, B. K. Sovacool, J. Eidsness, Cooking with gas: Policy lessons from rwanda's national domestic biogas program (ndbp). *Energy for Sustainable Development* **17** (2013) 347-356.

[28] E. Buysman, A. P. J. Mol, Market-based biogas sector development in least developed countries —the case of cambodia. *Energy Policy* **63** (2013) 44-51.

[29] M. A. Kader, M. R. Islam, M. Parveen, H. Haniu, K. Takai, Pyrolysis decomposition of tamarind seed for alternative fuel. *Bioresource Technology* **149** (2013) 1-7.

[30] A. V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy* **38** (2012) 68-94.

[31] K. S. Ro, K. B. Cantrell, P. G. Hunt, T. F. Ducey, M. B. Vanotti, A. A. Szogi, Thermochemical conversion of livestock wastes: Carbonization of swine solids. *Bioresour Technol* **100** (2009) 5466-

5471.

[32] Y. Uemura, W. N. Omar, T. Tsutsui, S. B. Yusup, Torrefaction of oil palm wastes. *Fuel* **90** (2011) 2585-2591.

[33] J. S. Tumuluru, C. T. Wright, J. R. Hess, K. L. Kenney, A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application. *Biofuels, Bioproducts and Biorefining* **5** (2011) 683-707.

[34] M. Verma, S. Godbout, S. K. Brar, O. Solomatnikova, S. P. Lemay, J. P. Larouche, Biofuels production from biomass by thermochemical conversion technologies. *International Journal of Chemical Engineering* **2012** (2012) 18.

[35] P. Basu, Chapter 5 - pyrolysis. In *Biomass gasification, pyrolysis and torrefaction (second edition)*. (Academic Press, Boston, 2013), pp. 147-176.

[36] S.-W. Park, C.-H. Jang, K.-R. Baek, J.-K. Yang, Torrefaction and low-temperature carbonization of woody biomass: Evaluation of fuel characteristics of the products. *Energy* **45** (2012) 676-685.

[37] N. Touray, W.-T. Tsai, H.-R. Chen, S.-C. Liu, Thermochemical and pore properties of goat-manure-derived biochars prepared from different pyrolysis temperatures. *Journal of Analytical and Applied Pyrolysis* **109** (2014) 116-122.

[38] X. Liu, Z. Li, Y. Zhang, R. Feng, I. B. Mahmood, Characterization of human manure-derived biochar and energy-balance analysis of slow pyrolysis process. *Waste Management* **34** (2014) 1619-1626.

[39] L. Wang, A. Shahbazi, M. A. Hanna, Characterization of corn stover, distiller grains and cattle manure for thermochemical conversion. *Biomass and Bioenergy* **35** (2011) 171-178.

[40] J. P. Cao, X. B. Xiao, S. Y. Zhang, X. Y. Zhao, K. Sato, Y. Ogawa, X. Y. Wei, T. Takarada, Preparation and characterization of bio-oils from internally circulating fluidized-bed pyrolyses of municipal, livestock, and wood waste. *Bioresour Technol* **102** (2011) 2009-2015.

[41] R. Wnetrzak, W. Kwapinski, K. Peters, S. G. Sommer, L. S. Jensen, J. J. Leahy, The influence of the pig manure separation system on the energy production potentials. *Bioresour Technol* **136** (2013) 502-508.

[42] M. H. Duku, S. Gu, E. B. Hagan, Biochar production potential in ghana—a review. *Renewable and Sustainable Energy Reviews* **15** (2011) 3539-3551.

[43] A. A. Boateng, C. A. Mullen, Fast pyrolysis of biomass thermally pretreated by torrefaction. *Journal of Analytical and Applied Pyrolysis* **100** (2013) 95-102.

[44] R. H. Venderbosch, W. Prins, Fast pyrolysis. In *Thermochemical processing of biomass*. (John Wiley & Sons, Ltd, 2011), pp. 124-156.

[45] T. Ogura, Y. Date, M. Masukujane, T. Coetzee, K. Akashi, J. Kikuchi, Improvement of physical, chemical, and biological properties of aridisol from botswana by the incorporation of torrefied biomass. *Scientific Reports* **6** (2016) 28011.

[46] Q. Chen, J. Zhou, B. Liu, Q. Mei, Z. Luo, Influence of torrefaction pretreatment on biomass

gasification technology. *Chinese Science Bulletin* **56** (2011) 1449-1456.

[47] L. J. R. Nunes, J. C. O. Matias, J. P. S. Catalão, A review on torrefied biomass pellets as a sustainable alternative to coal in power generation. *Renewable and Sustainable Energy Reviews* **40** (2014) 153-160.

[48] P. Basu, Chapter 4 - torrefaction. In *Biomass gasification, pyrolysis and torrefaction (second edition)*. (Academic Press, Boston, 2013), pp. 87-145.

[49] D. Ciolkosz, R. Wallace, A review of torrefaction for bioenergy feedstock production. *Biofuels, Bioproducts and Biorefining* **5** (2011) 317-329.

[50] B. Arias, C. Pevida, J. Fermoso, M. G. Plaza, F. Rubiera, J. J. Pis, Influence of torrefaction on the grindability and reactivity of woody biomass. *Fuel Processing Technology* **89** (2008) 169-175.

[51] W.-H. Chen, P.-C. Kuo, A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. *Energy* **35** (2010) 2580-2586.

[52] A. Pimchuai, A. Dutta, P. Basu, Torrefaction of agriculture residue to enhance combustible properties. *Energy & Fuels* **24** (2010) 4638-4645.

[53] B. Patel, B. Gami, H. Bhimani, Improved fuel characteristics of cotton stalk, prosopis and sugarcane bagasse through torrefaction. *Energy for Sustainable Development* **15** (2011) 372-375.

[54] M. J. C. van der Stelt, H. Gerhauser, J. H. A. Kiel, K. J. Ptasinski, Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass and Bioenergy* **35** (2011) 3748-3762.

[55] D. R. Nhuchhen, P. Basu, B. Acharya, A comprehensive review on biomass torrefaction. *International Journal of Renewable Energy & Biofuels* **2014** (2014) 1-56.

[56] R. H. H. Ibrahim, L. I. Darvell, J. M. Jones, A. Williams, Physicochemical characterisation of torrefied biomass. *Journal of Analytical and Applied Pyrolysis* **103** (2013) 21-30.

[57] Y. Uemura, W. Omar, N. A. Othman, S. Yusup, T. Tsutsui, Torrefaction of oil palm efb in the presence of oxygen. *Fuel* **103** (2013) 156-160.

[58] K. S. Ro, Kinetics and energetics of producing animal manure-based biochar. *BioEnergy Research* **9** (2016) 447-453.

[59] K. Y. Chan, L. Van Zwieten, I. Meszaros, A. Downie, S. Joseph, Using poultry litter biochars as soil amendments. *Soil Research* **46** (2008) 437-444.

[60] Y. Jin, X. Liang, M. He, Y. Liu, G. Tian, J. Shi, Manure biochar influence upon soil properties, phosphorus distribution and phosphatase activities: A microcosm incubation study. *Chemosphere*.

[61] B. Acharya, I. Sule, A. Dutta, A review on advances of torrefaction technologies for biomass processing. *Biomass Conversion and Biorefinery* **2** (2012) 349-369.

[62] W.-H. Chen, K.-M. Lu, W.-J. Lee, S.-H. Liu, T.-C. Lin, Non-oxidative and oxidative torrefaction characterization and sem observations of fibrous and ligneous biomass. *Applied Energy* **114** (2014) 104-113.

[63] Y. Uemura, S. Saadon, N. Osman, N. Mansor, K.-i. Tanoue, Torrefaction of oil palm kernel shell in

the presence of oxygen and carbon dioxide. *Fuel* **144** (2015) 171-179.

[64] K.-M. Lu, W.-J. Lee, W.-H. Chen, S.-H. Liu, T.-C. Lin, Torrefaction and low temperature carbonization of oil palm fiber and eucalyptus in nitrogen and air atmospheres. *Bioresource Technology* **123** (2012) 98-105.

[65] P. Rousset, L. Macedo, J. M. Commandré, A. Moreira, Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product. *Journal of Analytical and Applied Pyrolysis* **96** (2012) 86-91.

[66] C. Wang, J. Peng, H. Li, X. T. Bi, R. Legros, C. J. Lim, S. Sokhansanj, Oxidative torrefaction of biomass residues and densification of torrefied sawdust to pellets. *Bioresource Technology* **127** (2013) 318-325.

CHAPTER 3

Torrefaction of fresh dairy manure in an industrial rotary kiln combustion type reactor

3.0 Brief summary

In this chapter, direct usage of wet dairy manure as a feedstock for torrefaction using an industrial rotary kiln combustion type reactor is introduced. The torrefaction is investigated at three different temperatures (200 °C, 250 °C and 300 °C). The process started by feeding the manure to the input hopper of the reactor. The manure was crushed by the screw feeder and then transferred to the kiln for heat treatment. During the treatment, the kiln keep rotating and the heat flow along and the manure adsorbs the heat. Due to 4° of inclination, the kiln allows the gravity to assist in moving heated-manure through the higher end to the lower end of the rotary kiln. The manure at the lower end will discharge to the collecting tray. As a result, wet dairy manure was converted to a solid product and torrefied manure is produced.

3.1 Background

Most of the torrefaction studies used feedstock from plant-derived agricultural waste such as wood chip [1], wood [2, 3] and crops [4, 5]. Other agricultural sources such as livestock manure were also reported for biochar production [6, 7]. Biochar from animal

manure has higher nutrient content but with different characteristics [8] . For example, goat-manure-derived biochars are best used for soil amendment and environmental remediation rather than fossil fuel alternatives due to its porous structure and high mineral-ash content [9].

In this study, torrefaction of fresh dairy manure was carried out using an industrial rotary kiln combustion type reactor to produce solid bioenergy. At the time this study was conducted, limited data had been published related with the direct usage of high moisture content livestock manure as a feedstock for torrefaction. Generally, dried samples had been used for feedstock instead of wet samples. In addition, there was no information on wet manure that had been torrefied through an industrial rotary kiln reactor. However, a few studies have reported torrefaction with high moisture content biomass such as sewage [10], food waste [11] and tomato peels [12] and using a rotary kiln reactor [13-16]. Therefore, the goal of this study is to investigate the capability of high moisture content dairy manure to become a solid product through torrefaction at various temperatures using an industrial rotary kiln combustion type reactor. The results may improve biomass pretreatment for solid bioenergy production.

3.2 Materials and Methods

3.2.1 Sample collection

Fresh dairy manure was used as the biomass feedstock for torrefaction. It was collected from the experimental farm of the Field Science Centre for Northern Biosphere, Hokkaido University. The livestock manure was then placed into a covered bucket with a ten kilogram (10 kg) capacity. Three buckets of dairy manure were transferred to Kinsei Sangyo Co., Ltd. at Gunma Prefecture for torrefaction using an industrial reactor.

3.2.2 The torrefaction reactor

The experiment was carried out using a rotary kiln combustion type reactor. The reactor is divided into three major parts: the input hopper, the kiln, and the chimney. The torrefaction process takes place in the kiln. The kiln is positioned horizontally with an inclination angle of four degrees (4 °) and has a rotation speed of about 50 seconds per cycle. The maximum operation temperature of the reactor is 1200 °C with a mass processing capacity of 50 kg/h.

3.2.3 Torrefaction of fresh dairy manure

In principle, to achieve complete torrefaction through the rotary kiln combustion type reactor (Fig. 3.1), the manure must undergo a non-continuous heat-treated process. The torrefaction starts by feeding the manure (~10 kg) (no. 8) to the input hopper (no. 9) of

the reactor. The manure is crushed by the screw feeder (no. 10) and then is transferred to the kiln (no. 12) for heat treatment. In the kiln, the inside temperature is detected by the sensor (no. 7), which sends a signal to the thermal furnace burner (no. 3) to emit flame (no. 14) to control and maintain the heat at the set temperature. During the treatment, the kiln is constantly rotated, the heat flows and the manure adsorbs the heat. Due to the inclination angle of four degrees (4 °), gravity assists in moving the heated-manure through the higher end to the lower end of the rotary kiln. The manure at the lower end discharges to the collecting tray (no. 15). The heat-treated manure in the collecting tray is then weighed and 3-5 % of the total weight is taken for measurement of moisture content and other properties. The weighed manure is then sent back to the input hopper and torrefied, weighed and separated again for at least three cycles of the heat-treatment process. Consecutive heat treatments are denoted as T1, T2, T3, and T_n. No external gas is supplied to the reactor thermal during torrefaction. Color changes and time for every heat treatment are also recorded. For this study, we selected three temperatures for torrefaction: 200 °C, 250 °C, and 300 °C. The fresh dairy manure contained 84.1 % initial moisture content.

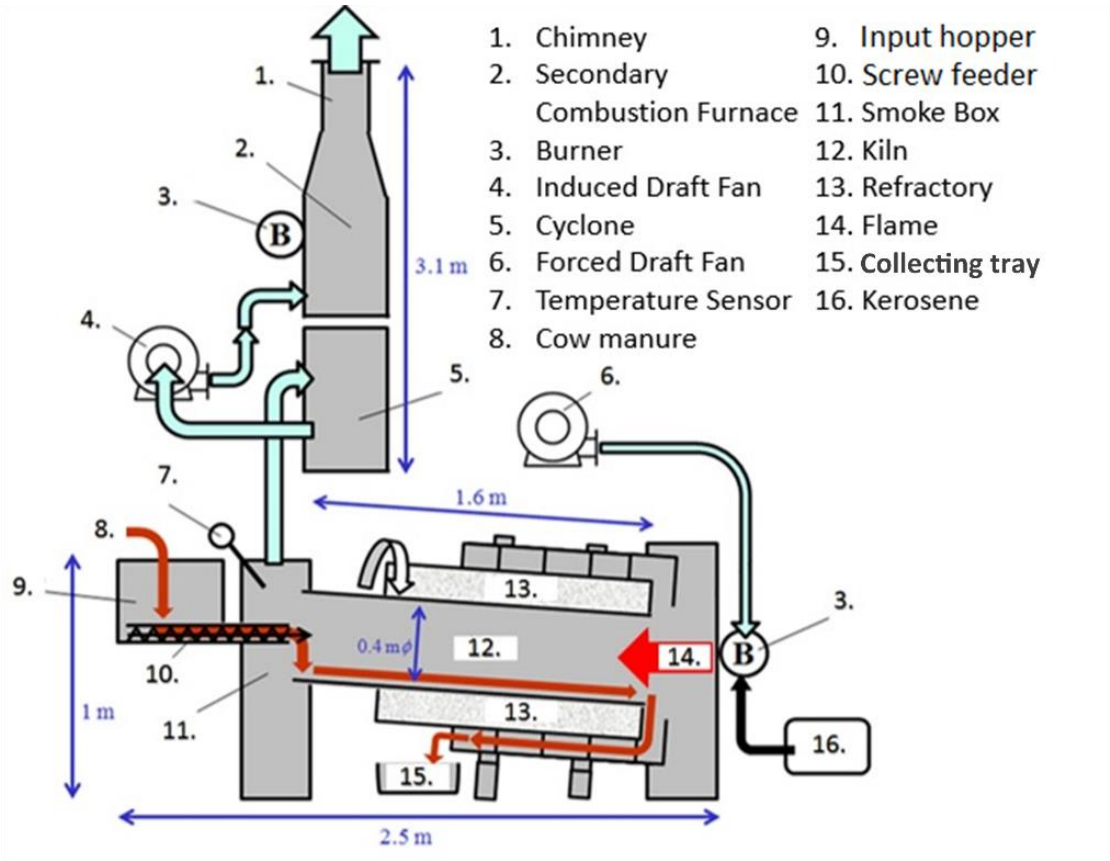

Figure 3.1 – Rotary kiln combustion type reactor.

3.2.4 Analysis

The manure was analyzed before and after torrefaction. Table 1 shows the properties of the fresh dairy manure used in this study. The moisture content, ash-free solid and ash content analyses were conducted as explained previously [17-19]. Moisture content was determined by the difference in weight before and after heating using an oven at 105 °C

Table 1 The properties of fresh dairy manure used in this study

Moisture (%,w.b)	84.1	± 0.2
Ash-free solid (%,d.b)	85.3	± 0.1
Ash (%,d.b)	14.7	± 0.2
Carbon (%)	43.2	± 0.1
Hydrogen (%)	5.9	± 0.3
Nitrogen (%)	2.1	± 0.2
HHV (MJ/Kg)	17.6	± 0.2

All values are expressed as a mean of three measurements ± standard deviation.

for 24 hours. After being oven-dried and weighed, the sample was placed in an electric furnace at 600 °C for 3 hours to determine the ash content. The ash content was determined by the weight difference before and after treatment in the furnace. For carbon, hydrogen and nitrogen content, a CHN analyzer (CE440, Exeter Analytical, Inc.) was used for the analysis. For calorific value, a bomb calorimeter (Ogawa Sampling Co., Ltd., Model OSK 200 digital calorimeter, Tokyo, Japan) was used for the measurement. About 0.5 g of the oven-dried dairy manure was used in the calorimeter for combustion with pure oxygen. Together with mass yield, the measurements were carried out in triplicate. All measurements were performed for the respective thermal treatments (T1, T2, T3 and T4). Mass yield percentage was calculated using equation (1) where Y is the mass yield,

$$Y_n = \frac{\prod_{r=1}^{n} M_{\mathrm{t}r}}{\prod_{r=1}^{n} M_{\mathrm{i}r\text{-}1}} \times 100 \qquad (1)$$

*n=1, 2, 3, 4, ...

n is the number of treatments, M_t is the mass of torrefied sample, and M_i is the initial mass. The ash-free solid content, was determined by the weight difference between oven-dried and ash as explained [17-19] in equation (2), where M_{dry} is the mass of oven-dried solid and M_{ash} is the ash mass.

$$\text{Ash-free solid} = \frac{M_{\text{dry}} - M_{\text{ash}}}{M_{\text{dry}}} \times 100 \qquad (2)$$

The production efficiency (η) of this study was also calculated as formulated in equation (3); where M_i is the initial mass (in dried basis), Y is the mass yield (in dried basis), HHV_t is the higher heating value of torrefied manure, Q is the evaporation heat of water, n is the number of treatments, and E_f and E_e are the fuel and electricity consumption by the reactor, respectively. From the equation, the production of torrefied dairy manure is considered efficient when it is greater than or equal to one.

$$\eta_n = \frac{M_{in} \times Y_n \times \left(HHV_t - Q\right)}{E_f + E_e} \times 100 \qquad (3)$$

$*n = 1, 2, 3, 4, \ldots$

3.3 Results and discussion

3.3.1 Time of heat treatment

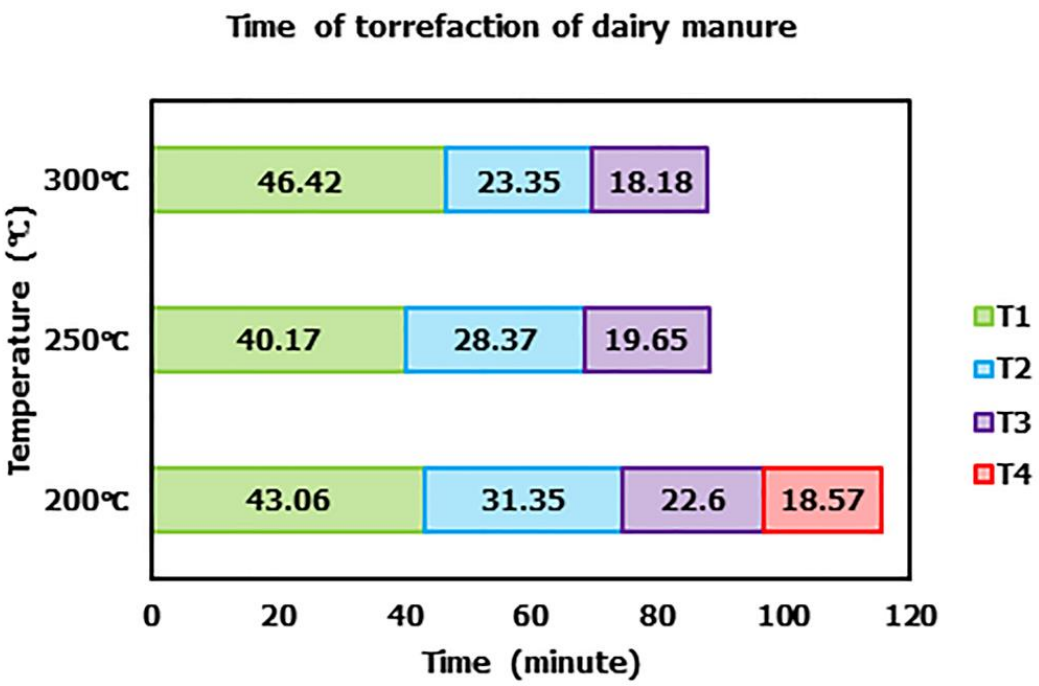

Figure 3.2 – Time of torrefaction at different temperatures.

It was found that four cycles of non-continuous heat treatment processes (T1-T4) were required at the 200 °C set temperature in order to complete the torrefaction of dairy manure. At 250 °C and 300 °C, the manure needed only three heat-treatment cycles for complete torrefaction (T1-T3). Thus, higher temperatures sped up the total time of the

torrefaction process. Torrefaction was completed in 87.95 min at 300 °C, 88.19 min at 250 °C, and 115.58 min at 200 °C. According to the stages of torrefaction, the results of each treatment are identified as follows: T1 is potentially a heating and drying stage and T2 is post-drying, while T3 is the torrefaction and cooling process. T1-T3 are applicable at 250 °C and 300 °C. However, for 200 °C, T1 and T2 are heating and drying, T3 is post-drying, and T4 is torrefaction and cooling. In Fig. 3.2, residence times of the kiln at T1, T2, and T3 for every temperature and T4 for 200 °C are stated accordingly.

3.3.2 Changes in color, retained mass and moisture content for each thermal treatment

Fig. 3.3 describes the sequential process of torrefaction with images tracking the dairy manure taken at T1-T3/T4. The percentage of retained mass and moisture content of the samples are also shown. Fig. 3.3 (a) shows a picture of the fresh dairy manure with its wet condition exposed in brown color. Thereafter, the manure undergoes the first heat treatment (T1) in the reactor at the prescribed temperatures. After approximately 40 minutes, granule and spherical shapes were visible, as shown in Fig. 3.3 (b), (f), and (i). At this stage, surface moisture of the fresh manure was evaporated and the surface no longer appeared wet. The color changed to light brown at 200 °C and 250 °C. However,

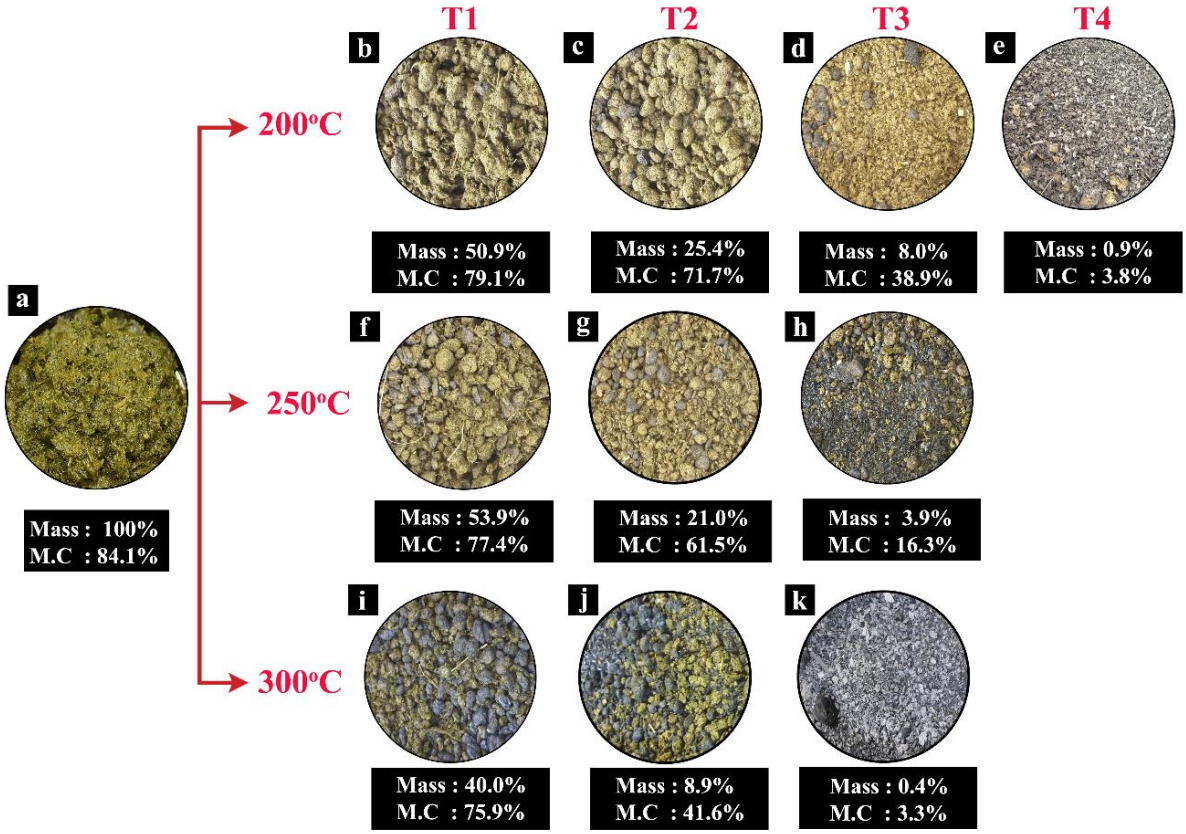

Figure 3.3 – Changes in color, retained mass and moisture content of dairy manure during torrefaction at each temperature.

dairy manure at T1 under 300 °C appeared brownish-black and its darker tones were highly visible compared with T1 at 200 °C and 250 °C. There are several factors that may affect the color changes during torrefaction. They include mass loss, surface and bound moisture, light volatile gases, composition of biomass, changes in the surface properties, formation of different chromophoric groups and the movement of sugar molecules [13]. However, the temperature of torrefaction is considered the key parameter that determines the color changes of torrefied biomass. In this experiment, the solid manure was heated

again in the reactor after T1. At T2, the mass loss was nearly 80 % of the initial mass at 200 °C and 250 °C and 90 % at 300 °C. Regarding the moisture content, there was little difference in the water loss at 200 °C between T1 and T2 because T2 is still considered to be a drying stage (Fig. 3.3 (c)). However, water losses at 250 °C (Fig. 3.3 (g)) and 300 °C (Fig. 3.3 (j)) were 23 % and 43 %, respectively. This is less than the initial moisture content. Additionally, the particle size of the torrefied manure at T2 was reduced (including T3 at 200 °C, Fig. 3.3 (d)). This is due to the reactive drying during the post-drying stage. At this time, bound water was substantially removed and permanent deformation of the biomass structure occurred [20]. At the same time, bonds between hydrogen and carbon were broken and a mild decomposition process took place during the post-drying stage. As a result, the granules were darker at this stage for all temperatures, with the color at 300 °C more pronounced and darker compared to those at 200 °C and 250 °C. Furthermore, the intensity of torrefaction was at its peak at T3 and T4 (for 200 °C), which can be observed from the size reduction of the solid-dried manure. The size of the granules was finer than at T1 and T2. The retained mass was less than 10 % of the original mass (Fig. 3.3 (d), (h), and (k)). Notably, the higher intensity of black color and a major reduction in water loss were also proof of the high torrefaction intensity. The retained moisture content at this torrefaction and cooling stage (T3 and T4) was about

3% except for at 250 °C. In addition, torrefied dairy manure became brittle and darker at all temperatures.

The color and size of the torrefied dairy manure were inhomogeneous. However, the inhomogeneous color and size trend were consistent throughout T1-T3/T4. The most probable reason for this is the non-uniform heat transfer from the rotary kiln reactor. In this kiln (Fig. 3.1), the flue gas from the flame (no. 14) through combustion in the burner is not supplied continuously. Instead, combustion and flame occurred only when the sensor detected that the internal temperature was less than the set temperature. Thus, the sample was heated by the remaining heat from the reactor wall, where the heat is transferred slowly to the biomass. This may result in a temperature gradient by low heat transfer and cause non-uniform heating of biomass in the reactor. From Figure 3.1, since the kiln-end wall (no. 12) is near the flame and burner (no. 14 and 3), it will be hotter than the middle and kiln-end near the input hopper (no. 9). During rotation of the kiln, the dairy manure receives heat from the wall, which is transferred slowly to the kiln-end. Due to the inclination angle of four degrees (4 °), the feedstock transfer at the kiln-end takes some amount of time before entering the collecting tray (no. 15). During this time, the hottest kiln-end wall, which is nearest the flame, results in combustion to some of the feedstock. Therefore, it is assumed that longer manure transfer time and non-uniform

heating in the kiln-end are key factors for the inhomogeneous color and size of the torrefied manure.

3.3.3 Mass yield, moisture content, ash-free solid and HHV

Fig. 3.4 (a) summarizes the reduction of mass, moisture content, ash-free solid and higher heating value (HHV) of dairy manure during torrefaction from T0 to T3/T4. Similar decreasing trends were observed at each temperature for every parameter. Also, a drastic decrease occurred for ash-free solid and HHV after T2 (post-drying stage) at 300 °C. Similar trends were also observed for elemental results of carbon, hydrogen and nitrogen in Fig. 3.4 (b). In contrast, ash content increased during torrefaction from T0 to T3/T4 for each temperature. However, unfavorable results at complete torrefaction were obtained when comparisons between low and high temperatures were made. At 200 °C, due to the four repetitive heat treatments to complete the torrefaction, a longer time was required, more ash-free solid was released and inorganic matter was retained in the form of ash. At the same time, the size of the solid-dried dairy manure during T3 was mostly reduced and further drying in T4 may have ignited combustion of some of the feedstock. These two factors likely contribute to the lower results of mass yield, moisture content, ash-free solid and HHV at 200 °C compared to 250 °C and 300 °C at complete torrefaction. In addition, the results from increasing ash and decreasing of elements further support the

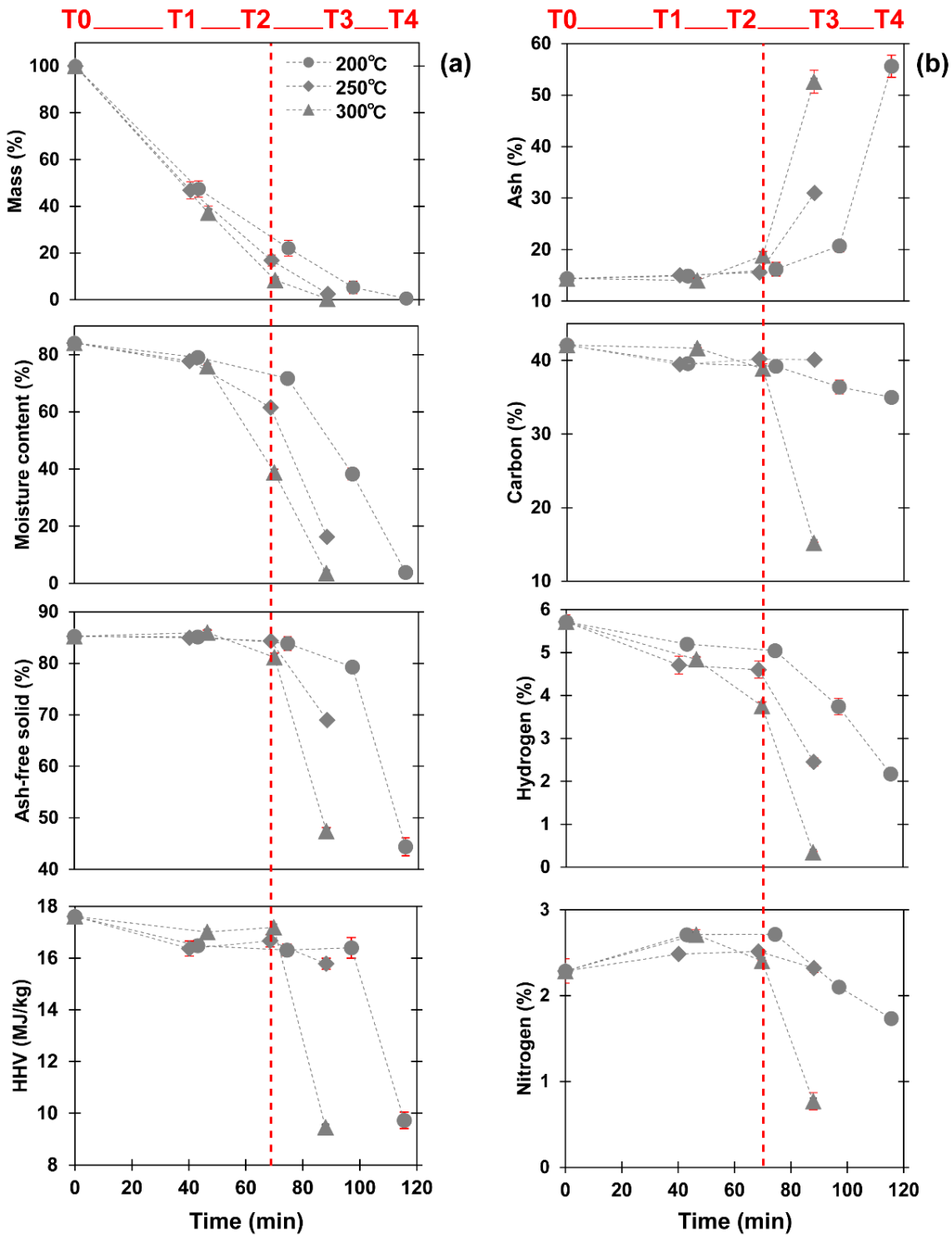

Figure 3.4 – Effect of temperature on (a) mass, moisture content, ash free solid, HHV and (b) ash, carbon, nitrogen and hydrogen of dairy manure during torrefaction over time. The straight dotted lines in red represent heat treatment at T2. The legends describe temperature in °C (error bars = standard deviation).

lower results of ash-free solid and HHV when almost no increment of carbon was observed. On the other hand, the results of the HHV are not in agreement with other studies that reported HHV of torrefied biomass is generally higher than the raw feedstock and increases with temperature [21-23]. In fact, HHV of the current study gives a lower amount compared to the raw feedstock and temperature at complete torrefaction. The trend of the HHV is reduction during the treatment (T1-T4) although a small increase occurred after T1 (for 250 °C and 300 °C) or T2 (for 200 °C). At complete torrefaction, torrefied manure at 250 °C gave the highest HHV at 300 °C it was the lowest. However, the HHV in the raw feedstock was the highest compared to torrefied dairy manure. Similar results were observed in a torrefaction study [24] on oil palm fiber (OPF) and eucalyptus using inert and oxidative conditions. They revealed that HHV of OPF conducted under air atmosphere decreased with temperature (250 °C to 350 °C). Furthermore, the HHV of torrefied OPF at 350 °C (14.9 MJ/kg) was lower than the raw material (17.1 MJ/kg). For eucalyptus, the highest HHV was at 275 °C (23.3 MJ/kg) and it decreased as temperature increased. In contrast, HHV of OPF and eucalyptus in an inert atmosphere provided desirable general torrefaction results of biomass as reported in other literature. Therefore, the lower HHV results of the current study on torrefied dairy manure presumably occurred under atmospheric conditions.

Additionally, the high amount of moisture was also likely a key factor for the lower HHV. Jenkins et al. [25] reported that biomass with high moisture content (about 90 %) required more energy to vaporize water. The vaporization energy necessary exceeded the amount of heating of that biomass. This explains why HHV in T1 was lower for every temperature than the raw feedstock. For example, in T1, the initial moisture content and HHV of fresh dairy manure were 84 % and 17.6 MJ/kg, respectively. When the heat treatment at T1 was completed, HHV decreased to 16.48 MJ/kg, 16.37 MJ/kg and 17.0 MJ/kg at 200 °C, 250 °C and 300 °C, respectively. The remaining moisture content at T1 was also considered high: 79.1 % at 200 °C, 77.4 % at 250 °C, and 75.9 % at 300 °C. The high moisture content of the raw feedstock contributed to the lower HHV because more energy was needed for vaporization. Jenkins et al. [25] also added that flame stability becomes better if the combustion system has less than 50-55 % moisture. Such moisture content sustains the flame and ignites combustion, especially in the presence of oxygen. This causes the drastic decrease of the HHV amount at 200 °C from T3 to T4 (16.40 MJ/kg to 9.73 MJ/kg), and at 300 °C from T2 to T3 (17.19 MJ/kg to 9.46 MJ/kg). For those heat treatments (T3 for 200 °C, and T2 for 300 °C), the moisture content of the feedstock was 38.9 % and 41.6 %, respectively. An amount of moisture lower than 50 % promotes combustion under atmospheric conditions, resulting in the lower HHV of

torrefied dairy manure of T4 and T3 at 200 °C and 300 °C, respectively. At 250 °C, the torrefied dairy manure at T3 was not affected by combustion because the moisture content of the feedstock at T2 was 61.5 %, which is more than 50-55 %. Hence, this resulted in the highest HHV at complete torrefaction at 250 °C, but the amount was still lower than the raw feedstock due to the higher moisture content and torrefaction that occurred under atmospheric conditions.

3.3.4 Production efficiency of dairy manure torrefaction

In order to determine the optimum torrefaction temperature for high moisture content dairy manure using an industrial rotary kiln combustion type reactor, the production efficiency was calculated. We defined a formula (equation 3) between output and input energies. Output energy is the energy gain from the torrefied manure while input energy is the energy used to produce torrefied manure during torrefaction. In this study, the torrefied manure retained a high amount of moisture. Generally, the moisture content of solid biofuels intended for energy purposes should be in the range of 10-15 % [26, 27]. Therefore, in order to determine the output energy, we must consider the energy that is used to evaporate water in the torrefied manure. This is calculated by subtracting the amount of evaporation heat of water (Q) from the calorific

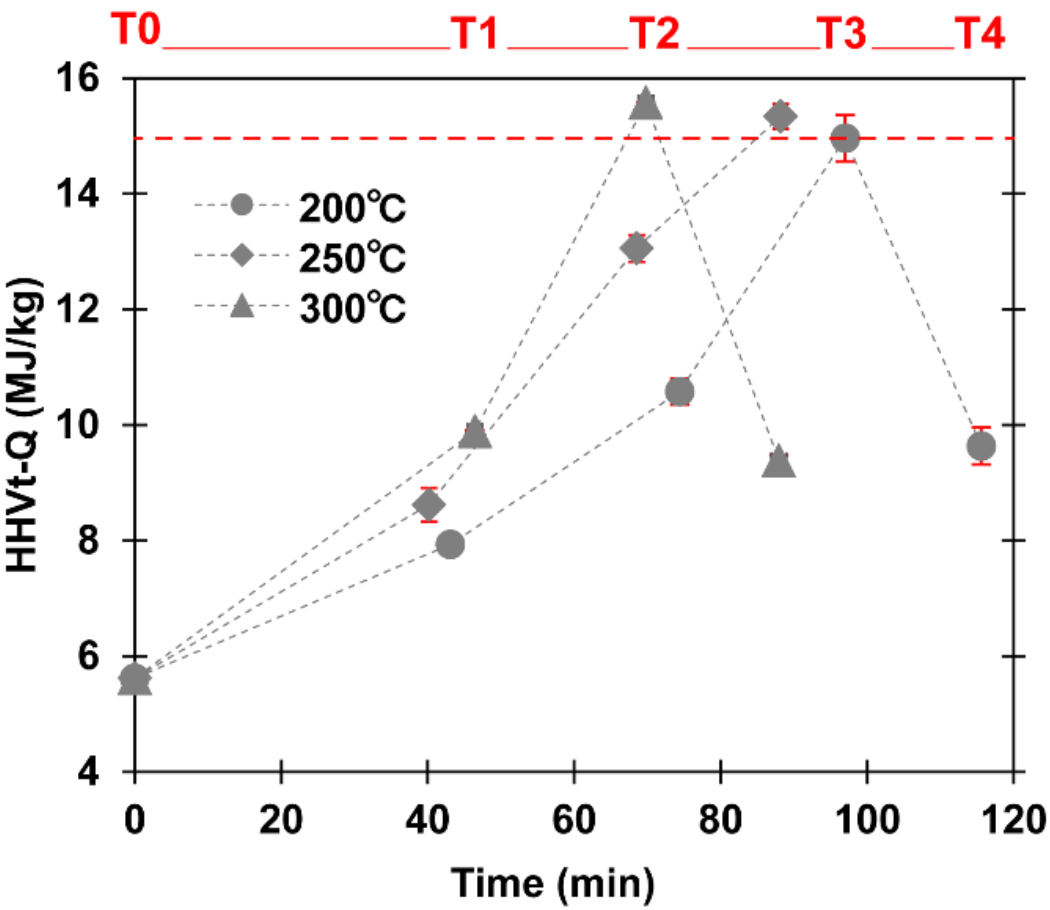

Figure 3.5 – Higher heating value of torrefied dairy manure after evaporation (HHVt-Q). The straight dotted line in red represent the amount of 15.0 MJ/Kg which is the average of the highest HHVt-Q for each temperature (error bars = standard deviation).

value of torrefied dairy manure (HHV_t). From equation (3), this is translated as (HHV_t - Q). Fig. 3.5 shows the calorific value of torrefied manure after evaporation (HHV_t - Q). On average, the highest calorific value after evaporation for each temperature was around 15.0 MJ/kg (dotted line). In particular, values of HHV_t - Q at 200 °C, 250 °C and 300 °C are 14.96 MJ/kg, 15.34 MJ/kg and 15.58 MJ/kg, respectively. Those values were used in equation (3) to determine the production efficiency for every temperature.

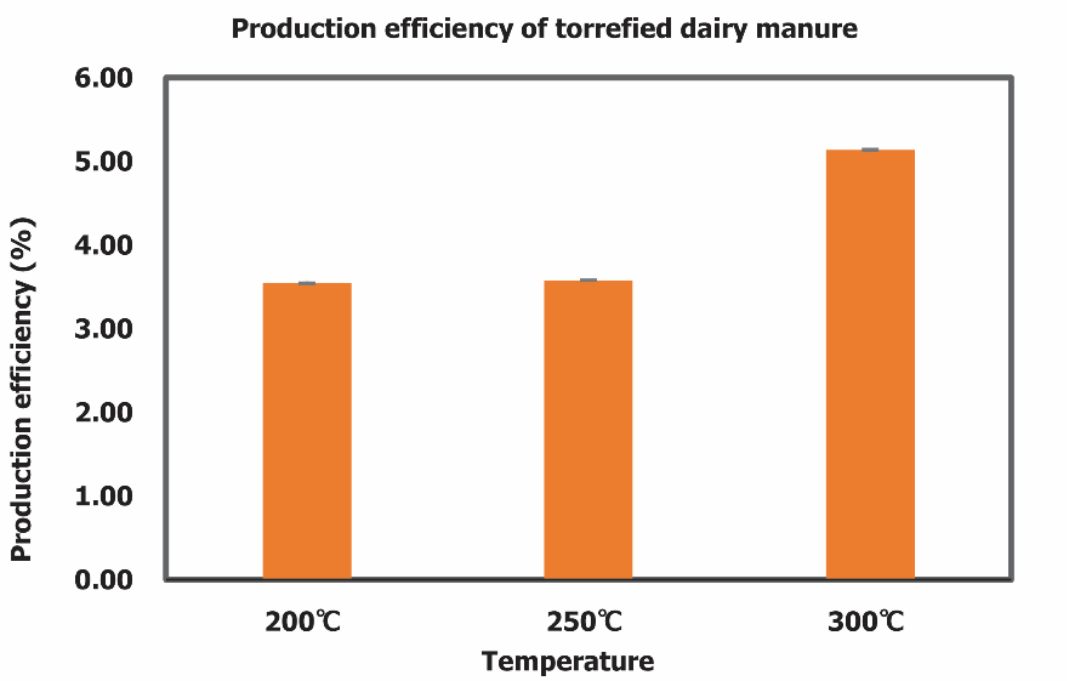

Figure 3.6 – Production efficiency of torrefied dairy manure (error bars = standard deviation).

Fig. 3.6 shows the production efficiency of torrefied dairy manure, which was calculated according to equation (3). From the graph, 300 °C is the optimum temperature for torrefaction of high moisture content dairy manure using an industrial rotary kiln combustion type reactor with 5 % efficiency. This is, followed by 250 °C and 200 °C, each with 3.5 % production efficiency. These results showed that torrefaction at higher temperature was more efficient because the least time was consumed for the heat treatment. This is further related to the consumption of less fuel and electricity for the shorter time. In the case of 300 °C, the efficiency was consider under the torrefied dairy

manure at T2, where the total heat treatment time (69.77 min) was shorter than T3 in the case of 250 °C (88.19 min) and 200 °C (97.01 min). This clarifies that production efficiency is better at higher temperature due to lower energy consumption and shorter treatment time. Therefore, torrefaction of high moisture content dairy manure using an industrial rotary kiln combustion type reactor is possible and recommended at 300 °C. However, the 5 % production efficiency at 300 °C is still considerably low. This low production efficiency using rotary kiln may be increased by improving electricity and fuel from the burner. Generally, rotary kilns tend to loses heat during operation. Therefore, the heat loss should be reduced so that high production efficiency can be achieved. One of the way is by applying heat recovery technology to the rotary kiln for minimizing heat loss [28]. For example, installing a heat recovery exchanger in the flue gas outlet. Controlling the emission of the flue gas could also presumably promote effective ventilation, such that the drying rate and residence time of the wet dairy manure torrefaction may be accurately predicted. At the same time, overheating may occur at the drum surface because of convection and radiation heat transfer from the kiln wall to the material during tumbling. Thus, adopting a heat recovery exchanger at the hot surface of the kiln [29-31] will also be beneficial for reducing convection and radiation heat loss to further enhance heat transfer between the kiln wall and the sample.

Mixing wet manure with agricultural residue is another alternative to improve energy consumption. An energetics study using a pyrolysis reactor [32] showed that a mixture of swine manure and rye grass (75 % and 10 % moisture content, respectively) only required 0.5 MJ of additional heating to produce 1 kg of value-added biochar. In comparison, 12.5 MJ/kg of energy was needed by the swine manure alone when pyrolyzed in a similar reactor. The study concluded that the energy efficiency of wet manure may be further increased by co-pyrolysis with more energy dense and drier sources such as waste plastic pellets to produce the same amount of biochar. Although this study was applied to pyrolysis, the co-digestion of manure and other biomasses may also be applicable for torrefaction to increase production efficiency since both technologies are similar, with the exception of the operation temperature.

3.4 Summary

In summary, torrefaction of fresh dairy manure in an industrial rotary kiln combustion type reactor was investigated. The wet dairy manure was converted to a solid product or torrefied manure. Due to its high moisture content, at least three cycles of non-continuous thermal treatment were required to complete the torrefaction. For the same reason, no increase of HHV was observed for the torrefied dairy manure in comparison

with the raw feedstock. Production efficiency calculations showed that the fresh dairy manure was torrefied better at higher temperatures (250 °C and 300 °C) with lower energy consumption and in a shorter time. The torrefaction of wet manure may be further enhanced in an upgraded industrial rotary kiln combustion type reactor with a heat exchanger or by combining the wet feedstock with other agricultural residue.

References

[1] D. Thrän, D. Peetz, K. Schaubach, Global wood pellet industry and trade study 2017. *IEA Bioenergy Task 40 Report* (2017).

[2] J. H. Peng, X. T. Bi, S. Sokhansanj, C. J. Lim, Torrefaction and densification of different species of softwood residues. *Fuel* **111** (2013) 411-421.

[3] S.-W. Park, C.-H. Jang, K.-R. Baek, J.-K. Yang, Torrefaction and low-temperature carbonization of woody biomass: Evaluation of fuel characteristics of the products. *Energy* **45** (2012) 676-685.

[4] B.-S. Chiou, D. Valenzuela-Medina, C. Bilbao-Sainz, A. P. Klamczynski, R. J. Avena-Bustillos, R. R. Milczarek, W.-X. Du, G. M. Glenn, W. J. Orts, Torrefaction of almond shells: Effects of torrefaction conditions on properties of solid and condensate products. *Industrial Crops and Products* **86** (2016) 40-48.

[5] Y. Mei, Q. Che, Q. Yang, C. Draper, H. Yang, S. Zhang, H. Chen, Torrefaction of different parts from a corn stalk and its effect on the characterization of products. *Industrial Crops and Products* **92** (2016) 26-33.

[6] X. Cao, W. Harris, Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource Technology* **101** (2010) 5222-5228.

[7] K. B. Cantrell, P. G. Hunt, M. Uchimiya, J. M. Novak, K. S. Ro, Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresour Technol* **107** (2012) 419-428.

[8] K. Y. Chan, L. Van Zwieten, I. Meszaros, A. Downie, S. Joseph, Using poultry litter biochars as soil amendments. *Soil Research* **46** (2008) 437-444.

[9] N. Touray, W.-T. Tsai, H.-R. Chen, S.-C. Liu, Thermochemical and pore properties of goat-manure-derived biochars prepared from different pyrolysis temperatures. *Journal of Analytical and Applied Pyrolysis* **109** (2014) 116-122.

[10] J. Poudel, T.-I. Ohm, S.-H. Lee, S. C. Oh, A study on torrefaction of sewage sludge to enhance solid fuel qualities. *Waste Management* **40** (2015) 112-118.

[11] J. Poudel, T.-I. Ohm, S. C. Oh, A study on torrefaction of food waste. *Fuel* **140** (2015) 275-281.

[12] P. Brachi, F. Miccio, M. Miccio, G. Ruoppolo, Torrefaction of tomato peel residues in a fluidized bed of inert particles and a fixed-bed reactor. *Energy & Fuels* **30** (2016) 4858-4868.

[13] D. R. Nhuchhen, P. Basu, B. Acharya, Torrefaction of poplar in a continuous two-stage, indirectly heated rotary torrefier. *Energy & Fuels* **30** (2016) 1027-1038.

[14] J. C. Carrasco, G. S. Oporto, J. Zondlo, J. Wang, *Observed kinetic parameters during the torrefaction of red oak (quercus rubra) in a pilot rotary kiln reactor.* (2014), vol. 9.

[15] Y. Mei, R. Liu, Q. Yang, H. Yang, J. Shao, C. Draper, S. Zhang, H. Chen, Torrefaction of cedarwood in a pilot scale rotary kiln and the influence of industrial flue gas. *Bioresource Technology* **177** (2015) 355-360.

[16] B. Colin, J. L. Dirion, P. Arlabosse, S. Salvador, Wood chips flow in a rotary kiln: Experiments and

modeling. *Chemical Engineering Research and Design* **98** (2015) 179-187.

[17] F. Miyatake, K. Iwabuchi, Effect of compost temperature on oxygen uptake rate, specific growth rate and enzymatic activity of microorganisms in dairy cattle manure. *Bioresource Technology* **97** (2006) 961-965.

[18] R. B. Saludes, K. Iwabuchi, A. Kayanuma, T. Shiga, Composting of dairy cattle manure using a thermophilic–mesophilic sequence. *Biosystems Engineering* **98** (2007) 198-205.

[19] R. B. Saludes, K. Iwabuchi, F. Miyatake, Y. Abe, Y. Honda, Characterization of dairy cattle manure/wallboard paper compost mixture. *Bioresource Technology* **99** (2008) 7285-7290.

[20] D. R. Nhuchhen, P. Basu, B. Acharya, A comprehensive review on biomass torrefaction. *International Journal of Renewable Energy & Biofuels* **2014** (2014) 1-56.

[21] S. Matali, N. A. Rahman, S. S. Idris, N. Yaacob, A. B. Alias, Lignocellulosic biomass solid fuel properties enhancement via torrefaction. *Procedia Engineering* **148** (2016) 671-678.

[22] J. Kihedu, Torrefaction and combustion of ligno-cellulosic biomass. *Energy Procedia* **75** (2015) 162-167.

[23] C. Wang, J. Peng, H. Li, X. T. Bi, R. Legros, C. J. Lim, S. Sokhansanj, Oxidative torrefaction of biomass residues and densification of torrefied sawdust to pellets. *Bioresource Technology* **127** (2013) 318-325.

[24] K.-M. Lu, W.-J. Lee, W.-H. Chen, S.-H. Liu, T.-C. Lin, Torrefaction and low temperature carbonization of oil palm fiber and eucalyptus in nitrogen and air atmospheres. *Bioresource Technology* **123** (2012) 98-105.

[25] B. M. Jenkins, L. L. Baxter, J. Koppejan, Biomass combustion. In *Thermochemical processing of biomass*, R. Brown, Ed. (John Wiley & Sons, Ltd, 2011), pp. 13-46.

[26] L. Chen, L. Xing, L. Han, Renewable energy from agro-residues in china: Solid biofuels and biomass briquetting technology. *Renewable and Sustainable Energy Reviews* **13** (2009) 2689-2695.

[27] P. D. Jensen, H. Hartmann, T. Böhm, M. Temmerman, F. Rabier, M. Morsing, Moisture content determination in solid biofuels by dielectric and nir reflection methods. *Biomass and Bioenergy* **30** (2006) 935-943.

[28] K. Sztekler, M. Komorowski, M. Tarnowska, Ł. Posak, Utilization of waste heat from rotary kiln for burning clinker in the cement plant. *E3S Web Conf.* **10** (2016) 00095.

[29] Q. Yin, W.-J. Du, X.-L. Ji, L. Cheng, Optimization design and economic analyses of heat recovery exchangers on rotary kilns. *Applied Energy* **180** (2016) 743-756.

[30] A. C. Caputo, P. M. Pelagagge, P. Salini, Performance modeling of radiant heat recovery exchangers for rotary kilns. *Applied Thermal Engineering* **31** (2011) 2578-2589.

[31] V. Karamarković, M. Marašević, R. Karamarković, M. Karamarković, Recuperator for waste heat recovery from rotary kilns. *Applied Thermal Engineering* **54** (2013) 470-480.

[32] K. S. Ro, K. B. Cantrell, P. G. Hunt, High-temperature pyrolysis of blended animal manures for

producing renewable energy and value-added biochar. *Industrial & Engineering Chemistry Research* **49** (2010) 10125-10131.

CHAPTER 4

Reaction mechanism of fresh dairy manure torrefaction

4.1 Brief summary

In this chapter, the highlight is to understand the reaction mechanism of high moisture content dairy manure during torrefaction. Thus, a continuous thermal degradation of high moisture content dairy manure in an atmospheric condition was conducted using a laboratory oven. The sample was a fresh dairy manure with mass approximately 100g and 84% moisture content with 1cm thick were put into a heat-resistant wired basket. The basket size was 10 (W) x 10 (L) and 10 (H) cm. The basket contained sample hung onto a mass balance for mass measurement. The balance was located on top of the oven and the reading from the balance was connected to the computer. Thermocouples was attached to the manure to determine sample temperature. For gas sampling, a teflon tube was placed 3cm distance from the surface of the sample to get the CO_2 reading using photoacoustic gas monitor. The experiments stop when the sample temperature reached the oven temperature. Resultant mass profile data confirmed that the torrefaction reaction involved a simultaneous process of drying and degradation. For a comprehensive prediction, we develop a simplified mathematical model for both process based on exponential model.

4.2 Background

In chapter 3, we identified that due to high moisture, at least three cycles of non-continuous thermal treatment were required to complete the torrefaction. Due to non-continuous steps, the thermal reaction of torrefaction on high moisture content biomass in atmospheric condition could not easily be determined from the industrial rotary kiln combustion type reactor. Nevertheless, on the basis of the characteristics and properties of solid torrefied manure, drying and thermal decomposition steps were strongly involved.

In this present work, a continuous thermal degradation of high moisture content dairy manure was conducted using a laboratory oven to further investigate the drying and decomposition processes involvement. The weight loss profile data was collected and treated as a major source to understand the reaction. Although several studies on thermal treatment of dairy manure have been reported [1-3], most of them are using dried dairy manure as a feedstock instead of wet. No data has been published related with the direct usage of fresh dairy manure for a continuous thermal treatment to the time this study was conducted. By using high moisture content biomass, the prediction for reaction mechanism of biomass through a continuous torrefaction processes can be determined accurately and may beneficial for real case scenario. Therefore, considering the points above, this research aims to better understand the thermal reaction mechanism of high

moisture content biomass from fresh dairy manure through a continuous torrefaction. We believe these results can accommodate the underlying mechanism during the dairy manure torrefaction.

4.3 Materials and methods

4.3.1 Sample collection

Fresh dairy manure was collected from experiment farm of Field Science Centre for Northern Biosphere, Hokkaido University. The fresh manure was stored in a laboratory fridge. Prior to experiment, the manure was rested at room temperature for 24 hours.

4.3.2 Wire-basket test

The experiment was carried out using a heat-resistant wire basket in a laboratory oven as illustrated in Figure 4.1. The heat-resistant wire basket is 10 (W) x 10 (L) and 10 (H) cm in size. Real-time data were recorded for mass, sample temperature and gas emissions using mass balance (Shimadzu UW1020H small pan model), midi logger (Graphtec corporation model GL220) and photoacoustic gas monitor (INNOVA 1412i Lumasense technologies) respectively. The wire-basket test is a thermogravimetric analysis (TGA)-like experiment. The sample, which was a fresh dairy manure with mass approximately 100g and 86.1 % moisture content with 1cm thick was put into a heat-resistant wire basket.

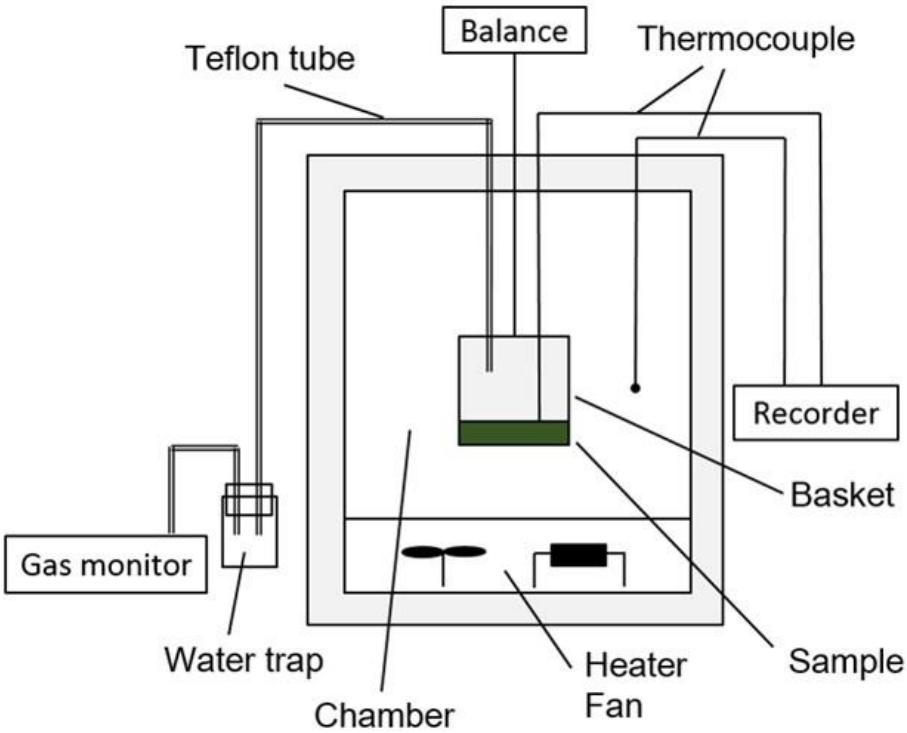

Figure 4.1 – Schematic diagram of the experiment set up using a laboratory oven.

The basket hung onto a mass balance for mass measurement where balance was located on top of the oven. Three 2-4 K-type thermocouples was attached to midi logger and the thermocouple was placed approximately 0.5 cm depth inside the sample to determine sample temperature. For gas sampling, a teflon tube that connected to the gas monitor was placed 3 cm distance from the surface of the sample to get the CO_2 reading. Intervals time was set 30 seconds for mass and sample temperature and 2 minutes for gas emission. The experiments stop when the sample temperature reached the oven temperature. All

data for mass, sample temperature and gas emission during were real time recorded and stored to in the experiment PC.

The experiments were replicated three times at a constant oven temperature at 200 °C, 250 °C, 300 °C and 350 °C respectively and the results obtained were almost identical. For mass reduction data, mass reduction rate (V_t, gmin^{-1}) curve was derived by taking the difference of mass at interval minute as shown in equation (1). *M* is the sample mass at time *t* while *n* is the minute of interval.

$$V_t = \frac{M_{(t-n/2)} - M_{(t+n/2)}}{n} \qquad (1)$$

From the preliminary experiments, it was found that no significant peak observed from mass reduction rate curve of fresh dairy manure torrefaction at 200 °C. Thus, additional treatment temperature were taken into account which were 260 °C, 270 °C, 280 °C and 290 °C to support the results from 250 °C. The experiments were replicated three times and were conducted similarly.

4.4 Results and discussion

4.4.1 Mass reduction, sample temperature and CO_2 emission

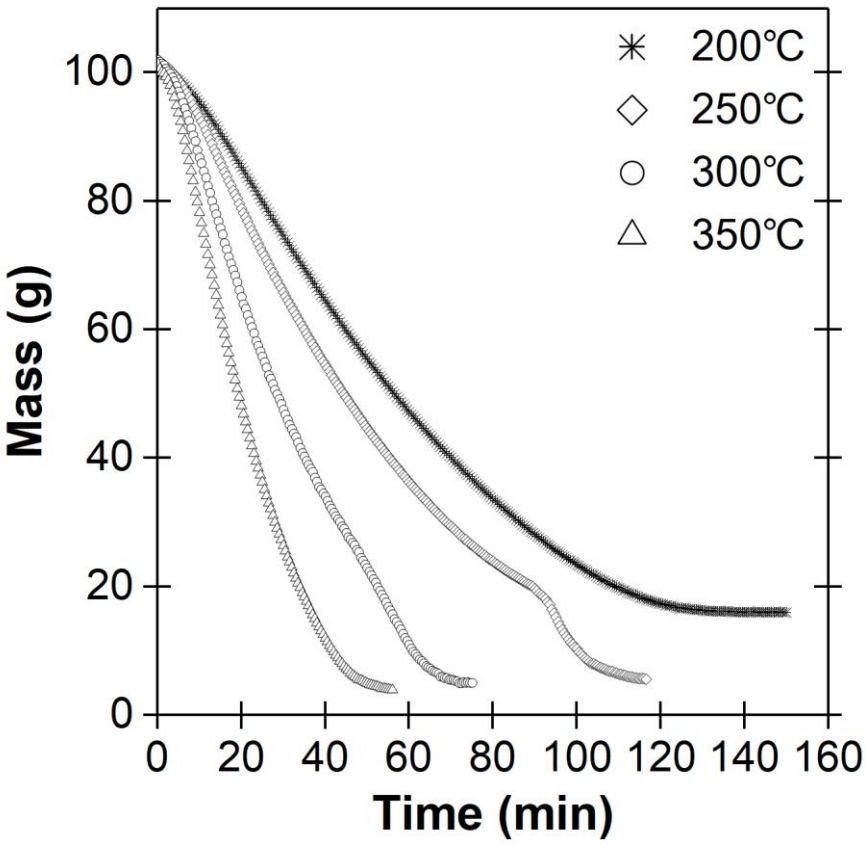

Figure 4.2 – Mass reduction of fresh dairy manure in atmospheric condition.

Figure 4.2 shows the mass reduction of fresh dairy manure at atmospheric condition for 200 °C, 250 °C, 300 °C and 350 °C. Higher temperature resulted in greater mass reduction, i.e., shorter torrefaction time. On the other hand, in exception with 200 °C, a distinct peaks at 90 min, 50 min and 40 min appear in mass reduction curves of 250 °C, 300 °C and 350 °C, respectively. Particularly in reference to 250 °C treatment results, the onset of the

distinct peak is well observed. The peaks distinguished the curve into two region. The region clarify two processes occurred simultaneously in the high moisture dairy manure: drying and decomposition processes. The onset of the peak is confirmed from a mass reduction rate ($gmin^{-1}$) curve (Figure 4.3).

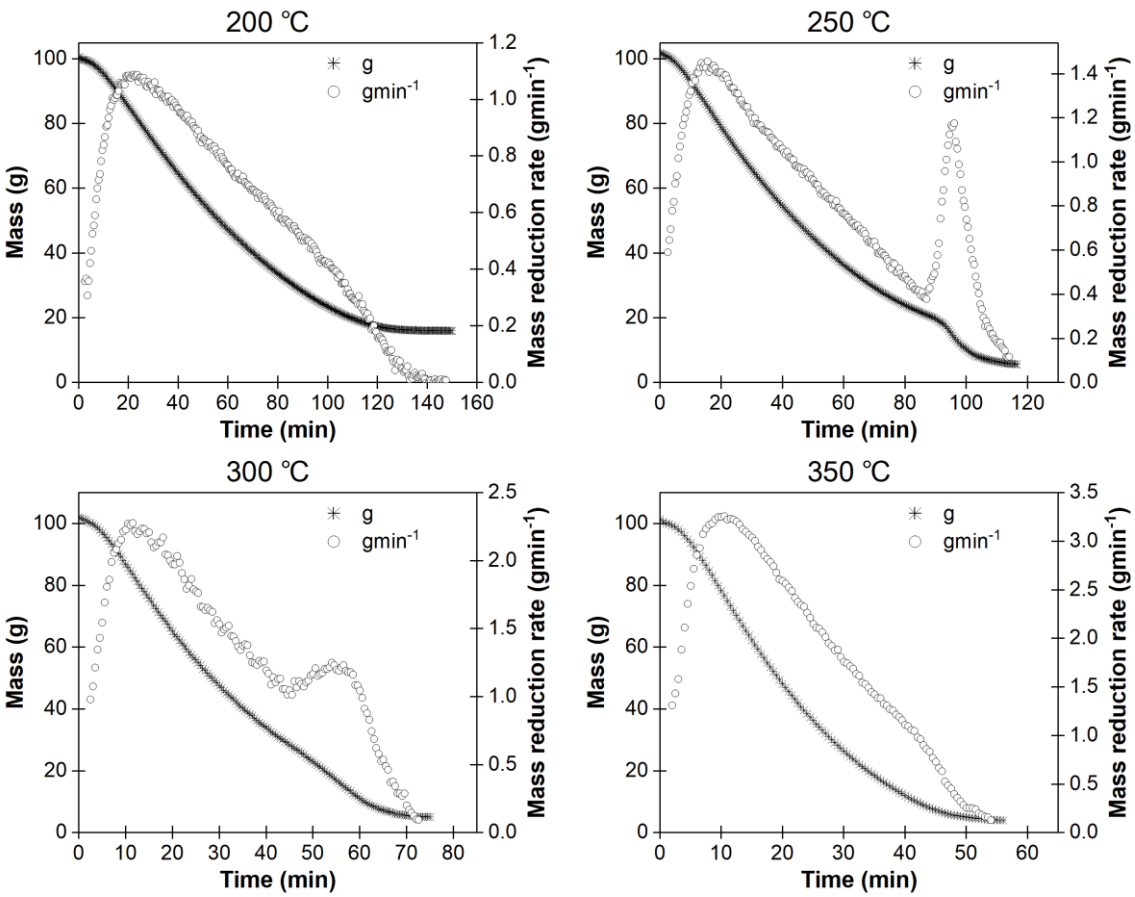

Figure 4.3 – Mass reduction and mass reduction rate curve.

In Figure 4.3, at 250 °C, the mass reduction rate ($gmin^{-1}$) curve (yellow) trend can be observed by four consecutive stages. First stage is preparation and initial heating

of the sample or preheat period. This stage takes about 15 minutes until the first peak appearance. In second stage, the sample goes through a drying process or drying period. This gives rise to a gradual mass reduction for about 75 minutes until a second peak appeared. The third stage is the torrefaction process or oxidation period. Here, a dramatic increase of the second peak was observed. At this point, devolatilization and decomposition process occurred for 10 minutes. Then, at the final stage, the second peak decreased gradually and occurred within 20 minute. Similar pattern of the mass reduction rate ($gmin^{-1}$) curve has also observed at 300 °C and 350 °C but the duration of the four consecutive stages reduced as the temperature increase. In general, torrefaction stages include heating, drying, post-drying, torrefaction, and cooling [4]. On the basis of our mass reduction curves results, the four consecutive stages are consistent with general stages of torrefaction. However, in this study, 200 °C could not satisfy those stages as only a single peak and a gradual mass loss have been observed. The absence of successive second peak translates to low impact of torrefaction in this temperature. Here, the unfavorable of 200 °C as torrefaction treatment temperature has been previously suggested by [5], which torrefaction rate under 220 °C is conceivably too low. In addition, temperatures equal or less than 240 °C have a low impact of biomass torrefaction [6]. Indeed, our finding is in agreement with the low impact of torrefaction at 200 °C. In regards to the drying and

decomposition of dairy manure from mass reduction profile, Figure 4.4 (a) and (b) presented the sample temperature and CO_2 emission data to confirmed the condition. CO_2 generated as a non-condensable product during torrefaction [7].In brief, one could clearly observed the curves appeared with a constant line and a dramatic peak from both parameters. These translated the occurrence of a simultaneous drying and decomposition in the torrefaction. The curves still appear in four consecutive steps for sample temperature and CO_2 emission, respectively. Nevertheless, sharp peak is still absent at 200 °C in comparison with 250 °C, 300 °C and 350 °C. The peak absence is due to low impact of torrefaction at 200 °C and only drying process occurrence. In particular, according to [4], drying in torrefaction classified into two types: reactive and non-reactive drying. In non-reactive drying, surface water of biomass is removed and occurs in temperature range of 50 - 150 °C. On the other hand, reactive drying removes the bound water and takes place from 150 - 200 °C.

From our result in Figure 4.4 (a) , although the treatment temperature in the oven were set higher from to 200, 250, 300 and 350 °C, the constant line of the sample temperature that presented drying process (~100 °C) took fairly some amount of time to reach oven temperature due to high moisture. This also can be explained due to the thermal movement from the outside surface of a biomass particle to the center [8] . Both

heating and drying processes started from the outside surface. Heat from the outside

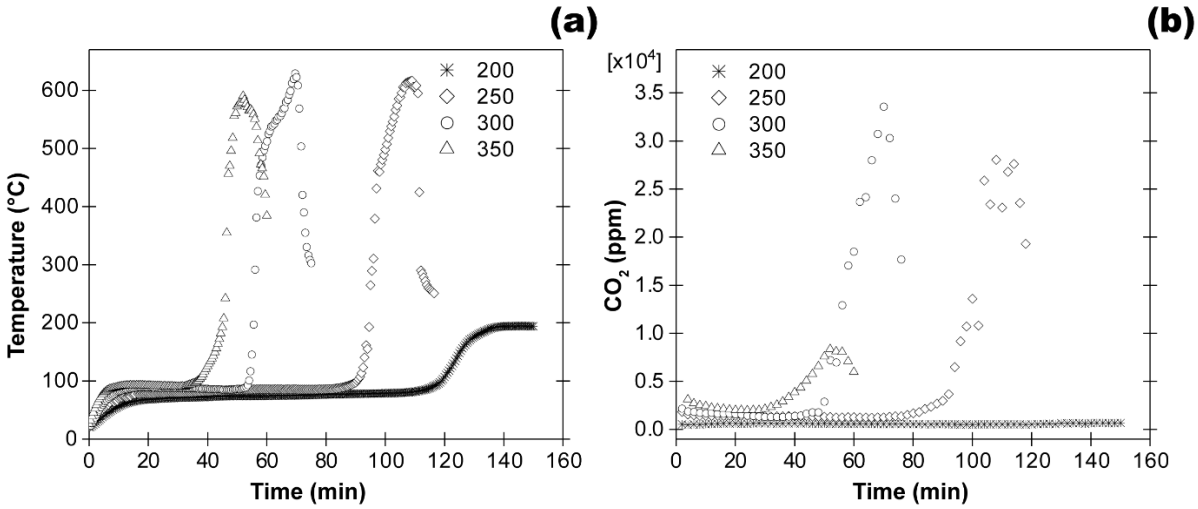

Figure 4.4 – (a) Sample temperature and (b) CO_2 emissions.

surface will move forward to the center to continue drying. In this study, the manure is set to be in room temperature prior treatment. Then, oven is set to desired reaction temperature. When the manure entered the oven, its outside surface's temperature increase immediately. On the contrary, the center's temperature increase slowly due to thermal movement lagging. Larger sample particle gives rise to longer delay of thermal movement. Thus, the constant line from inside temperature presented the drying temperature of fresh dairy manure at the center which is between 68 - 80 °C, 78-.90 °C, 80- 90°C, and 90- 100°C for thermal treatment of 200 °C, 250 °C, 300 °C and 350 °C respectively. In summary, the overview of torrefaction reaction of high moisture content biomass through fresh dairy manure is described in Fig. 4.5. Representative results from

250 °C treatment are taken to explain the phenomenon. Results of mass reduction, sample temperature and CO_2 emission are plotted accordingly to describe related processes. During mass reduction, drying process took place at the first 90 minutes including preheating for about 10 minute and followed by decomposition process (Fig. 4.5a). In sample temperature and CO_2 emission plots (Fig. 4.5b), drying and decomposition events are clearly understood by the constant line whilst decomposition process is signified by the rise and maximum point of the peak. At this point, the drying and decomposition phenomenon prominently led the torrefaction of high moisture content dairy manure. In correspond to those processes, the biomass water residue condition is inspected during transition from drying and decomposition. For this purpose, moisture content loss is plotted as in Fig. 4.5a. From the curve, the moisture content decrease gradually during the drying process. At the end of 90 minutes of drying, which is also marks the beginning of decomposition, some amount of water still remained at this transition point. When the decomposition process is about to begin, the moisture content fell steeply. Moisture content of biomass decrease faster in comparison to the mass reduction. In this situation, it is understood that during high moisture content dairy manure drying, the water may not completely vaporized. Instead, the remaining water loss rapidly during decomposition process, which explained the reason for steep fall of moisture content curve.

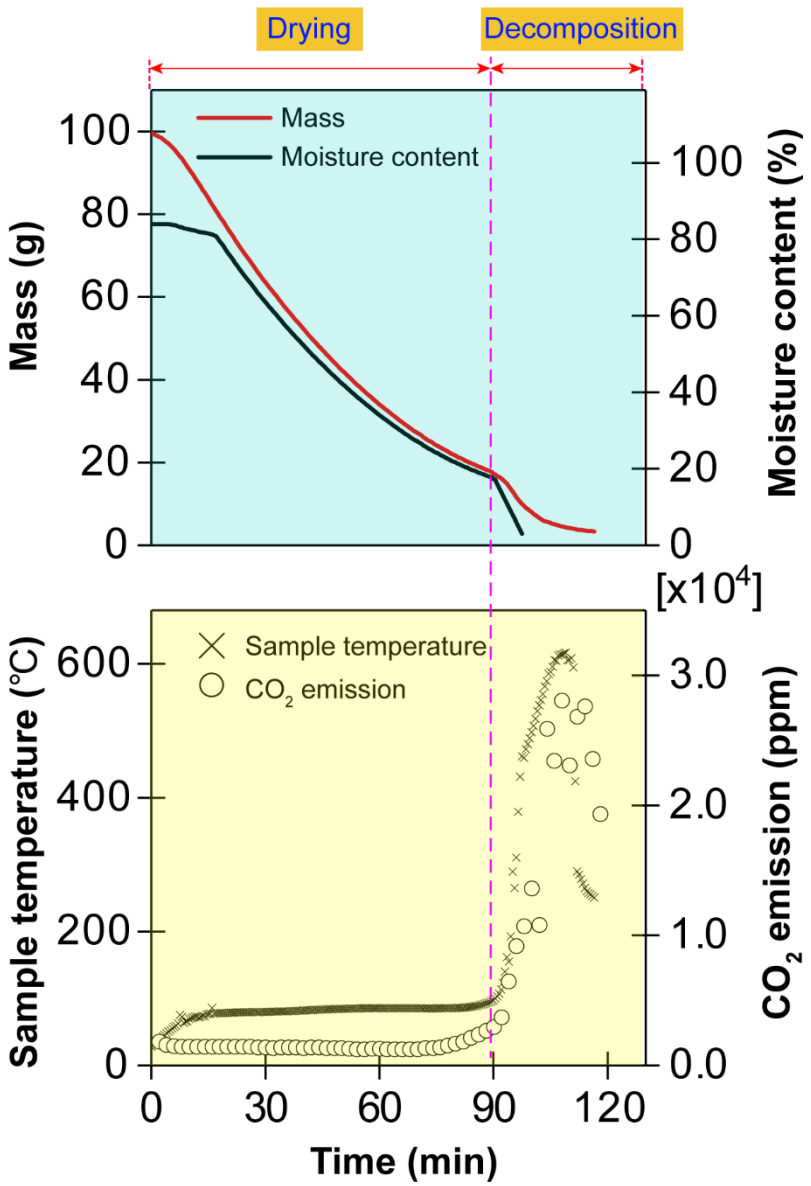

Figure 4.5 – An overview of torrefaction reaction of high moisture content biomass through fresh dairy manure. (a) Red and black lines are mass and moisture content, respectively. (b) Red plot is sample temperature and black plot is CO_2 emission.

4.4.2 Development of mathematical model

Now, based from the mass reduction curve in Fig. 4.5a, it is understood that drying and decomposition reactions are responsible for the wet dairy manure's torrefaction. In particular, moisture content still remained during transition from drying to decomposition process. In order to establish the mechanism explanation for this type of torrefaction, a mathematical model is necessary. Thus, the development of the model is explained. Driven by the fundamental mass reduction data, the principle behind the mathematical model is to estimate the time for drying process to end. For this purpose, three groups of variable are calculated and plotted: mass reduction rate, mass reduction acceleration and moisture content loss to determine the sampling area. In order to express these variables mathematically, the mass reduction rate v_t (g min^{-1}) and mass reduction acceleration a_t (g min^{-2}) are calculated as formulated in equation (1) and (2) respectively. Mass reduction rate (V_t; gmin^{-1}) was derived by taking the difference of mass at interval minute where M

$$v_t = \frac{M_{(t-n/2)} - M_{(t+n/2)}}{n} \quad (1)$$

$$a_t = \frac{v_{(t-n/2)} - v_{(t+n/2)}}{n} \quad (2)$$

is the sample mass at time t while n is the minute of interval. For mass reduction acceleration rate, a_t, it is obtained by the difference of mass reduction rate at interval time. Fig 4.7b illustrate the graph of equation (1) and Fig 4.7c for equation (2). Results from 250 °C treatment are taken to express the mathematical calculation into graph. Similar graph from temperature treatment of 260, 270, 280, 290, 300 and 350 °C are illustrated in Fig 4.7 (mass reduction rate, v_t) and 4.8 (mass acceleration rate, a_t).

From Fig. 4.6b and c, sampling data for the mathematical model is distinguished into three period and regarded as preheating and constant rate drying, decrease drying period, and a period of oxidation of organic matter. Herein, for simplicity, preheating period, decreasing period, oxidation period terms are used. Then, for each of three divided periods, a model for expressing time change of mass is created accrodingly. Meaning that, all three model from those periods were considered dependent on residence time and set temperature. In order to expres the temperature dependence, Arrhenius's equation is equation (equation 3) is adapted. k is the rate constant for drying. Here, i is an integer distinguishing each period, and it corresponds to the preheating period when i = 0, decreasing period when i = 1, and oxidation period when i = 2. The A_i is the frequency factor ([s^{-1}] and E_i is the activation energy (kJ mol^{-1}). R is the gas constant (J K^{-1} mol^{-1}) and T is the set temperature (K). Thereafter, the constant rate k for preheating, decreasing

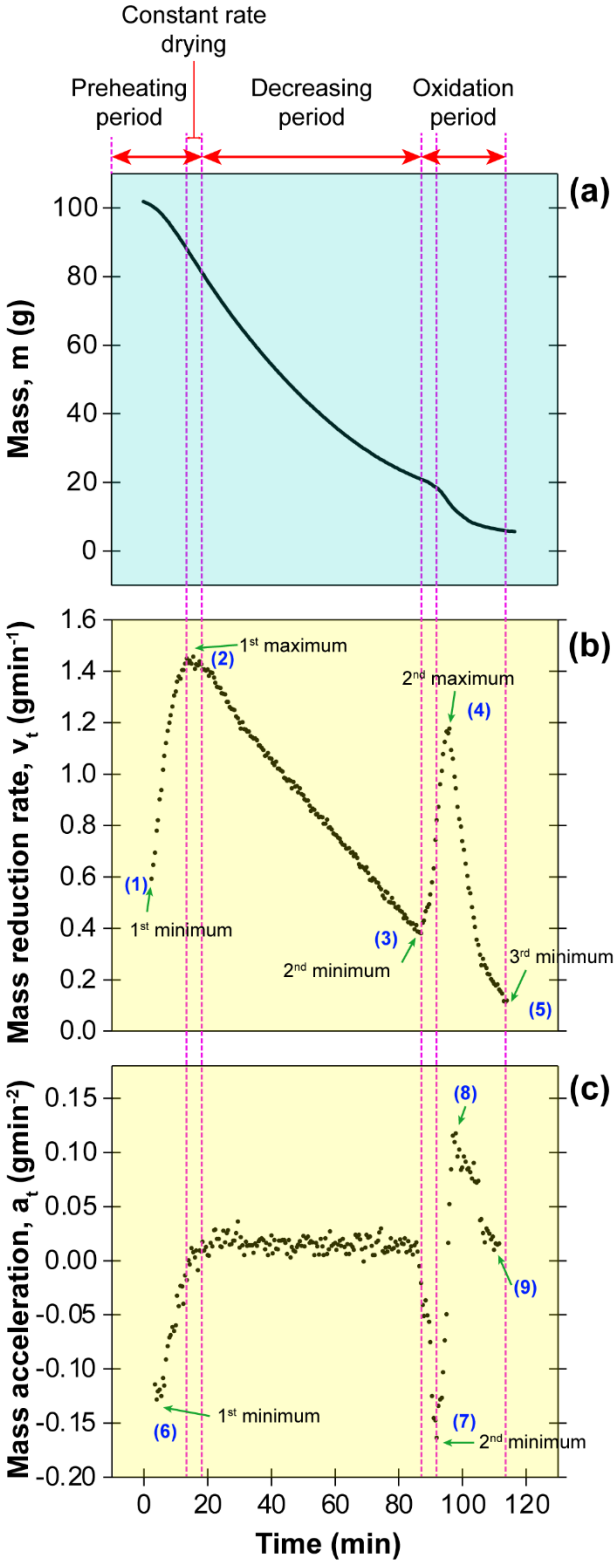

Figure 4.6 – Mass reduction, mass reduction rate, v_t and mass reduction acceleration rate, a_t of dairy manure.

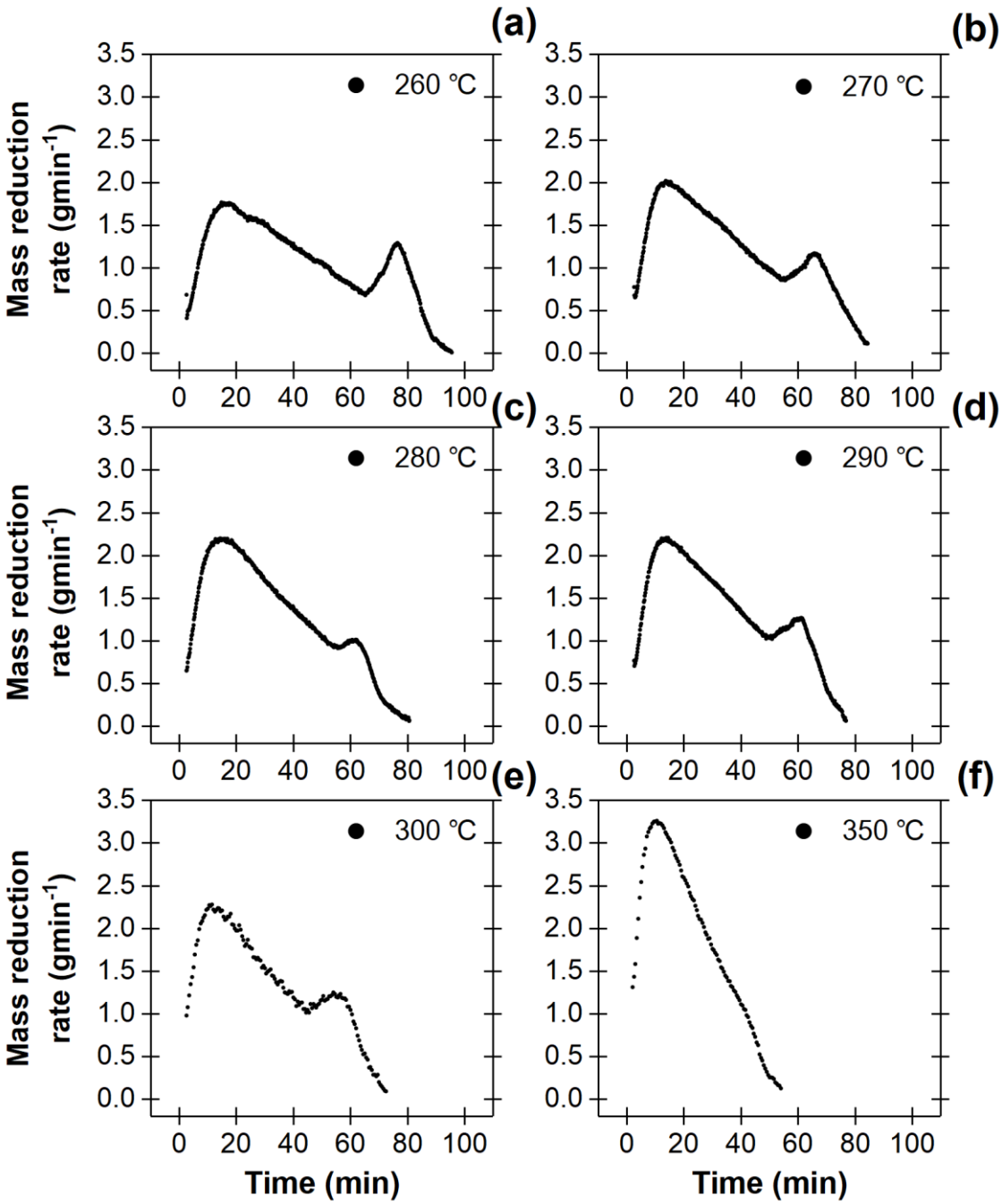

Figure 4.7 –Mass reduction rate, v_t of dairy manure.

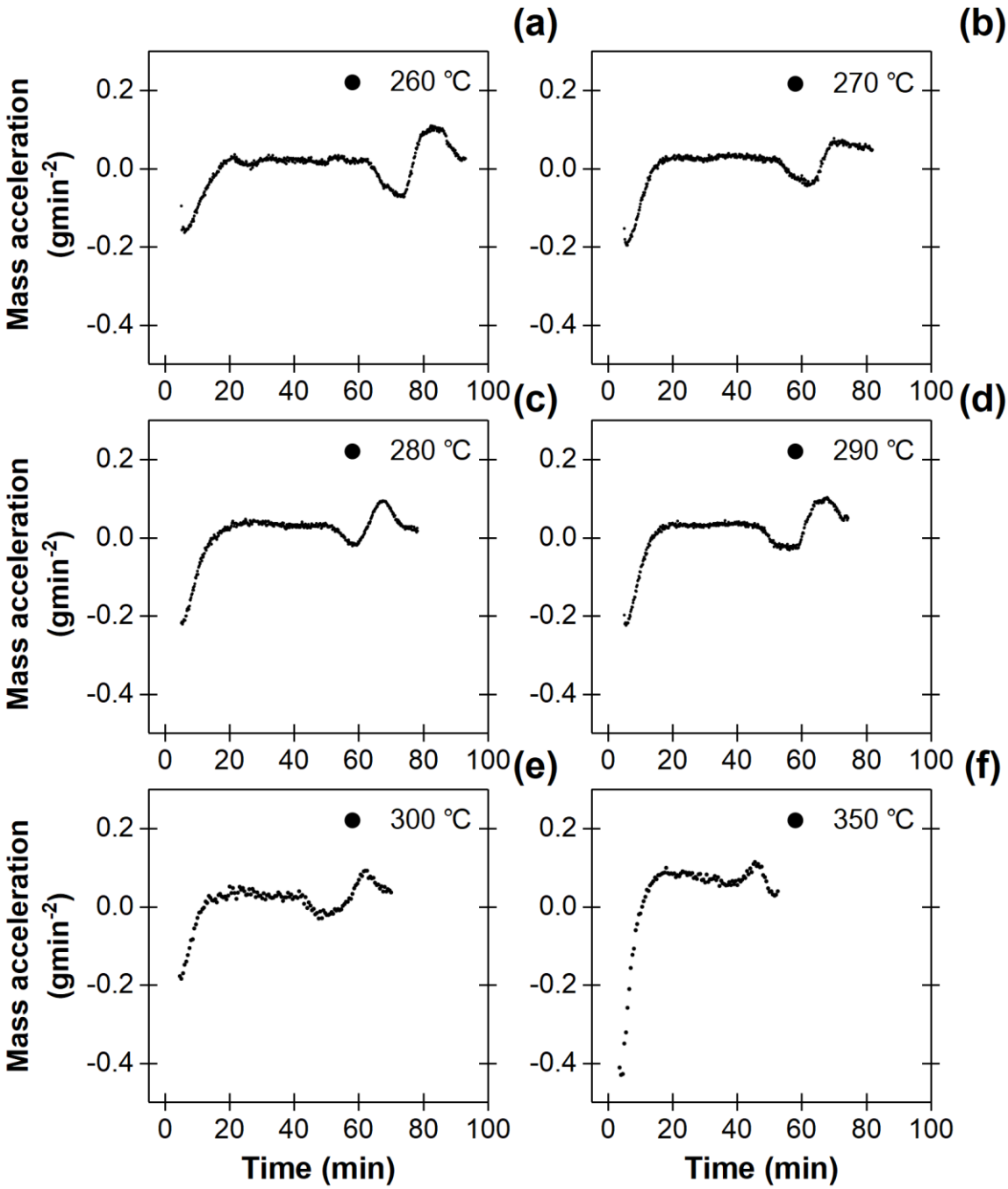

Figure 4.8 – Mass reduction acceleration rate, a_t of dairy manure.

and oxidation period is k_0, k_1 and k_2 respectively.

$$K_i = A_i \exp\left(-\frac{E_i}{RT}\right) \quad (3)$$

* (= 0 , 1 , 2)

4.4.2.1 Preheating period

The constant rate drying is very short as shown in 4.6. So it was identified as preheating period. Also, since the drying effect during the preheating period is weak, it is assumed that the constant rate drying process dominates preheating period. For this purpose, the model (4) is constructed. M is the moisture content (in dry basis; d.b) at the time t (min). M_0 (d.b.) is initial moisture content and k_0 is the rate constant (min^{-1}). The sampling area of mass is according to mass reduction rate graph (Fig. 4.6b). Sampling area for k_0 is from (1) to (2) when M at t = 0 until t=1st maximum. Modelling area is from (1) when M at t=0 until (2) according the time predicted by the regression equation of k_0.

$$M = M_0 - k_0 t \quad (4)$$

where time is

$$t = \frac{M_0 - M}{k_0}$$

if t=trd (at the end of Pre-heating period)

$$t_{rd} = \frac{M_0 - M_{rd}}{k_0} = \frac{0.4564}{k_0}$$

4.4.2.2 Decreasing period

In the decreasing period, the mathematical model is derived with reference to the Page equation used in the decreasing rate drying of agricultural products and foods. M is the moisture content (in dry basis; d.b) at the time t (min) and M_e is the moisture content at the equilibrium. In this study, $M_e = 0$, which is set as the termination state of drying process. M_{rd} (d.b.) is the moisture content at the start of decreasing period which is estimated at the 1st minimum (6) of mass acceleration rate graph in Fig 4.6c. While t_{rd}

$$\frac{M - M_e}{M_{rd} - M_e} = \exp\left(-k_1\left(t - t_{rd}\right)^a\right) \qquad (5)$$

where time is

$$t - t_{rd} = \left[\frac{\ln\left(\frac{M - M_e}{M_0 - M_e}\right)}{k_1}\right]^{\frac{1}{a}}$$

refer to time of M_{rd}. k_1 is the rate constant (min^{-1}) and a is the coefficient that derived together with k_1 during regression. In the experiment, however, the oxidation process took place before complete drying period is achieved. Thus, the residence time at the end of this process was defined as t_{ig} (min) and moisture content is M_{ig} (d.b.). M_{ig} (d.b.) was set to a value larger than $M_e = 0$. Thus, in this period, the sampling area is from (6) to (7) in accordance to mass acceleration rate graph (Fig. 4.6c) and modelling area is from (6) until M_{ig} which determine according the time predicted by the regression equation of M_{ig}.

$$\frac{M_{ig} - M_e}{M_0 - M_e} = \exp\left(-k_1 t_{ig}{}^{a}\right)$$

where time is

$$t_{ig} = \left[\frac{\ln\left(\frac{M_{ig} - M_e}{M_0 - M_e}\right)}{k_1}\right]^{\frac{1}{a}}$$

4.4.2.3 Oxidation period

When the oxidation process is reached, the organic matter corresponding to the dry matter is also related to the reaction. Therefore, the reaction is expressed as y (-) as in equation (6), where m_w (g) is the mass of water, m_s (g) is mas of solid matter, and m_{ash} (g) is mass of ash.

$$y = \left(m_w + m_s\right) / m_{ash} \qquad (6)$$

Here, y (-) decreases exponentially with the reaction according to k_2 (min^{-1}). Convergence occur at initial value y_0 (-) when the period starts. At the end, during oxidation period, all solid matter turned into ash.

$$\frac{y-1}{y_0-1} = \exp\left(-k_2\left(t - t_{rd} - t_{ig}\right)\right) \qquad (7)$$

where time is

$$t - t_{rd} - t_{ig} = \left[\frac{\ln\left(\frac{y-1}{y_0-1}\right)}{k_2}\right]$$

The initial value y_0 (-) of the oxidation period is defines as follows using Mig (d.b.)

$$y_0 = \left(M_{ig} m_s + m_s\right) / m_{ash} \qquad (6^*)$$

4.4.3 Derivation of parameters and boundary conditions

From here, parameters of the above model and value that become the boundary condition are actually derived.

4.4.3.1 Arrhenius plot

As described above, A_i and E_i are the frequency factor (s^{-1}) and the activation energy (kJ mol^{-1}) in each process. In order to derive this, relation between reaction rate constant K_i (min^{-1}) and the set temperature T = 473.15, 523.15, 573.15, 623.15 K are used. Equation (3) is modified to be equation (8). Then, Arrhenius plot is obtained.

$$\ln k_i = \frac{E_i}{RT} + \ln A_i \quad (i = 0,) \tag{8}$$

The reaction rate constant was obtained as a regression coefficient when regression analysis was performed on the experiment values in models (4), (5), and (7) for each set temperature condition. For the derivation of K_0 (min $^{-1}$), from the time t = 0 min of the data at the set temperatures 473.15, 523.15, 573.15, 623.15 K, three repeated data was used until the mass reduction rate v_t (g min $^{-1}$) reaches the 1st maximum. For the derivation of k_1 (min^{-1}) and a, under same set temperature, three repeated data was used

until 1st and 2nd minimum value of mass reduction acceleration a_t (g min^{-1}) are obtained. Here, the regression analysis of the experimental value corresponding to the falling rate drying period in Equation (5) yielded the reaction rate constants k_1 (min^{-1}) and a as regression coefficients. For the derivation of k_2 (min^{-1}) in the oxidation process, data at 473.15 K was excluded because no oxidation process was observed. Three repeated data was used until v_t (g min^{-1}) took the second maximum value. Fig. 4.9, 4.10, 4.11 and 4.12 are the results of Arrhenius plot for each process.

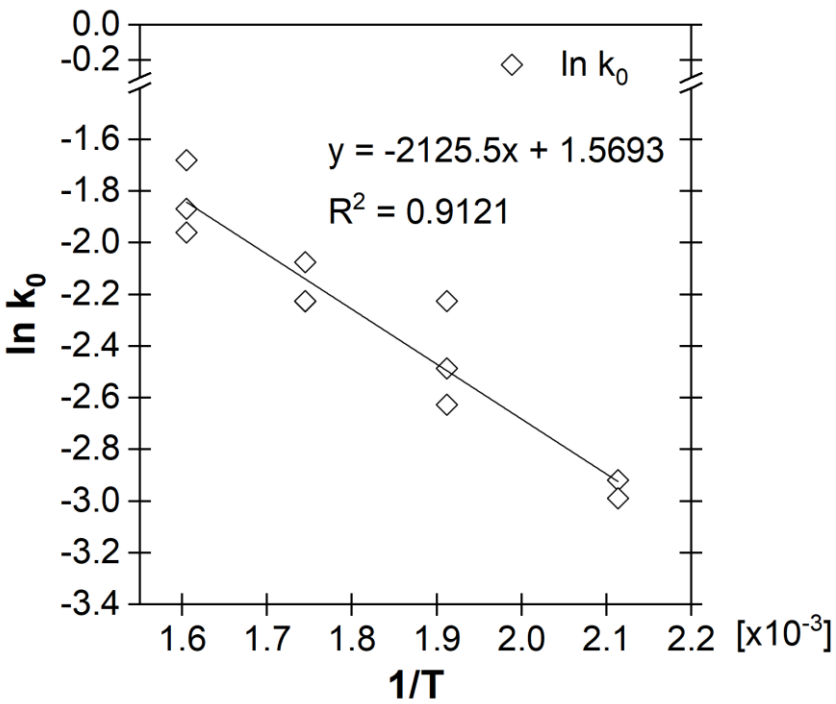

Figure 4.9 – Relation between K_0 and temperature treatment, A_0=4.803s^{-1}, E_0=1.767×10^{4}kJ·min^{-1}.

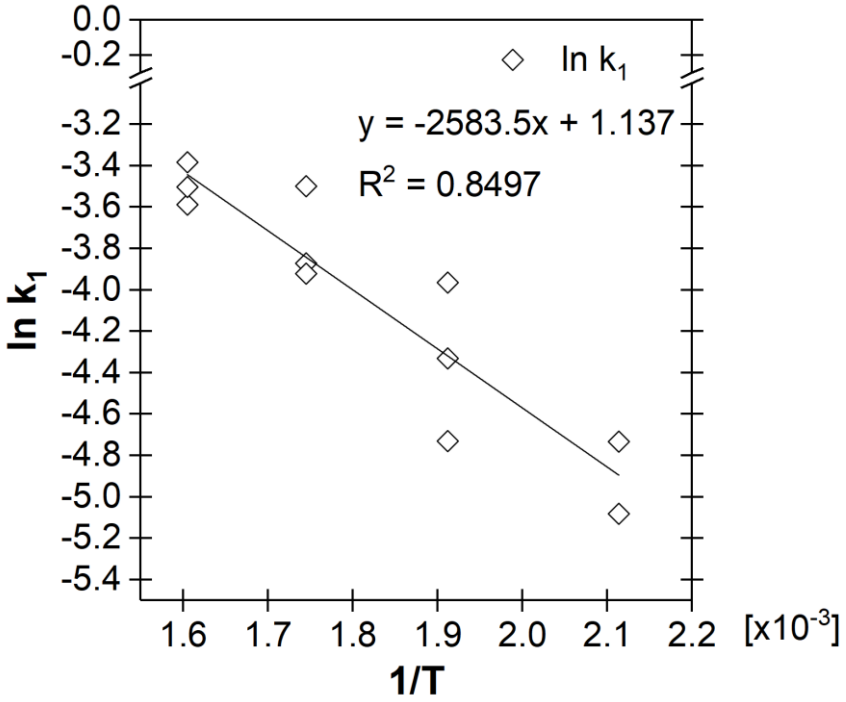

Figure 4.10 – Relation between K_1 and temperature treatment, A_1=1.137s^{-1}, E_1=9.718×10^3kJ·min^{-1}.

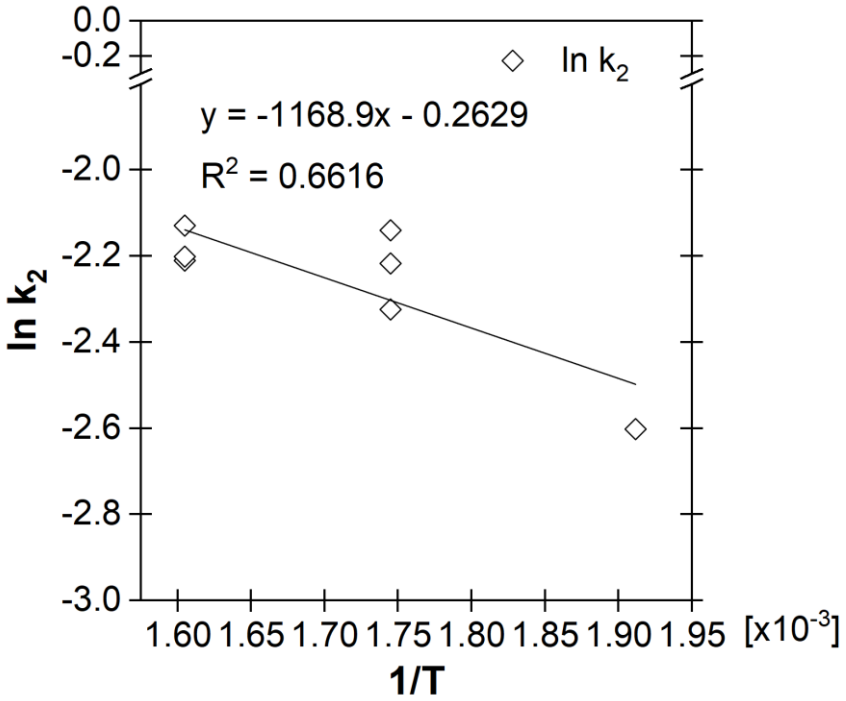

Figure 4.11 – Relation between K_2 and temperature treatment, A_2=0.7688s^{-1}, E_2=9.718×10^3kJ·min^{-1}.

Then, by plotting the set temperature and the coefficient a (Fig. 4.12), there is weak temperature dependence in between. Thus, based of regression equation, coefficient a calculation is expressed as function of set temperature (equation 9).

$$a = 4.967 \times 10^{-4}\theta + 1.3432 \qquad (9)$$

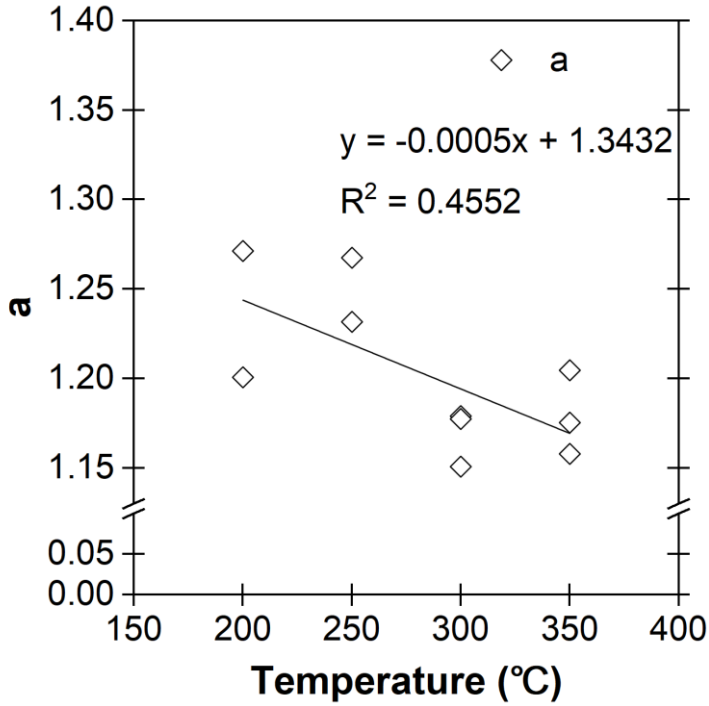

Figure 4.12 – Relation between the coefficient a in the Page equation and the set temperature.

4.4.3.2 Boundary condition

In this study, since the point convex upward in the curve of Fig. 4.6a coincides with the point at which the mass reduction acceleration takes a minimum value in Fig

4.6c, the point at which the mass reduction acceleration takes the minimum value is defined as the boundary condition. In regards to this mathematical model, it is necessary to set two boundary conditions which are M_{rd} (d.b.) and M_{ig} (d.b.). As mentioned earlier, M_{rd} (d.b.) is the moisture content at the start of decreasing period which is estimated at the 1st minimum (6) of mass acceleration rate graph in Fig 4.6c. The resultant moisture content are plotted in Fig. 4.13.

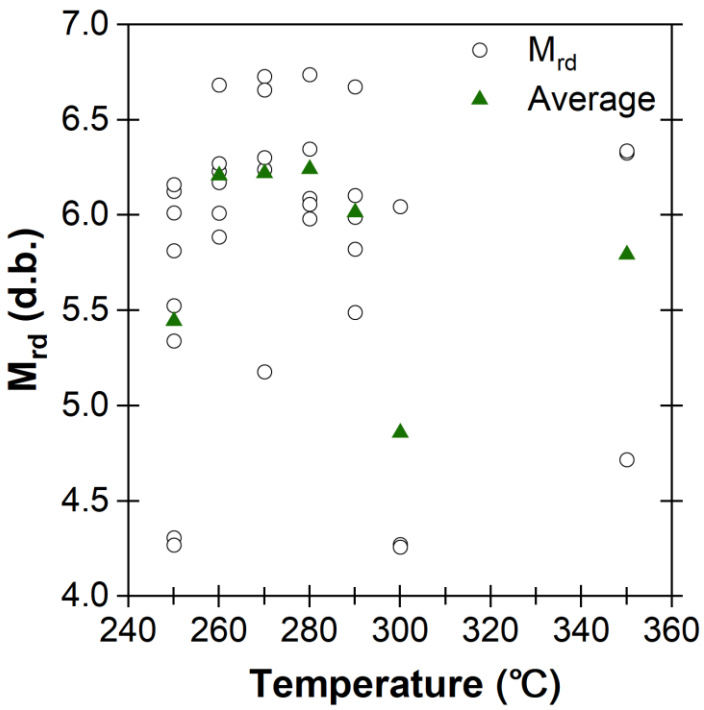

Figure 4.13 – Relation between moisture content and the set temperature at the end of preheating period.

From Fig. 4.13, it cannot be said that M_{rd} (d.b.) is influenced by the set temperature (°C). This is partly due to the fact that almost no time has elapsed since the start of heating. However, since M_{rd} (d.b.) is sufficiently considered to be affected by the initial moisture content M_0 (d.b.) at the beginning of decreasing period, the moisture content decreased from the initial moisture content was determined. And its relation with the set temperature is plotted as in Fig. 4.14.

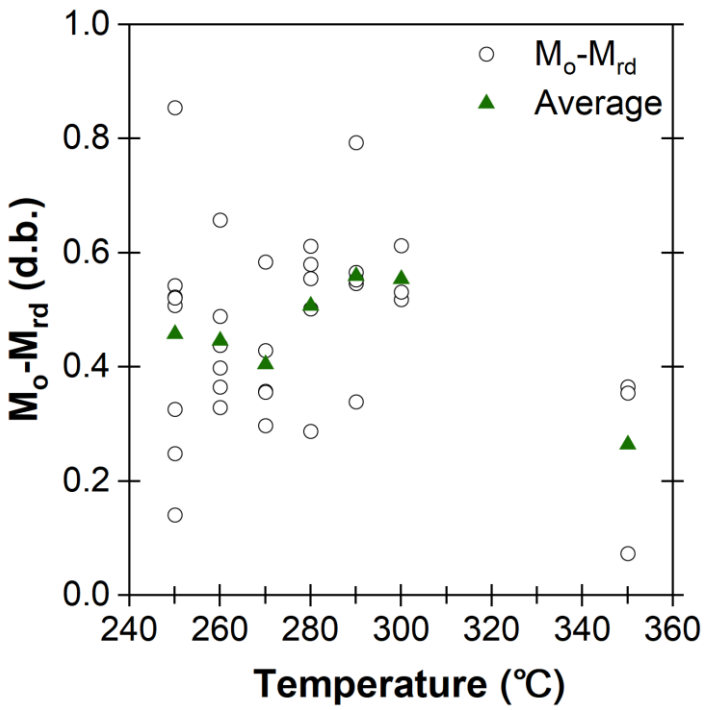

Fig. 4.14. Relation between the reduced moisture content and the set temperature at end of preheating period.

As in Fig. 4.13 and Fig 4.14, it cannot be said that the set temperature gives influence. Therefore, the average value of M_0-M_{rd} (d.b.) in Fig. 4.14 was obtained as 0.4564 (d.b.) and is expressed by equation 10.

$$M_{rd} = M_0 - 0.456 \qquad (10)$$

Next, the second boundary condition is $M_{ig.}$ Due to some amount of water that remained, the condition of shift from decreasing period to oxidation period is considered using the moisture content. The moisture content at the time when the acceleration a_t (g・min^{-2}) takes the 2nd minimum value is defined as M_{ig} (d.b.). This is the boundary when the transition to oxidation period occurred. In order to derive the M_{ig} (d.b.) hypothesis, multiple experiments with no oxidation reaction of organic matter at all were conducted on the set temperature conditions at 250-350 °C. Further, the relation between the set temperature and M_{ig} (d.b.) is plotted (Fig. 4.15). The data having common setting are subjected to temperature regression analysis.

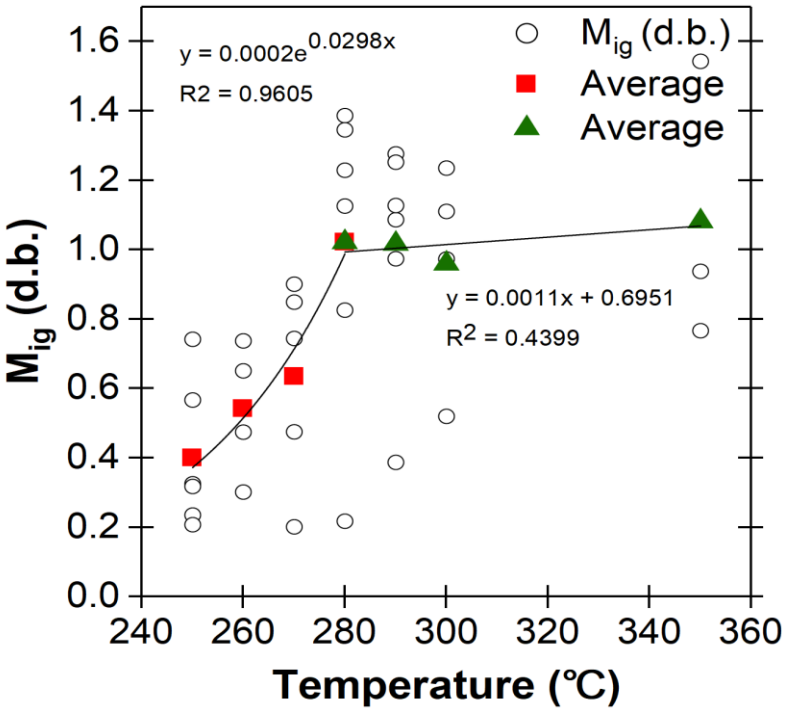

Fig. 4.15. Relation between the moisture content and the set temperature at the end of the decreasing period.

Based from the result, it can be said that the higher the set temperature, the more the sample can shift toward the oxidation period even there is still remaining moisture. It was also found that this effect stopped at M_{ig}≒1.0 (d.b.) when the set temperature is reached higher than 280 °C Therefore, M_{ig} (d.b.) is represented again using the set temperature T(°C) and the regression analysis as in equation 11 and 12.

$$\mathrm{M}_{ig} = 2.304\times10^{-4}\exp\left(0.0298\theta\right)\ \left(250^{o}\mathrm{C} \le \theta \le 280^{o}\mathrm{C}\right) \tag{11}$$

$$\mathrm{M}_{ig} = 1.068\times10^{-3}\theta + 0.6951\ \left(\theta \ge 290^{o}\mathrm{C}\right) \tag{12}$$

4.4.4 Model application to mass reduction data from experiment and rotary kiln reactor

In this section, we aimed to predict the behavior of fresh dairy manure when heated at various temperatures by using the created models from laboratory oven and the rotary kiln. The initial moisture content value is set to $M_0 \fallingdotseq 5.67$ g (d.b). This value linearly decreased until M_{rd} (d.b.) (equation 10) and the decrease is according to equation (4), which representing the preheating period. Further, it decreased exponentially according to equation (5), which represent the decrease period. Then, it fell to the moisture content M_{ig} (d.b.) as predicted by equation (11) or (12). Finally, it will be reduced exponentially according equation (7), which represent the oxidation period.

4.4.4.1 Model and mass reduction of laboratory oven

The mass reduction of the fresh dairy manure heated at temperatures of 250, 260, 270, 280, 290, 300, 350 °C is calculated. Then, the predicted mass reduction (-) by using the model is also calculated. The results is shown in Fig. 4.16. Overall, it can be said that the prediction of the mass reduction of the laboratory oven experiment through the preheating, decreasing and oxidation period was successful with the model. However, based from the result of M_{ig}, it is understood that there is still remaining moisture toward the oxidation period. It was also found that this effect stopped at $M_{ig} \fallingdotseq 1.0$ (d.b.) when the

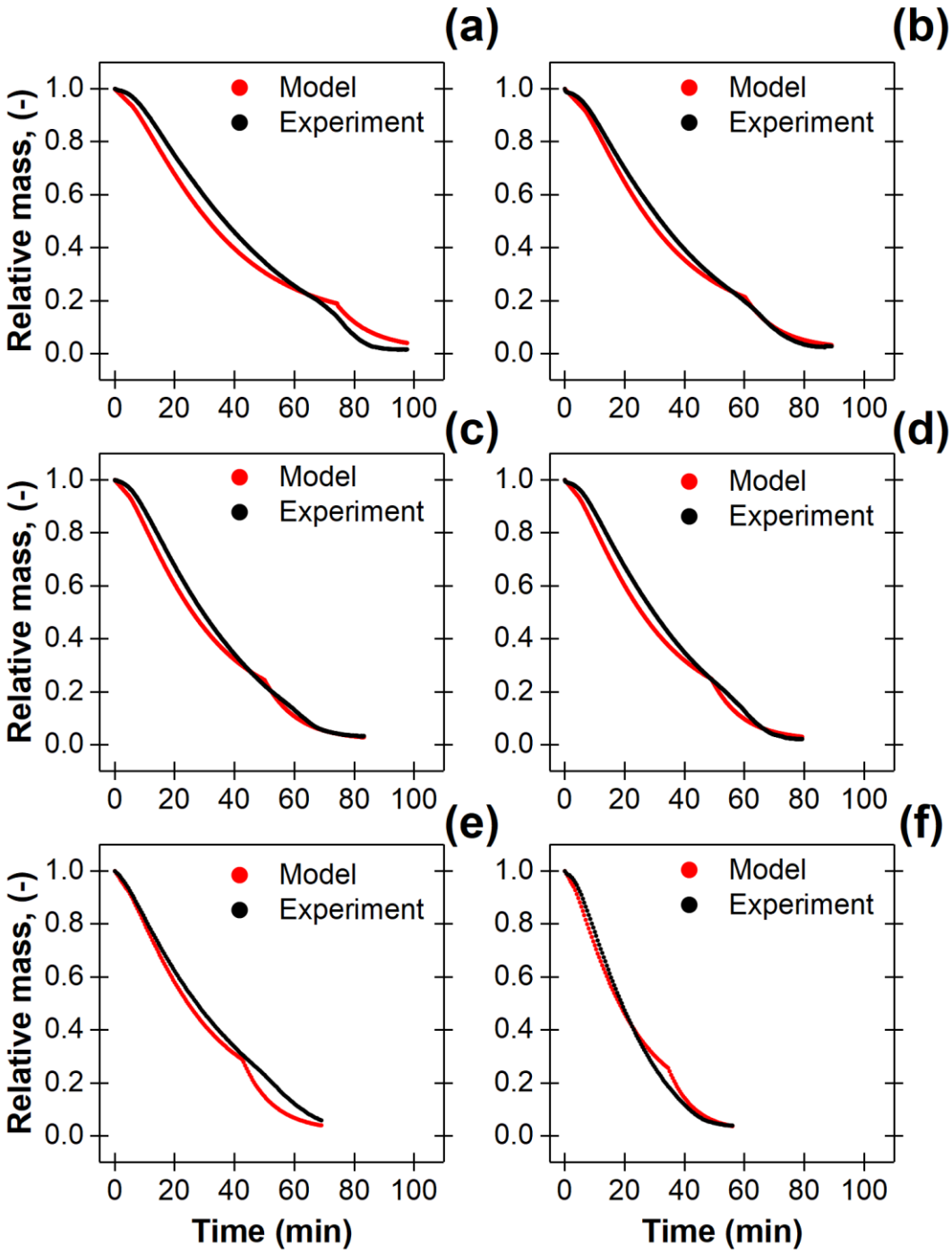

Fig. 4.16. Comparison between experimental and model results at (a) 260 °C, (b) 270 °C (c) 280 °C (d) 290 °C (e) 300 °C and (f) 350 °C.

set temperature is reached higher than 280 °C. Therefore, from M_{ig}, it seems that it is possible to indirectly predict the time of the start of thermal decomposition by using the result of tig for fresh dairy manure torrefaction using rotary kiln reactor. According to Bates and Ghoniem (2014) [9], time scale analysis allows to determine the dominant processes and able to recognize the rate controlling mechanism during drying and torrefaction.

4.4.4.2 Model and mass reduction of rotary kiln reactor

In previous explanation, it is understood that due to non-continuous steps, approximation of when the thermal decomposition occurring on high moisture content torrefaction using fresh dairy manure is not easily be determined from the industrial rotary kiln combustion type reactor. Thus, a continuous laboratory oven were conducted to understand the reaction mechanism and mathematical model developed for a close prediction.

Fig. 4.17 shows the mass reduction curve for model, experiment of the laboratory oven and rotary kiln reactor at 200 °C, 250 °C and 300 °C. It is shown that the summation of the plots between each other were quite accurate except for 200 °C. The model predicted the drying at 200 °C treatment temperature took ~170 minute to end which longer than the residence time of the rotary kiln reactor. Besides, the experiment of the

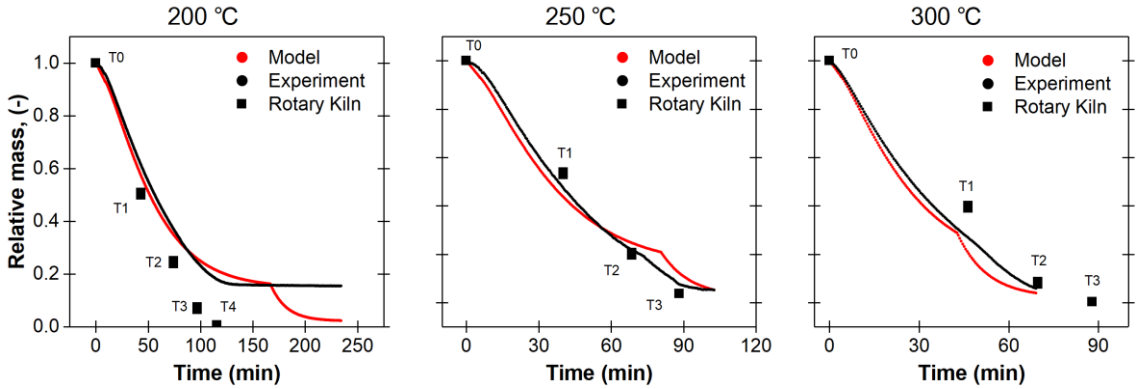

Fig. 4.17 Mass reduction of model, experiment of laboratory oven and rotary kiln reactor

oven in previous has proved that only drying process involve at 200 °C. In reference to the experiment curve, the drying process become almost stable in similar time to T4 that marks the completion of torefaction in rotary kiln. On the other hand, for 250 °C, it is shown that there is a good agreement between the model, experiment and the rotary kiln in comparison to the 200 °C. The model estimate the drying finish at 81.5 minute which is between T2 to T3 of the rotary kiln. In correspond to the solid degradation rate measurement of Saludes et al., (2008) [10], in 20 minute residence time of T3, 60 % of organic matter of dairy manure was decomposed. While for 300 °C, the model curve show that dairy manure may start to decompose between T1 to T2 at minute 43. The solid degradation rate is 30 % at the end of the T2 treatment.

In order to develop this model, the stable drying period during heat treatment is

focused. From the drying period, the condition of mass change with time can be represented with the model. Thus, the decreasing rate drying process can be expressed by a simple exponential model. The exponential expression is also considered for the experimental and industrial rotary kiln. In torrefaction, it necessary to has a simple models so that real phenomena can be predicted [11]. Here, an analytical time scale model that developed mainly from simple weight loss drying can be applied for torrefaction of high moisture content dairy manure through an industrial rotary kiln reactor.

4.5 Summary

In summary, a continuous thermal degradation of high moisture content dairy manure was conducted in order to understand the torrefaction from an industrial rotary kiln reactor. The reaction mechanism mainly involved two processes: drying and decomposition. Mass reduction, gas production and sample temperature were the determinant parameters during the experiments. From the result of mass reduction, the graph trend of 250 °C shows a gradual decrease and a sharp peak, accordingly referred as drying and decomposition. As the temperature increase, time for drying and decomposition become shorter. The gas production and sample temperature are in agreement with mass reduction profile trend thus, confirming the phenomena. However, moisture content still remained during transition from drying to decomposition process. In order to establish the mechanism explanation for this type of torrefaction, a mathematical model is necessary. In principle, an analytical time scale model was develop from three period; preheating, decreasing and oxidation. The model is mainly from simple weight loss drying which can be applied for torrefaction of high moisture content dairy manure through an industrial rotary kiln reactor. The model determine that drying process torrefaction at 250 and 300 °C finish at 81.5 and 43.5 minute respectively.

References

[1] H. Wu, M. A. Hanna, D. D. Jones, Thermogravimetric characterization of dairy manure as pyrolysis and combustion feedstocks. *Waste Management & Research* **30** (2012) 1066-1071.

[2] K. S. Ro, Kinetics and energetics of producing animal manure-based biochar. *BioEnergy Research* **9** (2016) 447-453.

[3] X. Cao, W. Harris, Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource Technology* **101** (2010) 5222-5228.

[4] D. R. Nhuchhen, P. Basu, B. Acharya, A comprehensive review on biomass torrefaction. *International Journal of Renewable Energy & Biofuels* **2014** (2014) 1-56.

[5] Y. Uemura, W. Omar, N. A. Othman, S. Yusup, T. Tsutsui, Torrefaction of oil palm efb in the presence of oxygen. *Fuel* **103** (2013) 156-160.

[6] K.-M. Lu, W.-J. Lee, W.-H. Chen, S.-H. Liu, T.-C. Lin, Torrefaction and low temperature carbonization of oil palm fiber and eucalyptus in nitrogen and air atmospheres. *Bioresource Technology* **123** (2012) 98-105.

[7] J. S. Tumuluru, C. T. Wright, J. R. Hess, K. L. Kenney, A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application. *Biofuels, Bioproducts and Biorefining* **5** (2011) 683-707.

[8] R. L. Bain, K. Broer, Gasification. In *Thermochemical processing of biomass: Conversion into fuels, chemicals and power,* R. Brown, Ed. (John Wiley & Sons, Ltd, West Sussex, UK, 2011), pp. 47-77.

[9] R. B. Bates, A. F. Ghoniem, Modeling kinetics-transport interactions during biomass torrefaction: The effects of temperature, particle size, and moisture content. *Fuel* **137** (2014) 216-229.

[10] R. B. Saludes, K. Iwabuchi, A. Kayanuma, T. Shiga, Composting of dairy cattle manure using a thermophilic–mesophilic sequence. *Biosystems Engineering* **98** (2007) 198-205.

[11] V. Repellin, A. Govin, M. Rolland, R. Guyonnet, Modelling anhydrous weight loss of wood chips during torrefaction in a pilot kiln. *Biomass and Bioenergy* **34** (2010) 602-609.

CHAPTER 5

Summary

5.1 General conclusion

The work of this thesis focused on the direct usage of high moisture content biomass as a feedstock during torrefaction. In particular, the feedstock is fresh dairy manure. By using high moisture content biomass, the prediction for whole biomass degradation processes allows accuracy to clarify the mechanism of biomass torrefaction.

In Chapter 2, I developed the understanding on importance of livestock manure and the torrefaction treatment technology in order to produce solid product.

In Chapter 3, direct usage of wet dairy manure as a feedstock for torrefaction using an industrial rotary kiln combustion type reactor is investigated. By using the reactor, the wet dairy manure was converted to a solid product or torrefied manure. Due to its high moisture content, at least three cycles of non-continuous thermal treatment were required to complete the torrefaction. No increase of HHV was observed for the torrefied dairy manure in comparison with the raw feedstock. Production efficiency calculations showed that the fresh dairy manure was torrefied better at 300 °C with lower energy consumption and in a shorter time.

In Chapter 4, the reaction mechanism and mathematical model of wet dairy torrefaction are described. The weight loss profile data was treated as a major source to understand the reaction. The reaction mechanism involved two processes: drying and decomposition. During transition from drying to decomposition process, water residue was inspected; i.e some amount of moisture content still remained. Thus, it is understood that, during high moisture content dairy manure drying, the water may not completely vaporized. Instead, the remaining water loss rapidly during decomposition process. In order to explain the phenomenon, a mathematical model is developed based on a drying process. The principle of the model is to estimate the time for drying to end. For this purpose, three groups of variable are calculated and plotted: mass reduction rate, mass reduction acceleration and moisture content loss to determine the sampling area. From there, three period clarified for modelling expression; preheating, decreasing and oxidation. The model is mainly from simple weight loss drying which can be applied for torrefaction of high moisture content dairy manure.

5.2 Future outlook

In this section, based on observations seen throughout this research, some ideas are introduced for further research. In similar principle, still, future work suggested involve the implementation of a direct usage of high moisture content livestock manure in an industrial reactor as the following:

1) with a continuous heat treatment
2) in an inert condition.

5.3 Final remarks

Overall, the concept of direct usage of wet biomass has been covered in this thesis. Although there is still more to explore for its applications in torrefaction technology, incorporation of scientific advances to open new perspectives in understanding wet biomass interaction during torrefaction has been done. An important point learned from this work is that even high moisture content biomass, if they are applied in in different way, can result in exciting breakthroughs.

List of publications

Journal

[1] **Sitty Nur Syafa Binti Bakri**, Kazunori Iwabuchi, Ryohei Yoshimoto and Katsumori Taniguro. 2018. Torrefaction of high moisture content biomass in an industrial combustion type reactor. Journal of the Japanese Society of Agricultural Machinery, 80 (2), X page

Proceeding

[1] **Sitty Nur Syafa Binti Bakri**, Kioto Ito and Kazunori Iwabuchi. 2017. Investigation of torrefaction reaction on high moisture content biomass using dairy manure. Proceedings of ASABE Annual International Meeting. 16-19 July, Spokane, USA. (doi:10.13031/aim.201700083)

[2] **Sitty Nur Syafa Binti Bakri**, Kazunori Iwabuchi, Ryohei Yoshimoto and Katsumori Taniguro. 2016. Effect of moisture content on dairy manure torrefaction. Proceedings of the 8th International Symposium on Machinery and Mechatronics for Agriculture and Biosystems Engineering (ISMAB), pp 967-972. 23-25 May, Niigata, Japan.

[3] **Sitty Nur Syafa Binti Bakri**, Yoshimoto Ryohei and Iwabuchi Kazunori. 2015. Preliminary study of dairy manure torrefaction for biochar production. Proceeding of ISER 9th international conference, pp 50-52. 30th October, Berlin, Germany. ISBN 978-93-85832-26-0.

Poster presentations

[1] **Sitty Nur Syafa Binti Bakri**, Kioto Ito and Kazunori Iwabuchi. 2017. Investigation of torrefaction reaction on high moisture content biomass using dairy manure. Proceedings of ASABE Annual International Meeting. 16-19 July, Spokane, USA. (doi:10.13031/aim.201700083)

[2] **Sitty Nur Syafa Binti Bakri**, Kazunori Iwabuchi, Ryohei Yoshimoto and Katsumori Taniguro. 2016. Effect of moisture content on dairy manure torrefaction. Proceedings of the 8th International Symposium on Machinery and Mechatronics for Agriculture and Biosystems Engineering (ISMAB), pp 967-972. 23-25 May, Niigata, Japan.

[3] **Sitty Nur Syafa Binti Bakri**, Kioto Ito and Kazunori Iwabuchi. Investigation on torrefaction mechanism of dairy manure. Hokkaido branch meeting of Waste Resources Circulation Committee 2016. Hokkaido University, Sapporo, Japan, 25 October 2016.

[4] **Sitty Nur Syafa Binti Bakri**, Kioto Ito and Kazunori Iwabuchi. Investigation on torrefaction mechanism of dairy manure. International Conference on Agricultural Biodiversity and Sustainability 2016 (CABS), Hokkaido University, Sapporo, Japan, 22-24 August 2016.

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