Study on Characteristics of Agricultural Wastes and Comparison between Aerobic Composting and Anaerobic Digestion Processes in Shanghai Suburbs, China

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Abstract

Aerobic composting and anaerobic digestion are encouraged methods for agricultural waste management in Shanghai, and many aerobic composting plants and anaerobic digestion projects have been built up or are under construction in order to solve the pollution problems from agricultural wastes. However, maturity evaluation system for aerobic composting and optimal operation conditions for anaerobic digestion have not been established based on the characteristics of local agricultural wastes.

In this study, besides the characteristic analysis of agricultural wastes in Shanghai suburbs, experiments were carried out on maturity evaluation for aerobic composting and operation optimization for anaerobic digestion. And their environmental impacts and economic benefits were also compared by using life cycle assessment.

The production amounts and pollution risk of animal manure and crop straws in Shanghai suburbs were evaluated spatially. The results showed that, serious attention should be paid to the potential pollution risk and N and P losses brought by land application of animal manure when the high application level of chemical fertilizers is taken into consideration. It was found that more than 80% of all the towns and the whole city were suffering from the potential pollution risk. The total amount of crop straws burned in the field was around 17,098 t a^{-1} in which rice straw occupied 73.33% and wheat straw occupied 26.67%. On the other hand, the total amount of crop straws discarded in the field was estimated to be 146,759 t a^{-1} in which rice straw was about 80.74% and wheat straw was about 19.26%. The burning and discarding activities of crop straws resulted in serious air and water pollution, especially in the harvest season in the areas with dense rice or wheat plantation. The results showed that swine manure and rice straw were the two main agricultural wastes in Shanghai suburbs, which could be used as raw materials for the aerobic composting plants and anaerobic digestion projects.

In the study on aerobic co-composting of swine manure and rice straw, the characteristics and establishment of maturity evaluation index system were investigated. Results indicated that the optimal composition for aerobic co-composting of swine manure and rice straw was determined as 3:2 (fresh weight). Mature compost could be achieved after 60 days' aerobic co-composting of swine manure and rice straw, and fast maturation was signaled by a relatively long thermophilic phase and high organic matter (OM) degradation rate, germination index (GI) and plant growth index (PGI). The findings in this study suggest that a comprehensive maturity evaluation index system consisting of chemical (C/N) and biological (GI or PGI) parameters is much more suitable and practical for the maturity assessment of compost. The suitable values of GI and PGI are proposed as greater than 120% and 1.00, respectively for mature compost.

In the experiments on anaerobic co-digestion of swine manure and rice straw, the effects of different amounts of inoculum and different pretreatment methods for rice straw on biogas production were explored. The optimal composition was determined to be higher than 2:1 (fresh weight) for swine manure and rice straw under anaerobic co-digestion at total solid (TS) of 10-20%. The anaerobic co-digestion process fitted the single-stage first-order model, and a small amount of biogas slurry inoculation could accelerate the digestion process. The biogas production rate constants, biogas yields and biogas productivities with 1.2%, 2.4% and 4.8% (TS basis) of biogas slurry inoculum were 0.0291-0.0314 d^{-1}, 286-297 L kg^{-1} TS-loaded and 769-773 L kg^{-1} TS-reduced, which increased by 40-51%, 3-7% and 7-8%, compared to 0.0208 d^{-1}, 278 L kg^{-1} TS-loaded and 714 L kg^{-1} TS-reduced without biogas slurry inoculum, respectively. Alkaline (NaOH) pretreatment of rice straw remarkably accelerated the co-digestion process which well fitted the two-stage first-order model. The biogas yields and biogas productivities with alkaline pretreated rice straw were 355-357 L kg^{-1} TS-loaded and 679-699 L kg^{-1} TS-reduced, which improved by 26-27% and 3-6%, compared to 282 L kg^{-1} TS-loaded and 660 L kg^{-1} TS-reduced without pretreated rice straw, respectively.

An environmental and economic life cycle assessment was conducted basing on an aerobic composting plant and an anaerobic digestion project with the treatment capacity of 10 tons of swine manure and rice straw in Shanghai suburbs. By using aerobic co-composting to treat 1 ton of agricultural wastes (swine manure and rice straw), the results indicated that the world’s environmental impact potentials per person for global warming potential (GWP), acidification potential (AP) and eutrophication potential (EP) were 0.91%, 3.61% and 0.38%, respectively. On the other hand, the three impact potentials were 1.27%, 0.92% and 0.06%, respectively for anaerobic co-digestion at the same scale. Meanwhile, aerobic composting had lower capital and operating expenditures and higher production profit but with higher environmental impacts, while anaerobic co-digestion had lower environmental impacts with higher capital and operating expenditures but lower production profit if calculated on the basis of current price system for electricity generation from biogas.

In conclusion, under the circumstances of National Pollution Emission Reduction Plan and National Climate Change Program in China, aerobic composting and anaerobic digestion have already been designated for the main encouraged approaches of agricultural waste management in Shanghai suburbs. Based on the characteristics of the agricultural wastes and the requirements of composting products and renewable energy, both techniques have the prospects for application and extension for the sustainable utilization of swine manure and rice straw. This study will provide the basic information and technical support for the establishment of maturity evaluation index system for aerobic composting and the operation optimization of anaerobic digestion when using swine manure and rice straw as feedstocks.

Keywords: Swine manure; Rice straw; Aerobic composting; Anaerobic digestion; Life cycle assessment

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Abbreviations

Abbreviation	Full name
AK	Alkaline pretreatment
AP	Acidification potential
CapEX	Capital expenditure
EP	Eutrophication potential
FA	Fulvic acid
GI	Germination index
GWP	Global warming potential
HA	Humic acid
MW	Microwave pretreatment
NBI	Nutrient balance index
NPI	Nutrient pollution index
OM	Organic matter
OpEX	Operational expenditure
OpIN	Operational income
RS	Rice straw
PGI	Plant growth index
ProPR	Production profit
SCOD	Soluble chemical oxygen demand
SM	Swine manure

Abbreviation	Full name
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TS	Total solid
VFA	Volatile fatty acid
VS	Volatile solid

Chapter 1 Introduction

1.1 Background

Swine breeding and rice production are the major agricultural industries in China. The annual amount of fattening pigs exceed 0.6 billion heads, and the annual generation of animal manure was nearly 0.3 billion tons, which could lead to serious water and air pollution if treated inappropriately. The sown area of paddy is about 30 million hectares with annual amount of 0.2 billion tons of rice straw being produced accordingly, which could cause severe water and air pollution if discarded or burned in open field (NBSC, 2011).

1.1.1 Pollution from animal manure

China has experienced one of the highest growth rates in livestock and poultry production and is currently the largest pork and poultry producer all over the world (NBSC, 2011), contributing more than 40% of the global pork supply (Orr Jr. and Shen, 2006). The following huge quantities of animal manure can be an economical source of plant nutrients and a valuable soil amendment to improve soil quality and maintain soil pH. Thus, animal manure can be a valuable asset to livestock and poultry production operation if its nutrients and organic matter are recycled through land application properly, and can replace the need for commercial fertilizer to some extent. On the other hand, animal manure may cause surface and ground water pollution if being mismanaged. The pollution from animal wastes has become one of the main sources of water quality deterioration according to the report on the first

China Pollution Source Census issued by Ministry of Environmental Protection in February, 2010. Especially in many economically developed regions with abundant water resource, such as Yangtze River Delta, nutrient losses from animal wastes have caused seriously adverse impacts on local water environment conservation, although the circumstances that the industrial and urban point source pollutions have been controlled efficiently. The key to a proper management for environmental protection is to determine the nutrient contents of the manures, the percentages of which are available to crops, and the nutrient requirements of the crops at a realistic yield target (Wei et al., 2013; Buerkert et al., 2005). Also, some heavy metals in the animal manure, such as copper and zinc originated from feed additives for increasing growth performance and preventing disease in livestock and poultry production, can enter the farmland simultaneously with direct land application and cause the accumulation of heavy metals, resulting in negative impacts on soil environment and plant growth (Xiong et al., 2010; Sun et al., 2011; Duan et al., 2012). However, the accumulation of heavy metals in the cropland soil of Shanghai suburbs has been investigated, appearing not a severe situation at present (Shen et al., 2006; Meng et al., 2008).

Therefore, the main pollution from animal manure is the nutrient losses caused by the inappropriate treatment, which could lead to severe water environment contamination.

1.1.2 Pollution from crop straws

Crop straws is mainly used for fuel (cooking and house heating), animal feed, fiber for pulping, and plowing into field, and meanwhile, it has been reported that a very large proportion of crop straws was burned or discarded in the field due to lack of cost-effective treatment approaches, leading to severe water and air pollution (Wang et al., 2008). Compared to the water pollution resulted from discarding in the field, the air pollutants emission from open field burning is the major problem for the treatment of crop straws. Burning of agricultural crop residues, including field burning of crop straws, is a common practice of land preparation and disposal of crop wastes in China. Especially in the economically developed area of China, such as Yangtze River Delta, the crop straws are not burned as domestic fuel because of the popularization of clean energy in the rural area, thus the field burning becomes an easier way with lower cost for crop straw treatment compared to the method of crushing and plowing into field by using machines (Zhang et al., 2011). The field burning of crop straws is an uncontrolled combustion process in which the products of burning are emitted into the atmosphere, such as CO_2, CO, CH_4, particle matters, NO_x, and SO_2, influencing both the local air quality and global climate (Ito and Penner, 2004; Tipayarom and Oanh, 2007; Viana et al., 2008; Maruf Hossain and Park, 2012). Furthermore, burning crop straws in the field may also contribute to the emission of harmful air pollutants, such as polycyclic aromatic hydrocarbon (PAH), polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs), threatening human health (Chen et al., 2008; Shih et al., 2008; Lai et al., 2009; Estrellan and Iino, 2010). In an extreme case, it was observed that smoke emitted from field burning reduces visibility drastically, leading to the variations of cloud condensation nuclei activation (Dusek et al., 2006). In Shanghai, the open field burning of crop straws contributed more than 4% of $PM_{2.5}$ in recent years (SMPG, 2013).

Consequently, the primary pollution from crop straws is the air pollutants emission caused by the open field burning, which would seriously affect the local air quality.

1.1.3 Resource utilization of agricultural wastes in Shanghai

Animal manure and crop straws could be largely utilized as resources of organic fertilizer and renewable energy. In recent years, the solutions of aerobic composting and anaerobic digestion have been adopted to solve the problems of agricultural waste treatment in Shanghai suburbs, including the following aspects:

(1) Construction of composting plants. In order to collect animal manure and crop straws for composting, composting plants have been built up in every district in Shanghai, and the construction of composting plants and the land application of commercial composts are encouraged with subsidy policies. Two-thirds of the investment for a composting plant construction was covered by municipal and district governments, while the land application of commercial compost was provided a subsidy of about 200 RMB t^{-1}. Under this circumstance, composting of livestock manure and crop straws was promoted remarkably in Shanghai suburbs, and its mature technique, aerobically mesophilic composting was adopted by most composting plants. However, due to the fact that the ratios of raw materials (animal manure to crop straws) always vary in different districts, the quality control of composting based on maturity has not been established, which still emphasized on

some physical and chemical parameters.

(2) Implementation of biogas production projects. For the waste treatment in large scale livestock and poultry farms, dozens of biogas production projects have been completed in Shanghai suburbs, and the utilization of large amount of biogas slurry becomes the main problem because the abundant rainfall and high level of groundwater in Shanghai. During the 12th Five-Year Plan period (2011-2015), the pollution emission reduction of intensive animal farms has been included into the national pollution emission reduction framework. Accordingly, Shanghai Municipal Government released the subsidy policy for the projects of animal manure treatment, in which 77% of the project investment would be covered by municipal and district governments for the treatment of animal manure. As for the biogas production projects, high solids (total solid above 10%) anaerobic digestion is the recommended technique. However, the feedstock composition and operation conditions for anaerobic co-digestion of livestock manure and crop straws still need to be studied in order to provide technical guidance for the anaerobic digestion projects.

1.2 Characteristics of the research area

Shanghai, the largest international city with rapid economic development in eastern China, hosts more than 20 million residents and occupies above 6,000 km^2, and has around 2,000 km^2 of arable land (SSB, 2009). It also has one of the most intensive livestock and poultry production industries to meet the demand of local markets, which are distributed in 101 towns in 9 suburbs (Figure 1.1). The paddy field accounts for more than 75% of arable land, and the breeding amounts of pig, cattle and poultry are about 2.67 million (for sale), 0.07 million (in fence) and 43 million (for sale) heads, respectively.

1.3 Objectives and originality of this study

As mentioned in section 1.1.3 and 1.2, Shanghai, as a Mega-City located in the plain river network area, not only shares the common and severe problems of pollution from animal manure and crop straws with other provinces, but also is confronting the specific and practical problems brought by animal manure and crop straws in local suburbs, which is attributable to the quality control in the aerobic composting plants and the operation optimization in the anaerobic digestion projects.

In this study, the characteristics of agricultural wastes in Shanghai suburbs was analyzed spatially, and the experiments on maturity evaluation for aerobic composting and operation optimization for anaerobic digestion were implemented in addition to the comparison of the environmental impacts and economic benefits between these two techniques for agricultural waste treatment in Shanghai suburbs. The objectives of this study are: (1) to figure out the spatial heterogeneity and pollution risk of agricultural wastes in Shanghai suburbs; (2) to establish the maturity evaluation index system for the aerobic composting plants and determine the optimal operation conditions for the anaerobic digestion projects based on the obtained characteristics of agricultural wastes in Shanghai suburbs; (3) to compare aerobic composting and anaerobic digestion through environmental and economic life cycle assessment.

The originality of this study could be concluded as follows:

(1) This study implemented a comprehensive and systematic investigation and

analysis on the spatial heterogeneity among townships with respect to the pollution risk of land application of animal manure, according to the nutrient balance between nutrient supplies from different animal manure and nutrient demands of different croplands. There is little information in the literature up to now. The results obtained in this study could provide specific information for the town-based pollution control of animal manure in Shanghai suburbs.

(2) Few research work focused on physical/chemical together with biological/agronomical parameters during the co-composition of swine manure and rice straw, and no maturity evaluation index system with agronomical parameters included is available in Shanghai. This study aimed to establish a comprehensive maturity evaluation index system consisting of chemical and biological parameters, which is much more suitable and practical for the maturity assessment of compost in Shanghai suburbs.

(3) Few trials have been conducted in the field to investigate the compositions and operation conditions of dry or semi-dry anaerobic co-digestion of swine manure with rice straw. This study tried to find the optimal operation conditions for the anaerobic co-digestion of swine manure with rice straw. Further, by using the first-order kinetics model and related analysis, the involved co-digestion mechanism was interpreted under the conditions of biogas slurry inoculation and rice straw pretreatment.

(4) A comprehensive comparison is still scarce for field studies between the aerobic composting and anaerobic digestion. This study gave detailed information

about the economic and environmental benefits of the two techniques based on field reaction systems in Shanghai suburbs.

1.4 Structure of this study

The contents of this study were divided into four parts so as to comprehensively evaluate the pollution status of agricultural wastes in Shanghai suburbs, establish the maturity evaluation index system for aerobic co-composting of swine manure and rice straw, optimize the operation conditions for anaerobic co-digestion of swine manure and rice straw, and compare the environmental impacts and economic benefits between aerobic composting and anaerobic digestion.

In the first part of this study (Chapter 2), through investigating animal husbandry and crop plantation in each town or district in Shanghai suburbs, the production of animal manure and crop straws were obtained. The animal manure in most towns exceeded the carrying capacity of arable land, especially in the circumstance of large amount of chemical fertilizers, while the crop straws in most districts still had the problems of field burning and discarding.

In the second part of this study (Chapter 3), based on the characteristics of agricultural wastes in Shanghai suburbs, swine manure and rice straw were chosen as the raw materials for the experiments of aerobic composting. The best composition of swine manure and rice straw for aerobic co-composting was obtained through 30 days' trials, and the physical, chemical and agronomical parameters were evaluated in the 90 days' experiments on the optimal composition of swine manure and rice straw. The maturity evaluation index system for aerobic co-composting of swine manure and rice straw was established.

In the third part of this study (Chapter 4), based on the characteristics of agricultural wastes in Shanghai suburbs, swine manure and rice straw were chosen as the raw materials for the experiments of anaerobic digestion. The best composition of swine manure and rice straw for anaerobic co-digestion was obtained through 45 days' trials, and the biogas and methane production was evaluated in the 60 days' experiments on different amounts of biogas slurry inoculum and different pretreatments for rice straw. The first-order kinetics of biogas production for anaerobic co-digestion of swine manure and rice straw was explored.

In the fourth part of this study (Chapter 5), according to the results of the second and third parts, the environmental impacts and economic benefits of the aerobic composting plant and anaerobic digestion project in Shanghai suburbs were compared by using the method of life cycle assessment.

The whole structure of this study was illustrated in Figure 1.2. The currently encouraged techniques of aerobic composting and anaerobic digestion in Shanghai suburbs would be comprehensively evaluated through the design and method for investigation, experiments and comparison in this study.

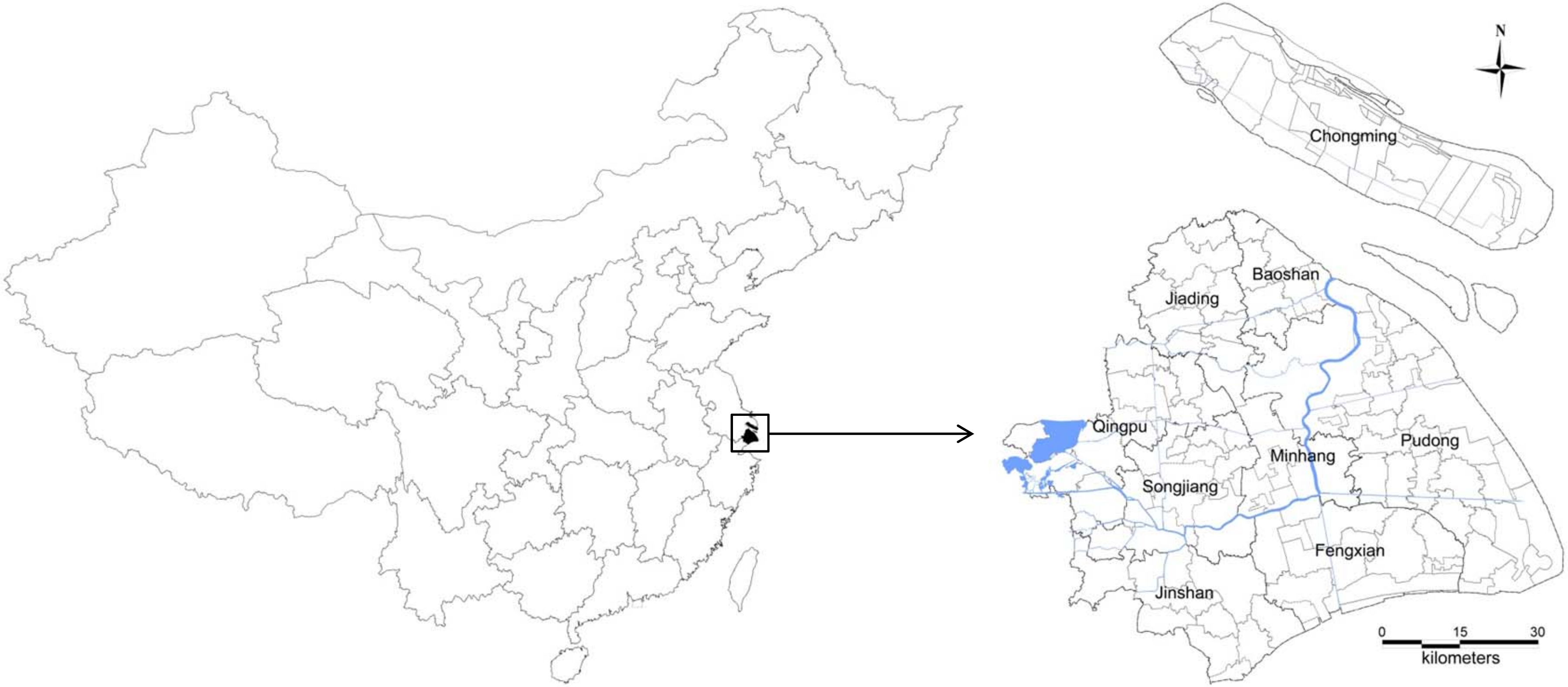

Figure 1.1 Shanghai metropolis suburbs and towns

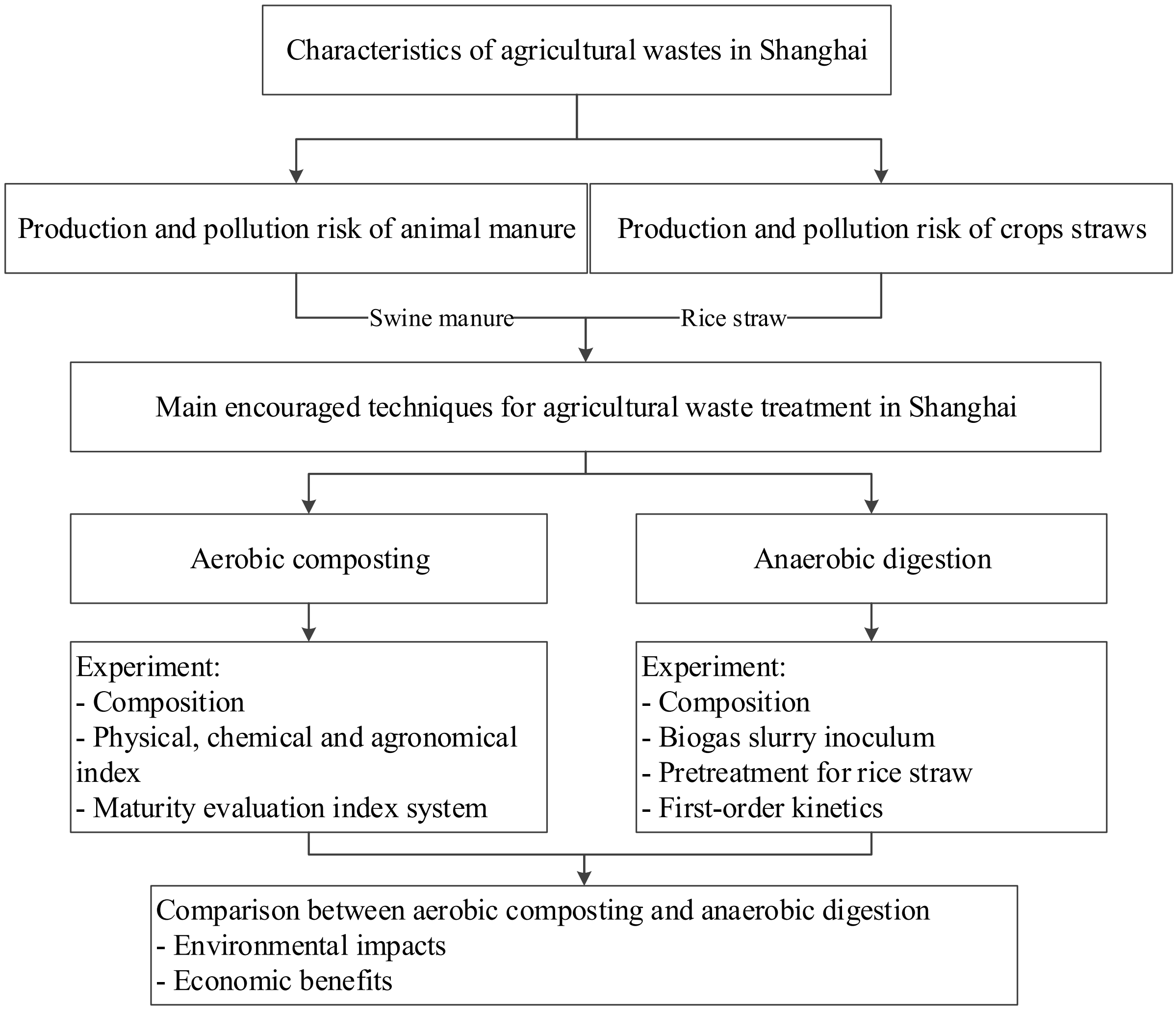

Figure 1.2 Structure of this study

Chapter 2 Evaluation on potential pollution risk of agricultural wastes in Shanghai suburbs

2.1 Introduction

Shanghai has limited agricultural land to receive animal manure from the surrounding provinces and the target treatment rate of municipal domestic wastewater will be greater than 85% before 2015 for the whole city, which is supposed to be realized by constructing more wastewater treatment plants and sewer networks. Along with the proper disposal of human extra, Shanghai Municipal Government has aimed to solve the nutrient disposal problems from animal manure, and has promulgated the Regulations of Shanghai Municipality on the Management of Livestock and Poultry Breeding in 2004 (SMPG, 2004), which greatly encouraged that animal manure should be returned to cropland properly and locally for the purpose of high nutrient cycling rate and less transportation cost. On the other hand, the overuse of chemical fertilizers in many areas of China is very common, regardless of crops, periods or specification (He et al., 2006; Zhang and Hu, 2011). The same status occurs in Shanghai, regardless of extra nutrient input from animal manure, although lots of techniques and strategies for the reduction of chemical fertilizer have been disseminated and extended. In this context, based on the existing application condition of plentiful chemical fertilizers, it is important to evaluate the nutrient balance and assess the potential pollution risk of land application of animal manure in Shanghai suburbs.

Burning of agricultural crop residues, field burning or burning as a domestic fuel, is a traditional practice of land preparation or disposal of crop wastes in China. It releases a large amount of pollutants into the atmosphere, including CO, CO_2, particulate matter, hydrocarbons, and other matters, bringing about serious local and regional impacts on the environment(Zhang, 2008; Yuan et al., 2010; Zhang et al., 2010a). In an extreme case, smoke emitted from field burning could reduce visibility drastically, leading to the variations of cloud condensation nuclei (CCN) activation (Dusek et al., 2006). In addition, smoke emitted from domestic fuel burning could cause reduced indoor air quality, contributable to acute and chronic respiratory diseases (Laumbach and Kipen, 2012). In the past decades, with the economic development in rural area of Shanghai suburbs, the cooking methods have already been changed from using crop straws to natural gas as fuel, resulting in no-collection of crop straws due to high labor cost. Thus field burning and discarding of crop straws become the sources of air and water pollution. To improve the utilization of crop straws, Shanghai municipal government announced the Plan of Comprehensive Utilization of Crop Straws in 2009 (SMDRC, 2009). In this plan, several encouraged methods, including crushing and plowing into cropland, fermentation with animal manure and cultivation substrates for mushrooms, were proposed. However, the field burning and discarding still exist in some areas. Under this circumstance, based on the encouraged methods of crop straws, it is also important to evaluate the treatment and pollution status of crop straws in Shanghai suburbs.

2.2 Materials and methods

2.2.1 Evaluation methods for potential pollution of animal manure

(1) Nutrient supplies from animal manure

Pig, cattle and chicken, as the main livestock and poultry types in Shanghai suburbs, have produced more than 95% of animal manure, and the perennial breeding amounts (the average number of every month's breeding inventory amount) of pigs, cattle and chickens were obtained from the statistical reports or yearbooks of each town (SSB, 2009). The amounts of feces and urine for each type of livestock and poultry and the corresponding nutrient contents of total nitrogen (TN) and total phosphorus (TP) were obtained from the data published by Ministry of Environmental Protection of China (Table 2.1) (MEP China, 2004). The nutrient supplies from animal manure were calculated according to the following equation.

$$S=\sum N_i\times(F_{ij}\times CF_{ij}+U_{ij}\times CU_{ij})\times 365\times 10^{-6} \tag{2-1}$$

where, S is the annual nutrient supply from animal manure (t); i is the livestock and poultry type; j is the nutrient type; N is the perennial breeding amount of livestock or poultry; F is the production amount of feces (kg d^{-1}); U is the production amount of urine (kg d^{-1}); CF is the nutrient contents of feces (g kg^{-1}); CU is the nutrient contents of urine (g kg^{-1}).

(2) Nutrient demands of croplands

The croplands in Shanghai suburbs could be divided to three main types: paddy field (rice, wheat, and rape), vegetable field (pimiento, spring corn, eggplant, pepper, wild rice stem, pumpkin, lettuce, cucumber, cauliflower, cowpea, green Chinese onion, melon, watermelon, pakchoi, celery, Chinese flat cabbage, tomato, radish, cabbage, spinach, green soy bean, Chinese cabbage, potherb mustard, potato, and others.) and orchard field (grass, grape, mulberry, sorb, aloe, clove, box, camphor, camellia, and others.), which cover more than 93% of the arable land. The areas of these three types of croplands were obtained from the statistical reports or yearbooks of each town, and the nutrient demands of each type were obtained from the previous study and listed in Table 2.2 (Shen et al., 2005). The nutrient demands of croplands were calculated according to the following equation.

$$D=\sum A_i \times C_{ij} \tag{2-2}$$

where, D is the annual nutrient demand of croplands (t); i is the cropland type; j is the nutrient type; A is the area of cropland (ha); C is the nutrient demand of cropland (t ha^{-1} a^{-1}).

(3) Nutrient inputs from chemical fertilizers

Besides animal manure, large quantities of chemical fertilizers were used in croplands for the purpose of high yields in Shanghai suburbs. The application amounts (net) of nitrogen and phosphorous fertilizer were obtained from the statistical reports or yearbooks of each town.

(4) Nutrient balance of land application of chemical fertilizer and animal manure

The status of nutrient balance of land application of chemical fertilizer and animal manure was defined by a nutrient balance index (NBI), which could be calculated by the following equation.

$$NBI=S_j/D_j \tag{2-3}$$

where, S is the annual nutrient supply from chemical fertilizer or animal manure (t); D is the annual nutrient demand of croplands (t); j is the nutrient type (TN or TP).

(5) Environmental risk of land application of animal manure

The potential pollution risk of land application of animal manure was evaluated by combining with the nutrient inputs from chemical fertilizer through a nutrient pollution index (NPI), which could be calculated by the following equation.

$$NPI=(S_j+C_j)/D_j \tag{2-4}$$

where, S is the annual nutrient supply from animal manure (t); C is the annual nutrient input from chemical fertilizer; D is the annual nutrient demand of croplands (t); j is the nutrient type (TN or TP).

2.2.2 Evaluation methods for potential pollution of crop straws

(1) Production of crop straws

Rice straw and wheat straw, as the main crop straws in Shanghai suburbs, amount to more than 95% of the total yield of crop straws, and the production of rice straw and wheat straw was calculated from the crop yields and their straw production coefficients. The yields of rice and wheat were obtained from the statistical reports or yearbooks of each district (SSB, 2009). The production of rice straw and wheat straw was calculated according to the following equation.

$$P_i=\sum E_i\times Y_i\times C_i \tag{2-5}$$

Where, P is the annual production amount of the crop straws (t a^{-1}); i is the type of crop straws; E is the plantation area of the crops (ha); Y is the annual yield of the crops per hectare ($t\ a^{-1}\ ha^{-1}$); C is the straw production coefficient of the crops investigated in Shanghai suburbs ($t\ t^{-1}$).

(2) Pollution status of crop straws

As the production of crop straws, including rice straw and wheat straw was calculated based on the range of districts, the proportions of field burning and discarding of crop straws in each district or county were investigated. The amounts of crop straws burned or discarded were calculated according to the following equations.

$$FB_i=\sum P_i \times PB_i \tag{2-6}$$

$$FD_i=\sum P_i \times PD_i \tag{2-7}$$

where, FB is the annual amount of the burned crop straws ($t\ a^{-1}$); i is the type of crop straws; P is the annual production amount of the crop straws ($t\ a^{-1}$); PB is the proportion of field burning of crop straws (%); FD is the annual amount of the discarded crop straws ($t\ a^{-1}$); PD is the proportion of field discarding of crop straws (%).

2.3 Results and discussion

2.3.1 Town-based pollution risk of land application of animal manure

(1) Areas of croplands and breeding amounts of livestock and poultry

In the investigated 101 rural towns where still had agricultural land and animal husbandry, the total area of agricultural land was around 190,000 hectares and the total amounts of pigs, cattle and chickens were 1.57 million, 0.044 million and 18 million respectively, according to the areas of croplands and the breeding amounts of livestock and poultry in each town (Table 2.3). From the district's distribution perspective, Chongming County, Jinshan District and Pudong District had the larger areas of agricultural land, which totally covered more than 65% of the total agricultural land. Meanwhile, Pudong District, Fengxian District, Chongming County and Jinshan District had the larger amounts of livestock and poultry breeding, which totally carried more than 80% of the total breeding amounts of pigs, cattle and chickens.

(2) Nutrient demands of croplands

According to the areas and nutrient demands of different types of croplands, the annual nutrient demands of croplands in each town were calculated and presented in district scale in Table 2.4. The annual TN demand of croplands was 46,833 t while the TP demand was 11,373 t, of which paddy field accounted for more than 50%.

(3) Nutrient supplies from animal manure

According to the breeding amounts and nutrient contents of different types of animal manure, the annual nutrient supplies from animal manure in each town were calculated and presented in district scale in Table 2.5. The annual TN supply from animal manure was 23,431 t while the TP supply was 9,581 t, of which pigs' manure accounted for more than 50%.

(4) Nutrient inputs from chemical fertilizer

The application levels of chemical fertilizer for different types of croplands in each town were investigated, and the annual average TN application levels from nitrogen fertilizer of paddy field, dry field and orchard field were 594.95, 717.97 and 467.15 kg ha^{-1} a^{-1} respectively, while the annual average TP application levels were 51.33, 132.98 and 130.06 kg ha^{-1} a^{-1} respectively (Figure 2.1). The application levels of each town varied largely due to the difference in soil fertility, cropping system, animal manure utilization, and profit motivation (Ma and Cai, 2007)

According to the areas and nutrient inputs for different types of croplands, the annual nutrient inputs from chemical fertilizer of each town were calculated and presented in district scale in Table 2.6. The annual TN input from chemical fertilizer was 112,550 t while the TP supply was 14,782 t, and the TN and TP inputs to paddy field accounted for more than 60% and 40% of the total TN and TP inputs from chemical fertilizer, respectively.

(5) Nutrient balance analysis of land application of animal manure

Assuming that all the animal manure could be applied to the local croplands in each town, the NBI for TN and TP were evaluated and the town-based spatial heterogeneity of nitrogen and phosphorus balances were presented in Figure 2.2. There were 14 towns with NBI>1 for TN, while 21 towns with NBI>1 for TP, which located mainly in the southeast area of Shanghai, meaning that the nutrient supplies from animal manure exceeded the nutrient demands of the local croplands in these towns. The highest NBI for TN and TP were calculated to be 15.37 and 33.34 respectively, in a town in Fengxian District, where totally had 50,000 pigs, 600 milk cows and 1,600,000 poultry.

From the perspective of total city area, the NBI for TN and TP were 0.50 and

0.87 respectively, indicating that the local croplands could accept all the animal manure if the distribution of livestock and poultry breeding could be properly programmed or the transportation system of animal manure could be established for appropriate land application according to the nutrient demands of croplands. Compared with the status of nutrient balance of land application of animal manure in Shanghai suburbs in 2004 (Shen et al., 2005), the nutrient loads of animal manure on croplands was decreased due to the controlling measures on the total amounts of livestock and poultry breeding.

(6) Nutrient balance analysis of land application of chemical fertilizer

The NBI for TN and TP from chemical fertilizer were evaluated and the town-based spatial heterogeneity of nitrogen and phosphorus balances was presented in Figure 2.3. There were 88 towns with NBI>1 for TN, while 63 towns with NBI>1 for TP, which located in all districts of Shanghai, meaning that the nutrient supplies from chemical fertilizer already exceeded the nutrient demands of the local croplands in these towns. The highest NBI for TN and TP were 5.94 and 4.09, respectively.

From the perspective of total city area, the NBI for TN and TP from chemical fertilizer were 2.40 and 1.30, respectively, indicating that the overuse of chemical fertilizer was pervasive in most of the towns, especially nitrogen fertilizer.

(7) Pollution risk assessment of animal manure application on arable lands

For the purpose of further exploring the potential pollution risk of land application of animal manure, the nutrient inputs of chemical fertilizer should be considered, and the NPI for TN and TP in each town were evaluated. The town-based spatial heterogeneity of potential pollution risk is presented in Figure 2.4. There were 92 towns with NPI>1 for TN, while 83 towns with NPI>1 for TP, meaning that most towns were experiencing nutrient surplus at the circumstance of high multiple-cropping index and yields expectation. The superfluous nutrients could be easily lost by rainfall runoff and leakage and then enter into the water environment under the condition of plenteous precipitation and abundant water resources (Li and Su, 2009; Sun and Wu, 2012).

From the perspective of total city area, the NPI for TN and TP were 2.90 and 2.14, respectively, signaling that the local croplands were carrying high potential pollution risk for nutrient losses when both animal manure and chemical fertilizer were considered for land application (Kim et al., 2013; Matsi, 2012). The TN nutrient was in the position of higher pollution risk than TP although the NBI for TN was lower than TP, indicating that much more nitrogen fertilizer was applied in the croplands besides animal manure. Therefore, in the towns with high NPI, the land application intensity of chemical fertilizer should be reduced and animal manure should be regarded as the most important source of nutrient supplies, because an ecological agriculture was the primary objective for the agricultural development in Shanghai suburbs.

2.3.2 District-based pollution risk of field burning and field discarding of crop straws

(1) Yields and straw production of rice and wheat

The areas of rice and wheat plantation and their yields and straw production in each district or county are listed in Table 2.7. The total area of rice and wheat plantation was about 136,000 ha, and the areas of rice and wheat accounted for 72.2% and 28.8% respectively. From the district's distribution perspective, Chongming County and Jinshan District had the larger areas of rice and wheat plantation, which totally covered nearly 50% of the total area of rice plantation and more than 60% of the total area of wheat plantation.

(2) Proportions of different treatments for rice and wheat straws

Table 2.8 shows the proportions of different treatments for rice and wheat straws in each district or county. The treatment methods including field burning (FDBN), field discarding (FDDC), crushing and plowing to field (CPFD), composting (COMP), forage (FORG), cooking fuel (CKFL), raw material (RWMR) and others (OTHR). The crushing and plowing to field and cooking fuel were the dominant methods in Shanghai suburbs, whose proportions reached 41.85% and 27.88% for rice straw, and 64.44% and 13.93% for wheat straw. From the perspective of district-based distribution, the proportions of crushing and plowing to field in the districts with more developed economics were generally higher than other districts, while the proportions of cooking fuel followed an opposite pattern. The average proportions of field burning and field discarding were 1.59% and 15.01% for rice straw and 1.64% and 13.66%, respectively.

(3) Pollution risk assessment on field burning and discarding of crop straws

Table 2.9 shows the amounts of field burning and discarding of rice and wheat straws in each district or county. The total amounts of field burning of crop straws were 17,098 t a^{-1}, including 73.33% of rice straw and 26.67% of wheat straw, while the total amounts of field discarding of crop straws were 146,759 t a^{-1}, including 80.74% of rice straw and 19.26% of wheat straw. The Chongming county and Jinshan district contributed the larger amounts of burning and discarding of crop straws, due to their larger areas of cropland.

These plentiful amounts of untreated straws could lead to serious air and water pollution when the burning and discarding is conducted or concentrated in the harvest season in the area with dense rice or wheat plantation.

2.4 Summary

The potential pollution risk of nitrogen and phosphorus losses from land application of animal manure should be seriously paid attention when the high application levels of chemical fertilizer were considered together. Results showed that more than 80% of the towns and the whole city were suffering the potential pollution risk. The plentiful amounts of untreated straws under field burning and field discarding could lead to serious air and water pollution when the burning and discarding is concentrated in the harvest season in the area with dense rice or wheat plantation. The above results, together with the consideration of resource utilization of agricultural wastes, indicated that swine manure and rice straw are the main agricultural wastes in Shanghai suburbs, which could be used as raw materials for aerobic composting plants and anaerobic digestion projects.

Table 2.1 Production amounts of feces and urine and the corresponding TN and TP contents for the main livestock and poultry in Shanghai suburbs.

Animal type	Manure type	Production amount ($kg\ d^{-1}$)	TN content ($g\ kg^{-1}$)	TP content ($g\ kg^{-1}$)
Pig	Feces	2.0	5.88	3.41
	Urine	3.3	3.30	0.52
Cattle	Feces	20.0	4.37	1.18
	Urine	10.0	8.00	0.40
Chicken	Feces	0.12	9.84	5.37
	Urine	-*	-	-

Source: MEP China, 2004.

*No urine for chicken.

Table 2.2 Annual nutrient demands for different cropland types.

Cropland type	TN demand (t ha^{-1})	TP demand (t ha^{-1})
Paddy field	211	64
Vegetable field	413	65
Orchard field	197	37

Source: Shen et al., 2005.

Table 2.3 Areas of different types of croplands and breeding amounts of livestock and poultry in Shanghai suburbs.

District/County	Area of agricultural land (ha)				Breeding amount of livestock and poultry (head)		
	Paddy field	Dry field	Orchard field	Total	Pig	Cattle	Chicken
Pudong	14,196	8,078	7,461	29,735	567,444	9,636	10,464,056
Minhang	1,051	1,560	312	2,923	30,715	359	136,996
Baoshan	1,197	829	1,130	3,155	21,469	3,597	48,931
Jiading	4,670	1,969	887	7,526	54,989	375	59,837
Jinshan	23,713	5,314	3,989	33,016	179,607	9,289	1,240,186
Songjiang	10,876	2,223	774	13,874	105,583	429	597,051
Qingpu	11,373	6,790	1,898	20,061	42,248	320	157,628
Fengxian	10,437	3,576	2,969	16,982	353,336	9,483	3,669,525
Chongming	44,872	7,940	6,812	59,624	214,842	10,118	1,687,451
Total	122,385	38,279	26,231	186,895	1570,233	43,606	18,061,661

Table 2.4 Nutrient demands for different types of croplands in Shanghai suburbs.

District/County	TN demand ($t\ a^{-1}$)				TP demand ($t\ a^{-1}$)			
	Paddy field	Dry field	Orchard field	Total	Paddy field	Dry field	Orchard field	Total
Pudong	3,000	3,337	1,467	7,804	917	528	275	1,720
Minhang	253	342	222	817	77	54	42	173
Baoshan	222	644	61	927	68	102	11	181
Jiading	987	813	174	1,974	302	129	33	464
Jinshan	5,011	2,195	784	7,990	1,532	347	147	2,026
Songjiang	2,299	918	152	3,369	702	145	29	876
Qingpu	2,404	2,805	373	5,582	735	443	70	1,248
Fengxian	2,206	1,477	584	4,267	674	233	110	1,017
Chongming	9,484	3,280	1,339	14,103	2,898	519	251	3,668
Total	25,866	15,811	5,156	46,833	7,905	2,500	968	11,373

Table 2.5 Nutrient supplies from animal manure in Shanghai suburbs.

District/County	TN supply (t a^{-1})				TP supply (t a^{-1})			
	Pig	Cattle	Chicken	Total	Pig	Cattle	Chicken	Total
Pudong	4,691	589	4,510	9,790	1,768	97	2,461	4,326
Minhang	254	22	59	335	67	36	12	115
Baoshan	177	220	21	418	96	4	32	132
Jiading	455	23	26	504	171	4	14	189
Jinshan	1,485	568	535	2,588	560	94	292	946
Songjiang	873	26	257	1,156	329	4	140	473
Qingpu	349	20	68	437	132	3	37	172
Fengxian	2,921	579	1,582	5,082	1,101	96	863	2,060
Chongming	1,776	618	727	3,121	669	102	397	1,168
Total	12,981	2,665	7,785	23,431	4,893	440	4,248	9,581

Table 2.6 Nutrient supplies from chemical fertilizer in Shanghai suburbs.

District/County	TN input (t a^{-1})				TP input (t a^{-1})			
	Paddy field	Dry field	Orchard field	Total	Paddy field	Dry field	Orchard field	Total
Pudong	10,280	4,098	3,725	18,103	721	810	1,277	2,808
Minhang	1,390	592	788	2,770	100	178	316	594
Baoshan	1,271	1,568	301	3,140	62	274	58	394
Jiading	3,109	1,396	508	5,013	191	248	137	576
Jinshan	14,644	2,316	1,728	18,688	868	805	499	2,172
Songjiang	4,410	2,973	133	7,516	165	454	30	649
Qingpu	6,222	6,004	694	12,920	562	947	264	1,773
Fengxian	4,800	3,660	913	9,373	407	701	253	1,361
Chongming	26,689	4,876	3,462	35,027	3,206	672	577	4,455
Total	72,815	27,483	12,252	112,550	6,282	5,089	3,411	14,782

Table 2.7 Yields and straw production amounts of rice and wheat in Shanghai suburbs.

District/County	Rice			Wheat			Total straw (t a^{-1})
	Area (ha)	Yield (t ha^{-1} a^{-1})	Straw (t a^{-1})	Area (ha)	Yield (t ha^{-1} a^{-1})	Straw (t a^{-1})	
Pudong	12,711	7.64	102,960	1,741	3.58	7,489	110,449
Minhang	914	7.27	7,040	650	4.68	3,651	10,691
Baoshan	1,174	7.01	8,723	1,153	5.08	7,031	15,754
Jiading	4,595	7.64	37,222	3,477	4.29	17,899	55,121
Jinshan	21,805	7.37	170,320	8,793	4.11	43,358	213,678
Songjiang	10,901	7.55	87,186	457	4.43	2,428	89,614
Qingpu	10,659	7.80	88,143	3,455	4.56	18,912	107,054
Fengxian	10,216	7.98	86,449	3,296	4.50	17,809	104,259
Chongming	25,311	7.50	201,158	14,816	4.79	85,175	286,333
Total	98,287	/	789,199	37,838	/	203,752	992,952

Table 2.8 Proportions of different treatments for rice and wheat straws in Shanghai suburbs (Unit: %).

District/County	FDBN	FDDC	CPFD	COMP	FORG	CKFL	RWMR	OTHR
Rice straw								
Pudong	1.45	5.71	48.14	2.11	4.00	14.23	6.60	17.78
Minhang	0.00	0.00	98.28	1.72	0.00	0.00	0.00	0.00
Baoshan	0.00	23.66	65.69	0.91	7.67	0.00	0.00	2.07
Jiading	2.71	19.33	44.24	0.89	0.00	11.03	1.05	20.75
Jinshan	0.47	19.78	39.02	3.75	0.21	27.69	5.83	3.25
Songjiang	0.08	19.27	39.20	1.56	0.42	34.62	4.25	0.60
Qingpu	0.84	11.93	44.11	1.13	0.00	36.82	1.10	4.07
Fengxian	3.40	4.66	35.75	2.17	1.05	25.91	23.42	3.64
Chongming	2.73	19.05	40.35	2.02	0.72	34.34	0.71	0.08
Average	1.59	15.01	41.85	2.20	1.00	27.88	5.51	4.96

District/County	FDBN	FDDC	CPFD	COMP	FORG	CKFL	RWMR	OTHR
Wheat straw								
Pudong	1.52	9.72	69.76	0.00	1.38	12.75	0.94	3.93
Minhang	0.00	0.00	96.96	0.00	0.00	0.00	0.00	3.04
Baoshan	0.00	19.64	30.41	0.00	24.72	7.59	13.87	3.77
Jiading	3.01	11.19	75.59	0.00	0.74	9.47	0.00	0.00
Jinshan	0.37	14.76	73.87	0.00	0.00	9.28	0.43	1.29
Songjiang	0.12	22.76	68.44	0.00	0.00	8.68	0.00	0.00
Qingpu	3.16	11.82	49.99	0.00	0.00	35.03	0.00	0.00
Fengxian	3.65	21.63	45.63	0.00	0.00	27.87	1.22	0.00
Chongming	2.93	11.38	69.28	0.00	0.80	14.74	0.17	0.70
Average	1.64	13.66	64.44	0.00	3.07	13.93	1.85	1.41

FDBN, field burning; FDDC, field discarding; CPFD, crushing and plowing to field; COMP, composting; FORG, forage; CKFL, cooking fuel; RWMR, raw material; OTHR, others.

Table 2.9 Amounts of field burning and discarding of rice and wheat straws in Shanghai suburbs (Unit: t a^{-1}).

District/County	Rice straw		Wheat straw		Total	
	Field burning	Field discarding	Field burning	Field discarding	Field burning	Field discarding
Pudong	1,488	5,877	114	728	1,602	6,605
Minhang	0	0	0	0	0	0
Baoshan	0	2,064	0	1,381	0	3,445
Jiading	1,009	7,195	539	2,003	1,547	9,198
Jinshan	801	33,689	160	6,400	961	40,089
Songjiang	70	16,801	3	553	73	17,353
Qingpu	740	10,515	598	2,235	1,338	12,751
Fengxian	2,939	4,029	650	5,277	3,589	9,305
Chongming	5,492	38,321	2,496	9,693	7,987	48,013
Total	12,538	118,490	4,560	28,269	17,098	146,759

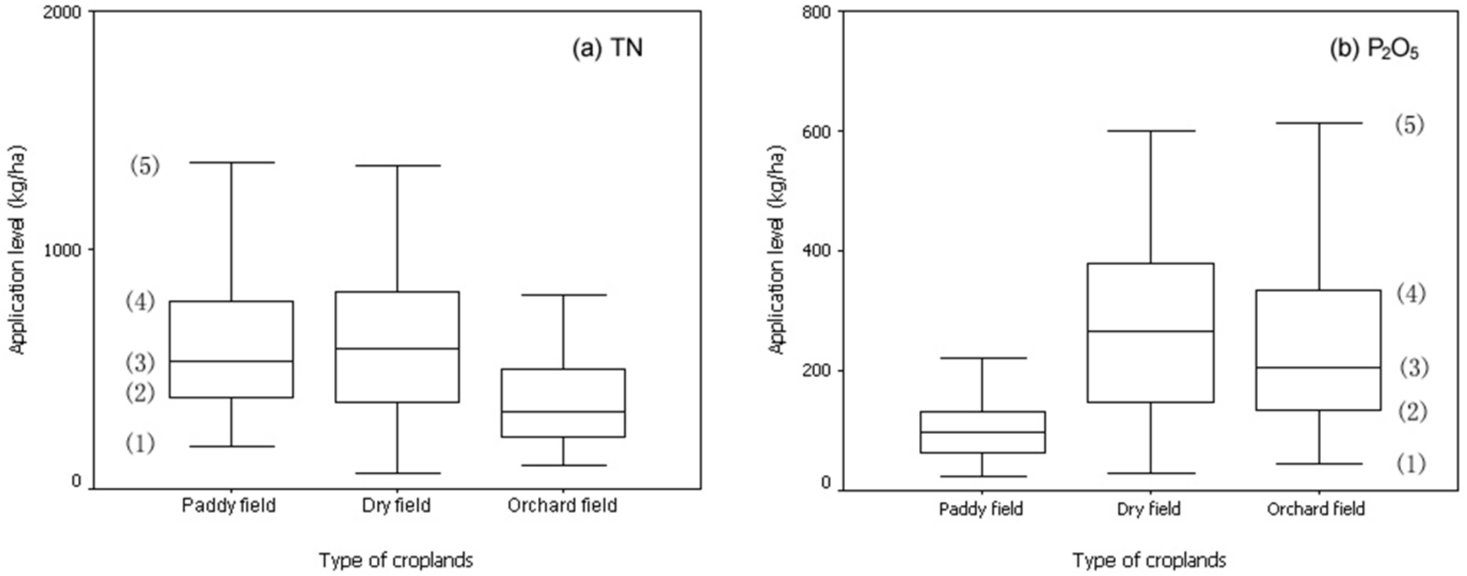

Figure 2.1 Application levels of chemical fertilizer for different types of croplands in Shanghai suburbs.

In the box plot, (1) represents the smallest value, (2) represents the first quartile, (3) represents the median, (4) represents the third quartile, and (5) represents the largest value.

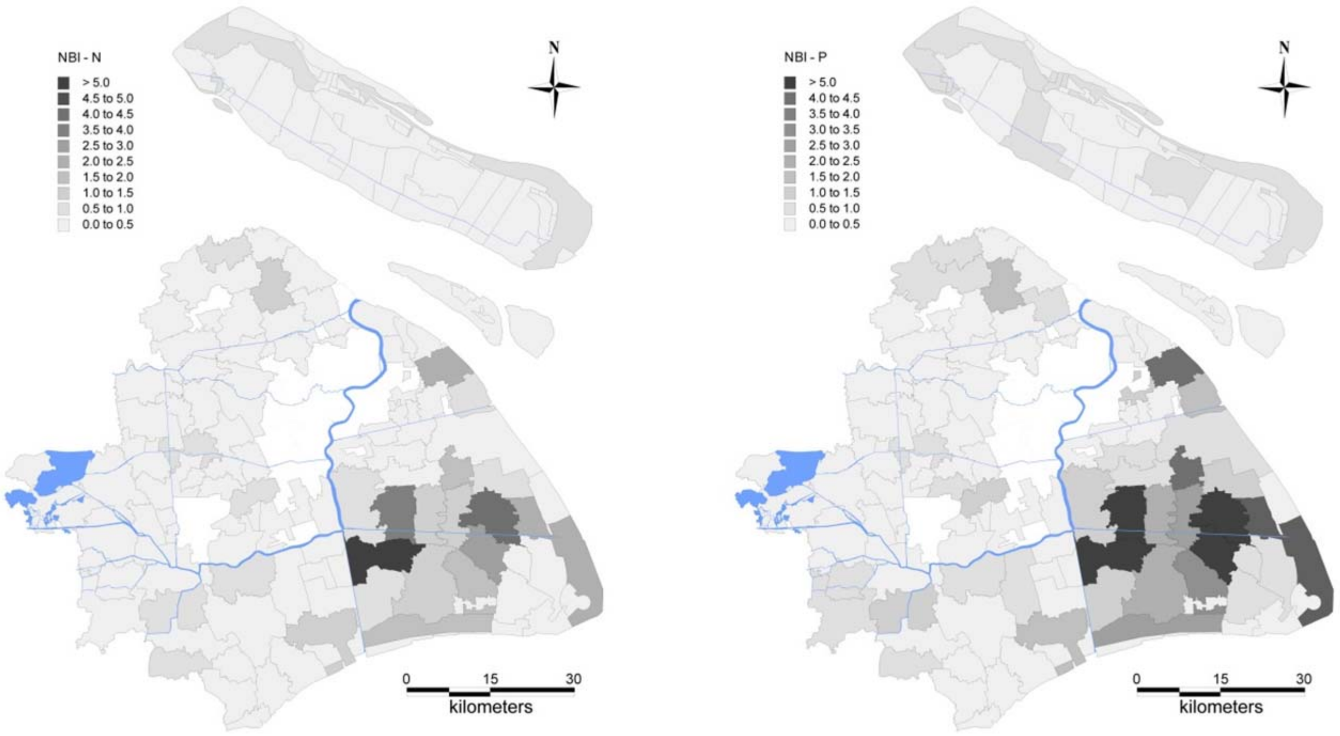

Figure 2.2 Town-based spatial heterogeneity of nitrogen and phosphorus balances for land application of animal manure in Shanghai suburbs. (NBI, nutrient balance index. *NBI=S/D*, where *S* and *D* are the annual nutrient supply from animal manure and annual nutrient demand of croplands, respectively.)

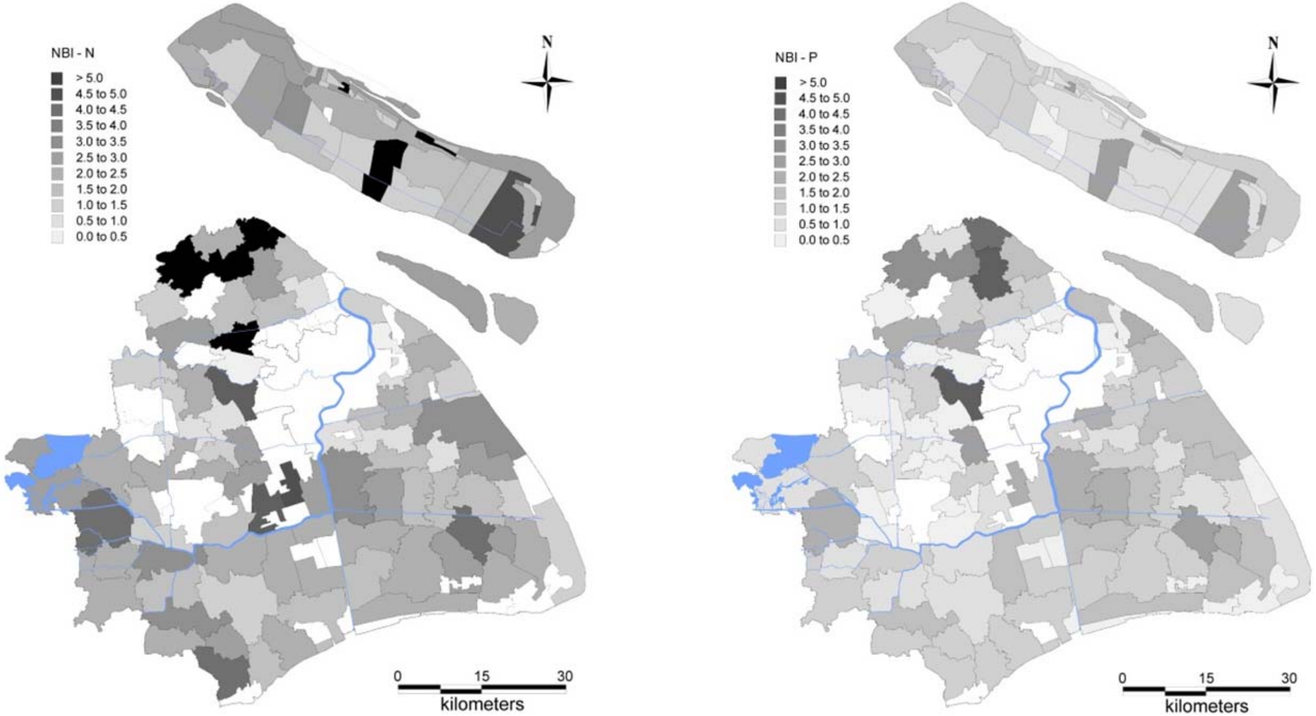

Figure 2.3 Town-based spatial heterogeneity of nitrogen and phosphorus balances for land application of chemical fertilizer in Shanghai suburbs. (NBI, nutrient balance index. *NBI=S/D*, where *S* and *D* are the annual nutrient supply from chemical fertilizer and annual nutrient demand of croplands, respectively.)

Figure 2.4 Town-based spatial heterogeneity of potential pollution risk for land application of animal manure in Shanghai suburbs.

(NPI, nutrient pollutant index. $NPI=(S+C)/D$, where S and C are the nutrient supply from animal manure and chemical fertilizer, respectively; D is the annual nutrient demand of croplands.)

Chapter 3 Establishment of maturity evaluation index system for aerobic co-composting of swine manure and rice straw

3.1 Introduction

Aerobic composting is a biological process in which organic matter (OM) can be utilized by aerobic thermophilic and mesophilic microorganisms as substrate and mainly converted into mineralized products (CO_2, H_2O, NH_4^+) or stabilized OM (mostly as humic substances) (Bernal et al., 2009; He et al., 2009). Although composting has been widely practiced with its final products being used as fertilizer or soil amendment, there are still knowledge gaps in understanding it due to the high variety and heterogeneity of feedstocks (Li et al., 2013b; Himanen and Hänninen, 2011). Besides, various composting systems add some difficulty in this understanding, probably resulting in the complexity of compost maturity evaluation system (Gao et al., 2010). Bernal et al. (2009) and Nolan et al. (2011) pointed out that compost maturity couldn't be well described by a single property or parameter. In China, the standards for composts focus on the physical and chemical parameters like pH, moisture, TN and OM without biological or agronomical parameters being considered, resulting in a less comprehensive and systematical assessment with respect to the maturity of composts and a potential risk of land application of unstable and immature composts (Gao et al., 2010). The principal requirement of compost for its being safely used in agricultural soil is a high degree of maturity or stability (Bernal et al., 2009). Some attempts have been tried on testing the effects of different feedstocks on process performance (Zhu, 2007; Li et al., 2008; Himanen and Hänninen, 2011; Gigliotti et al., 2012), and on evaluating compost maturity by using different parameters (Grube et al., 2006; Ko et al., 2008; Gómez-Brandón et al., 2008). Up to now, for the co-composition of the main agricultural wastes in Shanghai suburbs (swine manure and rice straw), still little information can be found when these two aspects (*i.e.*, physical/chemical and biological/agronomical parameters) are taken into consideration simultaneously, thus no maturity evaluation index system with agronomical parameters included is available. In addition, the relationship between the physical/chemical properties and biological/agronomical parameters is also scarce for the co-composition of the two main feedstocks, swine manure and rice straw.

3.2 Materials and methods

3.2.1 Raw materials

The swine manure was collected from a swine farm in Pudong District, Shanghai, China with a productivity of 8,000 heads per year, and the rice straw was sampled from a paddy field in Qingpu District, Shanghai, China. Besides fresh swine manure and rice straw, one kind of commercial compost was obtained from local market for the maturity test, which was produced by Shanghai Yunong Composting Plant mainly by using swine manure and rice straw as raw materials. Table 3.1 lists the main characteristics of raw materials and commercial compost used in this study. In the trials, rice straw was milled to the size of 1-2 cm, and mixed with fresh swine manure thoroughly.

3.2.2 Experimental design

(1) Reactor of aerobic composting

All composting piles weighted about 50 kg, and after being mixed completely, the piles were put into foam boxes (50×50×50 cm^3) which were then placed in a climate chamber. The chamber was controlled at temperature of 30±1 ℃ and humidity of 70±5 %, respectively. During the composting process, the pile was manually mixed every 7-10 d and sampled every 15 d or 30 d for the determination of the related parameters. The compost sample was obtained by mixing 5 sub-samples from 5 random sites of the pile at the same time.

(2) Design of 30 days' pre-trials and 90 days' trials

a) 30 days' pre-trials

For the purpose of obtaining the best composition for co-composting of swine manure with rice straw, the feedstock mixtures with five proportions of 1:1, 3:2, 2:1, 3:1, 4:1 and 5:1 on fresh weight basis (w.m.) for swine manure and rice straw (SM:RS) were prepared, and each mixture was run in triplicate.

b) 90 days' trials

In order to establish the index system of composting quality control, the feedstock mixture with the optimal composition for co-composting of swine manure with rice straw on fresh weight basis (w.m.) was prepared, and the mixture had six replicated piles, in which two piles were taken out for the testing of germination index (GI) and plant growth index (PGI) after 30 days, 60 days and 90 days.

3.2.3 Testing parameters

(1) 30 days' pre-trials

During the composting, the temperature of the core of the composting piles, pH and moisture were measured every 7-10 days, and the TN, total organic carbon (TOC) and ammonia nitrogen (Ammonia-N) were detected before and after 30 days.

(2) 90 days' trials

During the experiments, the following parameters were measured including the temperature of the core of the composting piles, pH, moisture, OM, TN, TOC, Nitrate-N, Ammonia-N, humic acid (HA), fulvic acid (FA), GI and PGI after 30, 60 and 90 days.

3.2.4 Analytical methods

The core temperature was measured by a thermometer (ZDR-21, Hangzhou Zeda Equipment Co, Ltd., China) equipped in each feedstock at the depth of 25 cm, and monitored every 24 h. The pH of the raw material or compost sample was detected by a pH meter (SenION1 portable pH meter, HACH, USA) in a 1:5 (w/v) water-soluble extract. The moisture content and dry matter of the samples was obtained by drying at 105℃ in an oven for 12 h, and the OM was determined by the weight loss after ignition at 430℃ for 24 h (Zhu, 2007). TN and TOC were measured in accordance with Zhu (2007). Ammonia-N was determined by the indophenol blue photometric method based on Berthelot's reaction (Ko et al., 2008). Nitrate-N was determined by ion chromatography (WIC-II ion chromatographer, Shanghai Cany Precision Instrument Co., Ltd., China) in a 1:20 (w/v) water extract. HA and FA fractionations were determined according to Ko et al. (2008).

OM loss was calculated from the initial (X_1) and final (X_2) ash contents according to the Equation (3-1) (Bustamante et al., 2008):

$$OM\_loss(\%) = 100 - 100\frac{[X_1(100 - X_2)]}{[X_2(100 - X_1)]} \qquad (3\text{-}1)$$

GI was calculated using seeds of *Lepidium sativum* L. (He et al., 2009). The experiment was conducted in a 1:2 (w/v) of the water-soluble extract. The extract was obtained by centrifuge the mixture (compost + distilled water) at 3200 rpm (1147×g) for 30 min, and then filtration through filter paper. The resultant solution was mixed with distilled water in the proportion of 100%, 75% and 50%, respectively, and 100% of distilled water was used as control in the experiment. Two ml of the mixture was added into a petri dish (9 cm) with filter paper laid previously, and 10 seeds of garden cress (*Lepidium sativum* L.) were spread on the filter paper. Then all the petri dishes were placed in an incubator at temperature of 25±1℃ for 72 h. The number of germinated seeds and root length were measured, and the GI was calculated according to Equation (3-2):

$$GI(\%) = \frac{(G_{100\%} \times R_{100\%}) + (G_{75\%} \times R_{75\%}) + (G_{50\%} \times R_{75\%})}{G_{0\%} \times R_{0\%} \times 3} \times 100\% \qquad (3\text{-}2)$$

where $G_{100\%}, G_{75\%}, G_{50\%}$ and $R_{100\%}, R_{75\%}, R_{50\%}$ were the numbers of germinated seeds and the average root length of treatments (100%, 75% and 50% of compost extracts) respectively, $G_{0\%}$ and $R_{0\%}$ were the numbers of germinated seeds and the average root length of the control (100% of distilled water).

Plant growth index (PGI) determination was conducted on the mixture of compost and peat at different ratios of 0%, 20%, 40%, 60%, 80% and 100% (v/v). Plastic pots with volume of 1000 ml were used to hold the mixtures and 125 seeds of garden cress (*Lepidium sativum* L.) were spread on the surface and covered with small amount of peat. The pots were placed in a climate chamber at temperature of 25±1 ℃, humidity of 75±5 % and 12/12 of light/dark cycle and incubated for 3 weeks. The pots were irrigated with de-ionized water at a same interval determined previously. On the day of termination the seedlings were cut close to the substrate surface, dried and weighed. The PGI was expressed by the ratio of average weight of the treatments (20%, 40%, 60%, 80% and 100% of compost) to the weight of the control samples (0% of compost).

The Solvita maturity index was also used and tested by following the guide to Solvita testing for compost maturity index (Woods End Research, 2002).

3.2.5 Statistical analysis

The first-order kinetic model, Equation (3-3) was adopted for OM degradation during the composting process in this study (Bustamante et al., 2008). And the related kinetics calculation was completed by using the SPSS 17.0 and ORIGIN 8.0 computer program.

$$OM\_loss\ (\%) = A\ (1-e^{-kt}) \tag{3-3}$$

where A is the maximum degradation of OM (%), k the rate constant (d^{-1}) and t the composting duration (d). The residual mean square (RMS) was calculated to indicate the kinetic model fittings of the experimental results.

The results presented in this study were mean values±standard deviations. Bivariable square Pearson's correlation analysis was applied to disclose the relationship between different maturity parameters. Significance was assumed if the p

<0.05.

3.3 Results and discussion

3.3.1 Characterization of co-composting during 30 days' pre-trials

(1) Changes of physical and chemical parameters

a) Change in temperature

Figure 3.1 shows the temperature changes in the composting piles with different compositions of swine manure and rice straw. A similar temperature-rising phenomenon was observed for all the piles at the beginning, and the temperature of the pile with composition of 3:2 rose much faster during 5-10 days, and kept above 50 ℃ until the end of experiment.

b) Moisture change

Figure 3.2 shows the moisture changes in the composting piles with different compositions of swine manure and rice straw. A decrease in moisture was detected in most of the piles, and the moisture decreased remarkably in the pile with a composition of 3:2 (swine manure and rice straw).

c) pH change

Figure 3.3 shows the pH changes in the composting piles with different compositions of swine manure and rice straw. The results indicated that during the early period of composting, the pH of all piles decreased, possibly attributable to the production of organic acids because of anaerobic condition resulted from the high moisture and low oxygen content in the composting materials; then in the later period, pH increased and reached stable.

d) TN change

Figure 3.4 shows the contents of TN, Ammonia-N and TOC before and after the composting under different compositions of swine manure and rice straw. The results indicated that some nitrogen loss occurred in the composting process. Maybe it's caused by NH_3 volatilization during the high temperature stage, and NO_x volatilization from denitrification might also have some contribution under appropriate conditions of high moisture and anaerobic environment in the composting piles. Ammonia-N contents remarkably rose in all the composting piles, and TOC contents in most of the piles decreased slightly except the piles with compositions of 4:1 and 5:1, maybe due to lower carbon degradation and higher ammonia nitrogen loss during the anaerobic status caused by high moisture in these piles (Li et al., 2013a).

e) Determination of the optimal composition

Table 3.2 lists the scores (from 0 to 5) for 6 indices of the composting products with different compositions of swine manure and rice straw. The scores of temperature, moisture, pH, TN, ammonia-N and TOC were subjectively evaluated based on practical values, and the score of 5 presented the best performance while the score of 0 presented the worst performance. The scores of the pile with a composition of 3:2 were the highest, indicating that this composition maybe the best ratio for co-composting of swine manure with rice straw in this study.

3.3.2 Characterization of co-composting during 90 days' trials

(1) Changes of physical and chemical parameters

a) Change in temperature

In the composting piles, the average temperature reached the thermophilic phase (max. T = 69.8 ℃) within 2 days, and fell to the ambient temperature in about 60 days (Figure 3.5). Four obvious temperature peaks were observed. The temperature drop between peaks may be attributable to the large amount of heat loss caused by manually mixing, and some time interval is needed for heat accumulation to reach the subsequent peaks. This observation is somewhat in agreement with the reports by de Guardia et al. (2010) and Himanen and Hänninen (2011), slightly different in the duration of thermophilic phase and the maximum temperatures. Bernal et al. (2009) concluded that 40-65 ℃ was the optimum temperature for composting and above 55 ℃ was required to eliminate pathogenic microorganism. In this study, the piles maintained this range for a period of 4-5 weeks and stayed above 55 ℃ for around 2 weeks.

b) Change in pH

The initial pH values in the composting piles (Figure 3.6a) are within the suitable range 6-8 for composting (Bernal et al., 2009; Troy et al., 2012), and the rapid increase in the initial 15 days could be attributed to the degradation of acid-type compounds and the mineralization of proteins, amino acids and peptides to ammonia. Then the pH values tended to be stable at 7.50-8.50 and the peaks were detected at 8.33 on day 30, reflecting the high ammonia production (Fig. 3.6e). The final pH values decreased to 7.80, due to microbial nitrification (Nolan et al., 2011). The pH variation profiles are similar to Zhu (2007) and Li et al. (2008) who did co-composting of animal manure and rice straw.

c) Change in moisture

The moisture contents decreased gradually in the piles, averagely from an initial 51.04% to final 20.58% in the composting piles (Figure 3.6b).

d) Changes of TOC and OM

TOC and OM were detected to decrease gradually during the composting process in the piles. The initial TOC of 42.21% decreased to 35.65% in the final composts, (Figure 2c). The OM contents gradually decreased from initial values of 72.77% to final values of 61.45% in the composting piles (Fig. 3.6c).

e) Changes of different N forms

The changes of TN, ammonia-N and nitrate-N are presented in Figures 3.6d and 3.6e. A rapid increase in TN was observed in the initial stage, and in contrast with the relatively stable nitrate-N levels, ammonia-N remained stable till day 60 and then decreased clearly in the composting piles. This phenomenon may be closely associated with the activity and community evolution of the inhabited ammonification and nitrifying bacteria in the composting piles, and high temperature and volatilization may also have some contribution to the loss of ammonia-N in the composts (Huang et al., 2004). Much less change in nitrate-N was observed during the composting, implying less risk of nitrate contamination of the groundwater when the compost is used for land application (Bernal et al., 2009).

f) Changes of humus

The average HA content fluctuated during the composting process and the FA seemed to change in an opposite pattern with HA in the piles (Fig. 3.6f), reflecting the humification of OM. This observation doesn't agree with the previous studies (Ko et al., 2008; Gigliotti et al., 2012), in which an increase of HA and decrease of FA was reported, probably attributable to the different origin and nature of the feedstocks used in this study.

(2) Changes of agronomical parameters

The parameters of GI and PGI can be used to indicate the phytotoxicity of composts to plants. Table 3.3 shows the GI and PGI values increased with the progress of composting, and reached greater than 100% for GI and above 1.00 for PGI after 90 d, signaling no phytotoxicity problems in the final compost (Huang et al., 2004; Himanen and Hänninen, 2011).

(3) Changes of C/N, HA/FA, and Solvita maturity index

The C/N ratio decreased fast in the composting piles, especially at the first 30 days of the composting process. The C/N ratios almost reached < 25 after 60 days' composting, higher than the results (C/N=9-17) obtained by Huang et al. (2004) due to much higher initial C/N ratios (> 40) in the raw materials.

From Table 3.3, it can be seen that the ratio of HA to FA (HA/FA), *i.e.* degree of polymerization, in the composting piles didn't clearly display a classic increase trend throughout the composting process observed by Bernal et al. (2009) and He et al. (2009). However, this observation is similar with the results from the co-composting of cattle/poultry manure with distillery wastes by Bustamante et al. (2008) and the co-composting of poultry manure with sawdust by Dias et al. (2010), partly attributed to the different origin of raw materials.

Although no clear trend was found in HA/FA ratio in this study, the gradual increase of Solvita maturity index till the end of composting in the piles signals the maturation process. Based on Solvita maturity index, the compost maturity of the piles can be comparable to the commercial products after 90 days' composting (Table 3.3).

3.3.3 Kinetics of OM degradation during 90 days' trials

In the bio-oxidative phase of composting, substantial OM losses can be observed with the lowest OM mineralization in the maturation phase (Bernal et al., 2009). The OM degradation followed a first-order kinetic equation in the piles, namely OM loss $= A(1-e^{-kt})$ (Fig. 3.7). The following parameters were obtained from the curve fitting of experimental data:

$A=69.37\pm5.54,\ k=0.00985\pm0.00112\ d^{-1},\ RMS=0.9982\ (p<0.001)$

where A values obtained in this study is in agreement with the result of 55%-72.5% obtained by Bustamante et al. (2008).

3.3.4 Maturity evaluation index system

Many parameters have been used to indicate the maturation process of composting and included in the maturity parameters systems (Grube et al., 2006; Ko et al., 2008; Gómez-Brandón et al., 2008). In this study, the Solvita maturity index, widely recognized and obtained by simple tests, is taken as a standard index. Table 3.4

lists the correlation coefficients between Solvita maturity index and some commonly used maturity parameters by bivariable square Pearson’s correlation analysis. Except HA/FA ratio, the other maturity parameters such as C/N ratio, GI and PGI are significantly correlated with the Solvita maturity index. Therefore, the C/N ratio, GI and PGI can be included into the maturity evaluation index system in order to assess the compost maturity effectively. The negative coefficients between C/N ratio and other maturity parameters (including Solvita index, GI and PGI) imply the decrease trend of C/N ratio during the maturation process. Both GI and PGI can be used as the indicators of compost phytotoxicity. GI test is a quick method for evaluating phytotoxicity within a short period, while PGI test can give a better estimation of compost impact on plant growth for a longer time, thus the application of GI or PGI test can be determined from practical needs and on time requirement.

According to the results of maturity test for the composting piles and the commercial compost, a suitable C/N ratio is difficult to define due to different carbon and nitrogen sources (thus different C/N ratio) in the feedstocks. In this study, however, suitable values of GI and PGI could be proposed for composting products from the tests of livestock manure and rice straw, greater than 120% and 1.00, respectively.

3.4 Summary

Mature compost could be achieved after 60 days’ aerobic co-composting of swine manure and rice straw, and exhibited fast maturation signaling by a relatively long thermophilic phase, high OM degradation rate, GI and PGI. A comprehensive maturity evaluation index system consisting of chemical (C/N ratio) and biological (GI or PGI) parameters was established, much more suitable and practical for the maturity assessment of compost. The suitable values of GI and PGI are proposed as greater than 120% and 1.00, respectively for mature compost.

Table 3.1 Characteristics of the raw materials used in the aerobic composting and commercial compost product (dry weight).

Parameters	Swine manure	Rice straw	Commercial compost
Moisture (%)	81.95±0.56	11.07±1.00	27.08±0.86
TOC(%, d.w.)	42.20±0.45	38.73±0.99	36.19±1.13
TN (%, d.w.)	3.17±0.07	0.54±0.07	1.63±0.05
C/N ratio (TOC/TN)	13.31	71.72	22.20
TP (%, d.w.)	1.28±0.13	0.09±0.02	2.09±0.15
pH	7.64±0.43	N.D.	7.45±0.03

The data are expressed as mean±standard deviation for triplicate determinations. N.D., no determination.

Table 3.2 Scores for the main physicochemical parameters during co-composting under different compositions of swine manure and rice straw.

Composition	Temperature	Moisture	pH	TN	Ammonia-N	TOC	Total score
1:1	2	0	1	5	5	4	17
3:2	5	5	4	5	3	4	26
2:1	2	1	4	3	3	3	16
3:1	3	4	2	3	3	5	20
4:1	0	0	5	4	1	0	10
5:1	1	0	3	2	1	0	7

The scores of temperature, moisture, pH, TN, ammonia-N and TOC are subjectively evaluated based on practical values. 5 denotes the best while 0 indicates the worst performance.

Table 3.3 Changes of principal maturity parameters during aerobic co-composting of swine manure with rice straw.

Composting duration (days)	C/N	HA/FA	Solvita index	GI	PGI
Composting piles: swine manure + rice straws					
0	42.21	1.67	N.D.	N.D.	N.D.
30	28.57	1.02	5	68%	1.03
60	24.86	1.68	6	86%	1.04
90	22.92	1.22	8	129%	1.12
Commercial compost: swine manure + rice straws					
70	22.20	N.D.	8	145%	1.09

C/N, ratio of total organic carbon and total nitrogen; HA/FA, ratio of humic acid to fulvic acid; GI, germination index; PGI, plant growth index. N.D., no determination.

Table 3.4 Coefficients between Solvita maturity index and some commonly used maturity parameters through bivariable square Pearson's correlation analysis.

Parameters	Solvita index	C/N	HA/FA	GI	PGI
Solvita index	1	-0.987**	0.471	0.912*	0.818*
C/N	-1.000**	1	-0.461	-0.917*	-0.825*
HA/FA	0.471	-0.461	1	0.068	-0.122
GI	0.912*	-0.917*	0.068	1	0.982**
PGI	0.818*	-0.825*	-0.122	0.982**	1

$^{*}p<0.05$; $^{**}p<0.01$.

C/N, ratio of total organic carbon and total nitrogen; HA/FA, ratio of humic acid to fulvic acid; GI, germination index; PGI, plant growth index.

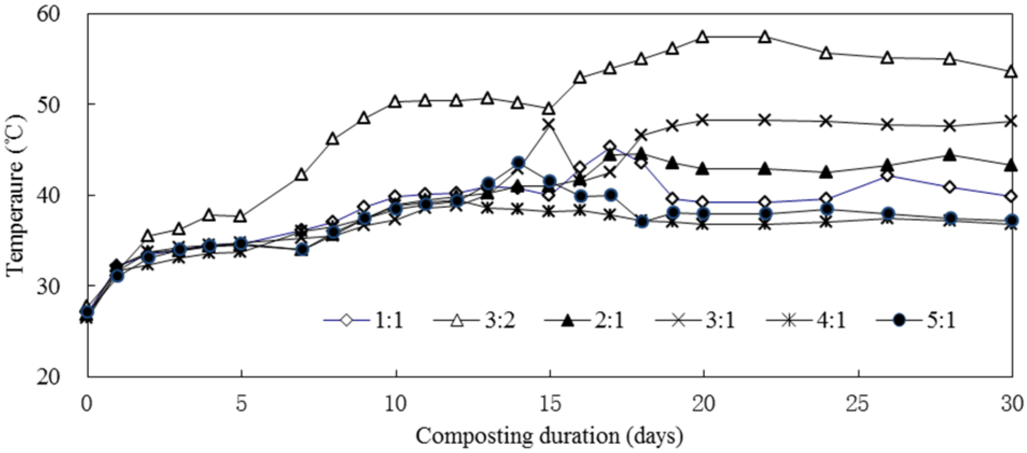

Figure 3.1 Temperature change in the composting piles with different compositions of swine manure and rice straw.

(1:1, 3:2, 2:1, 3:1, 4:1 and 5.1 denote the proportions of swine manure to rice straw on fresh weight basis)

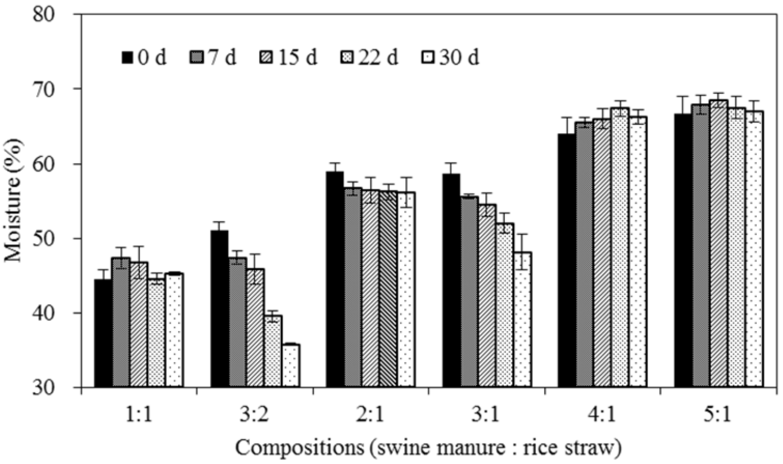

Figure 3.2 Moisture change in the composting piles with different compositions of swine manure and rice straw.

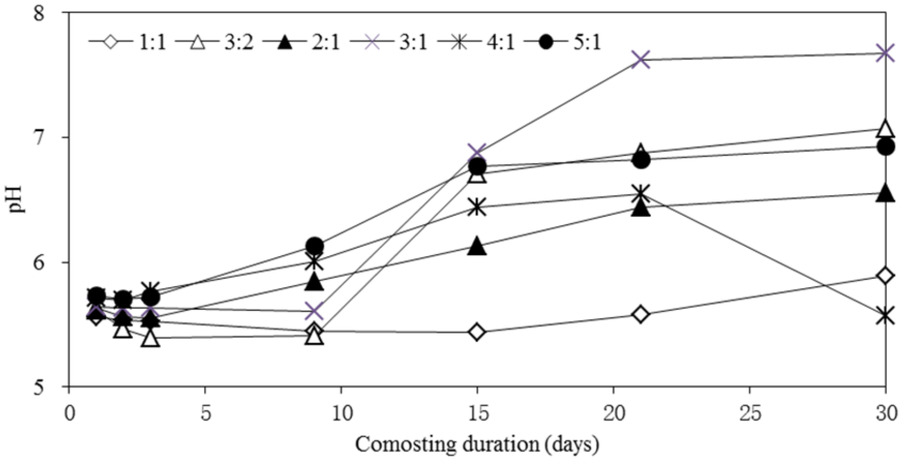

Figure 3.3 pH change in the composting piles with different compositions of swine manure and rice straw.

(1:1, 3:2, 2:1, 3:1, 4:1 and 5.1 denote the proportions of swine manure to rice straw on fresh weight basis)

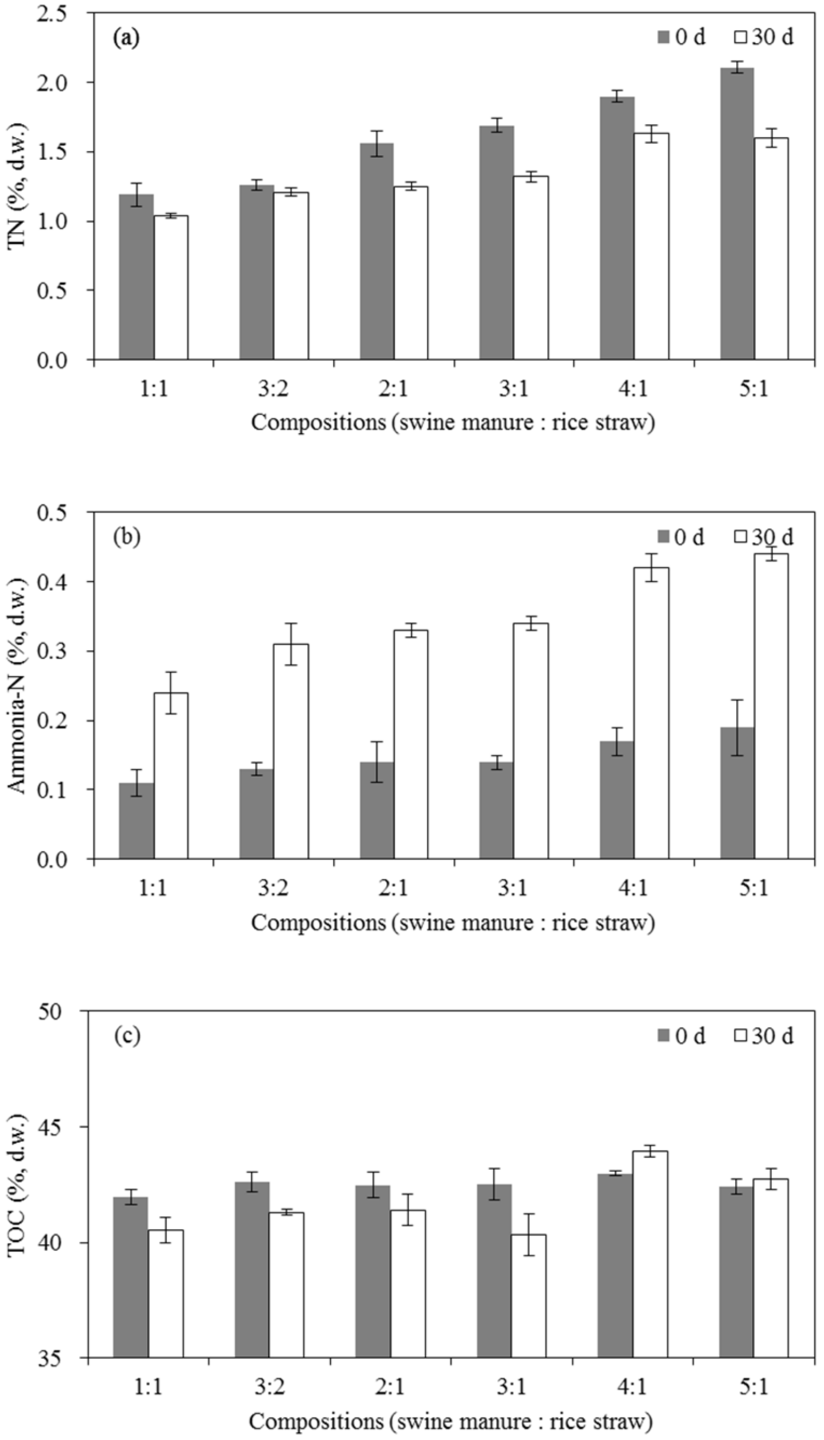

Figure 3.4 Comparison of TN, Ammonia-N and TOC contents in the composts under different compositions of swine manure and rice straw after 30 days' pre-trials. (a: TN; b: Ammonia-N; c: TOC)

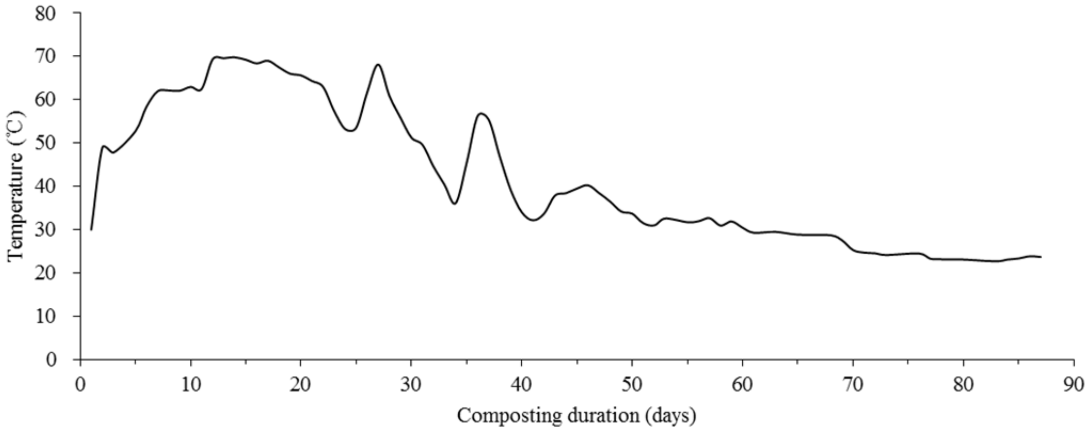

Figure 3.5 Average temperature change in the composting piles under the optimal composition of swine manure and rice straw (3:2 on fresh weight).

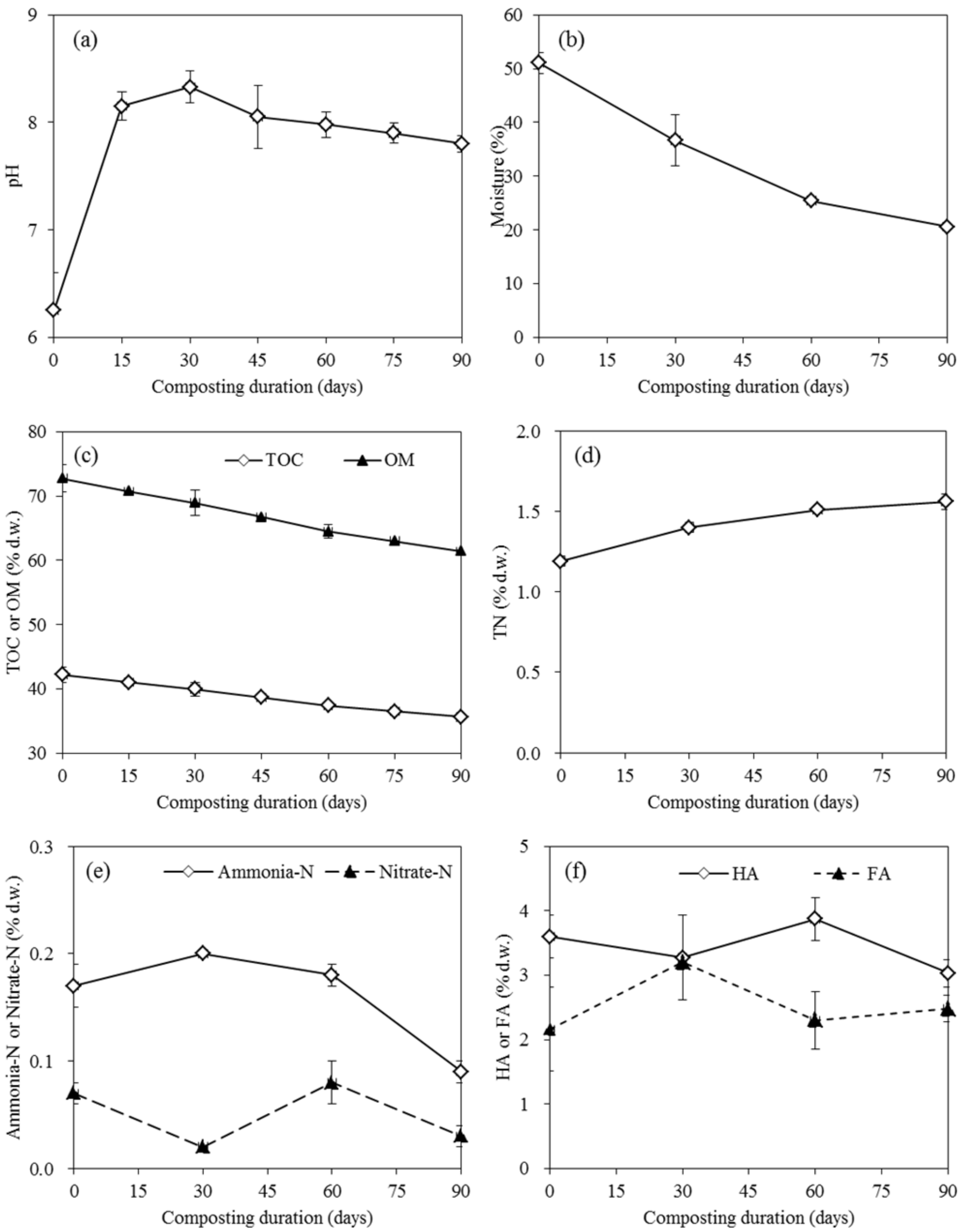

Figure 3.6 Average changes in physicochemical parameters for the composting piles under optimal composition of swine manure and rice straw (3:2 on fresh weight). pH(a), moisture (b), TOC and OM (c), TN (d), Ammonia-N and Nitrate-N (e), and HA and FA(f)

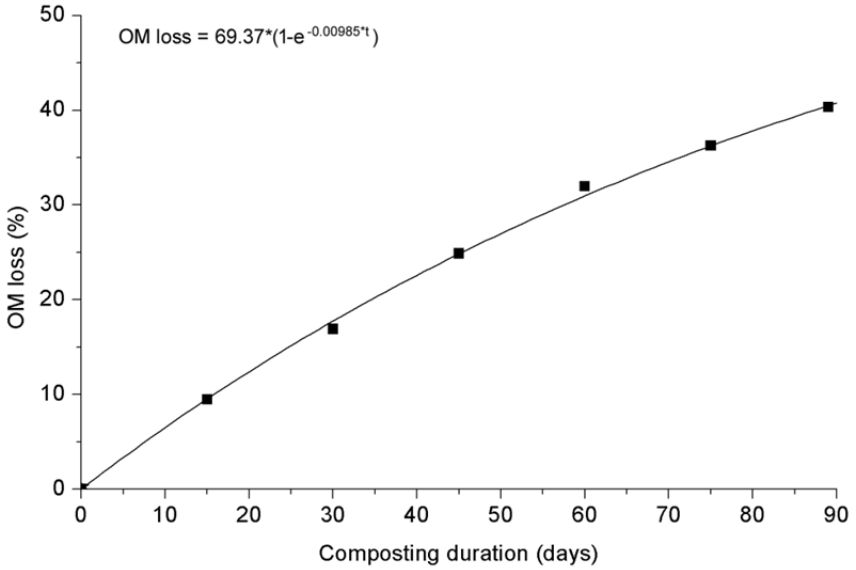

Figure 3.7 Organic matter (OM) loss in the composting piles under optimal composition of swine manure and rice straw (3:2 on fresh weight). (The line is the curve-fitting by using experimental data.)

Chapter 4 Exploration on optimal operation conditions for anaerobic co-digestion of swine manure and rice straw

4.1 Introduction

Anaerobic digestion is a biological process wherein diverse groups of microorganisms convert the complex organic matters into simple and stable end products in the absence of oxygen. This process is very attractive because it yields biogas, a mixture of methane (CH_4) and carbon dioxide (CO_2), which can be used as renewable energy resources (Raposo et al., 2011; Zhong et al., 2011; Niu et al., 2011; Lei et al., 2010). In this view, anaerobic digestion of solid waste is a process that is rapidly gaining momentum to new advances especially dry anaerobic fermentation which has become a major focus of interest in waste management throughout the world. This process appears to be the reliable and promising one for the treatment of organic solid wastes, including swine manure and rice straw. Nowadays, there are two main types of anaerobic digestion processes classified according to the solids content in the solid wastes, i.e. low-solids (wet, TS<10%) and high-solid (semi-dry, 10%<TS<20%; dry, TS>20%) anaerobic digestion. The biogas yield and production rate are high in the systems where the waste is kept in its original solid state without dilution with water. Indeed, dry systems have already being proven to be reliable in France and Germany for the biomethanization of mechanically sorted organic fraction of municipal solid wastes (Juanga, 2005). The specific features of high solid batch systems such as simple design and easy process control, small water consumption and lower investment cost make them particularly attractive for developing countries

(Sinpaisansomboon et al., 2007). However, to some extent this kind of system demonstrates various limitations including large inoculation, mixing, and instability and difficulty in overcoming this instability (Ahn et al., 2010; Bollon et al., 2011; Krishania et al., 2013). In order to overcome these limitations, some approaches have been put forward, such as total solid (TS) and C/N control, appropriate inoculums, material pretreatment, and reaction temperature control. In China, dry or semi-dry anaerobic digestion for agricultural wastes is still at its developing stage. Some studies have been conducted to explore the operation conditions of different compositions of dairy manure and wheat or corn straws (Wang et al., 2012; Ye et al., 2013; Liang et al., 2014), and few attempt has been tried to study the composition of swine manure and rice straw for dry or semi-dry anaerobic co-digestion. This study aims to explore the best operation conditions of anaerobic co-digestion of swine manure with rice straw by using the methods of inoculation and pretreatment, with the expectation of overcoming its limitations.

4.2 Materials and methods

4.2.1 Raw materials

The swine manure was collected from a swine farm in Pudong District, Shanghai, China with a productivity of 8,000 heads per year, and the rice straw was sampled from a paddy field in Qingpu District, Shanghai, China. Table 4.1 lists the main characteristics of raw materials used in this study. In the trials, rice straw was milled to the size of 1-2 cm, and mixed with fresh swine manure thoroughly.

4.2.2 Experimental design

(1) Experimental setup for anaerobic co-digestion

The anaerobic digesters used in this study were 1-L glass bottles with working volume of 500 mL. Each bottle was sealed using a rubber stopper with a glass tube connected to exit biogas. The digester was connected to a gas collection system consisting of a biogas displacement cylinder and a saturated $NaHCO_3$ solution beaker (Figure 4.1). Prior to operation, the reactors were purged with nitrogen gas for 5 min to ensure anaerobic conditions. Thereafter, the digesters were placed in a water bath controlled at 35±1℃.

(2) Design of 45 days' pre-trials and 90 days' trials

a) 45 days' pre-trials

For the purpose of obtaining the optimal composition for anaerobic co-digestion of swine manure with rice straw, the feedstock mixtures with three proportions of 2:1, 1:1 and 1:2 on fresh weight basis (w.m.) for swine manure and rice straw and three TS concentrations of 10%, 20% and 30% were prepared, and each mixture was run in duplicate (Table 4.2). Besides, each mixture was simultaneously prepared for 4 tubes (50 mL) of replicates in order to test the parameter of volatile fatty acids (VFAs) every 7-10 days.

b) 60 days' trials

In order to explore the best operation conditions of anaerobic co-digestion of swine manure with rice straw, the feedstock mixture with the optimal composition was prepared with different amounts of biogas slurry inoculum and different pretreated rice straw, and each mixture was run in triplicate (Table 4.3).

For the trial of biogas slurry inoculation, 4 treatments were prepared: (a) CK (control reactor), 140 g swine manure, 60 g rice straw, 270 mL distilled water; (b) BS-1, 140 g swine manure, 60 g rice straw, 34 mL biogas slurry, 236 mL distilled water; (c) BS-2, 140 g swine manure, 60 g rice straw, 69 mL biogas slurry, 201 mL distilled water; (d) BS-1, 140 g swine manure, 60 g rice straw, 137 mL biogas slurry, 133 mL distilled water.

For the trial of rice straw pretreatment, 4 treatments were prepared: (a) CK, 140 g swine manure, 60 g rice straw without pretreatment, 137 mL biogas slurry, 133 mL distilled water; (b) MW, 140 g swine manure, 60 g rice straw with microwave pretreatment (put in the microwave oven at 900 W for 5 min), 137 mL biogas slurry, 133 mL distilled water; (c) AK, 140 g swine manure, 60 g rice straw with alkaline pretreatment (soaked in the solution of 10% NaOH for 75 min and then washed to neutral), 137 mL biogas slurry, 133 mL distilled water; (d) AK+MW, 140 g swine manure, 60 g rice straw with alkaline and microwave pretreatment (put in the microwave oven at 900 W for 5 min, then soaked in the solution of 10% NaOH for 75 min followed by washing to neutral), 137 mL biogas slurry, 133 mL distilled water.

4.2.3 Testing parameters

(1) 45 days' pre-trials

Biogas production was monitored every day, and soluble chemical oxygen demand (SCOD) was determined before and after 45 days. VFAs were detected every 7-10 days.

(2) 60 days' trials

Biogas production and methane content were checked every day, and pH, TS and Volatile solid (VS) were measured before and after about 60 days.

4.2.4 Analytical methods

Biogas production was measured by water displacement and methane content was measured by portable CH_4 detector (Shenzhen Keernuo Electronics Technology Co., Ltd., China). TN, TOC, TS, VS and SCOD were determined using standard methods (APHA, 1998). pH was detected by a pH meter (SenION1 portable pH meter, HACH, USA) in a 1:5 (w/v) water-soluble extract. VFA samples were prepared in 2% formic acid and measured by a gas chromatograph (Agilent 7890) with a flame ionization detector.

Besides, the yields and productivities of biogas or methane after about 60 days were calculated following equations (4-1) and (4-2).

$$C_{yield} = \frac{P_{\text{total}}}{S_{\text{loaded}}} \times 10^{-3} \tag{4-1}$$

$$C_{productivity} = \frac{P_{\text{total}}}{S_{\text{reduced}}} \times 10^{-3} \tag{4-2}$$

where, C_{yield} is the biogas/methane yields (m^3 kg^{-1} TS or VS-loaded); C_{prod} is the biogas/methane productivity (m^3 kg^{-1} TS or VS-reduced); P_{total} is the total production amount of biogas or methane (mL); S_{loaded} is the loaded amount of TS or VS in the reactor (g); $S_{reduced}$ is the reduced amount of TS or VS in the reactor (g).

4.2.5 Statistical analysis

One-way ANOVA was performed to evaluate the data for any significant difference in terms of biogas or methane production and methane content. Biogas yield was calculated as the volume of biogas or methane production per unit weight of straw TS or VS loaded, and biogas productivity was referred to the volume of biogas or methane production per unit weight of straw TS or VS reduced. First-order kinetic models, the simplest models applied to one- or two-phase anaerobic digestion of complex substrates, have been successfully used to quantify the extent of process inhibition, assess the substrate availability, and discover the rate-limiting steps such as hydrolysis (Lopes et al., 2004; Lei et al., 2010; Kafle and Kim, 2013; Liang et al., 2014). In this study, a first-order model was also used to compare the digestion performance of different reactors. The biogas or methane production rate constant (*k*) was obtained from the following Equation (4-3) using the data analysis and graphing software (Origin 8.5).

$$G = G_T(1 - e^{-kt}) \tag{4-3}$$

where G (mL) is the cumulative biogas or methane production, G_T (mL) is the total biogas production in the anaerobic co-digestion, k (d^{-1}) is the first-order biogas production rate constant, and t (d) is the operation time, respectively.

4.3 Results and discussion

4.3.1 Characterization of co-digestion during 45 days' pre-trials

(1) Biogas production

Figure 4.2 shows the cumulative biogas production in the reactors of anaerobic co-digestion under different compositions of swine manure and rice straw. The cumulative biogas yields varied from 62.09 to 204.74 L/kg-TS loaded. The reactors with a composition of 2:1 (SM:RS) produced higher biogas yields at different contents of TS, probably contributed by the higher methane productivity of swine manure resulted from a higher proportion of swine manure in these reactors (Møller et al., 2004). The reactors with 20% of TS achieved higher biogas yields than the other TS conditions (10% and 30%), possibly due to the inhibition of microorganisms responsible for anaerobic digestion at high solid concentration and the insufficient degradable compounds at low solid concentration. This observation is almost in agreement with previous work of Fernández et al. (2010) and Motte et al. (2013).

It could be concluded that, a higher proportion of swine manure in the anaerobic co-digestion of swine manure with rice straw may have a better performance of biogas production, especially at TS of about 20%.

(2) SCOD and VFAs changes

Figure 4.3 shows the SCOD changes in the reactors under anaerobic digestion with different compositions of swine manure and rice straw. The initial SCOD concentrations varied from 5405 to 19091 mg/L, and decreased to 3091 to 13216 mg/L at the end. Since SCOD concentration could reflect the progess of hydrolysis/acidification process, a higher SCOD concentration was accompanied by a higher VFA concentration (Ahn et al., 2010). The reactors with a composition of 2:1 (SM:RS) at different TS contents generally produced higher SCOD concentrations, probably brought about by its higher proportions of swine manure and thus more readily biodegradable organic materials (Wang et al., 2012).

Figure 4.4 shows the VFAs changes in the reactors under anaerobic digestion at different compositions of swine manure and rice straw. As an indicator of the metabolic status of an anaerobic degradation system (Ye et al., 2013), the VFAs concentrations increased firstly and two obvious peaks appeared before decreasing slowly to below 4 g/L. In addition, the VFAs concentrations in the reactors with a composition of 2:1 (SM:RS) at TS of 10% and 20% were generally higher than other reactors, which agrees with the variation of SCOD in the reactors.

(3) Determination of the optimal composition

The results of 45 days' pre-trials indicated that, the composition of 2:1 (SM:RS) at TS of 10-20% had the better performance on biogas production and SCOD and VFAs evolution. In this view, the 60 days' trials with different amounts of biogas slurry inoculum and different pretreated rice straw adopted the composition of around 2:1 (SM:RS) at TS of about 15%, in order to ensure a continuous and stable operation of anaerobic co-digestion process.

4.3.2 Characterization of co-digestion with biogas slurry inoculation during 60 days' trials

(1) Biogas and methane production evaluation

a) Daily biogas production

Figure 4.5 shows the daily biogas production in the reactors of anaerobic co-digestion under different amounts of biogas slurry inoculation. The daily biogas production in all the reactors gradually increased from day 4 on, and reached the first peak on day 10, which was followed by a gradual decreasing tendency. Thereafter, the daily biogas production in the reactors with biogas slurry addition reached the second peaks on day 20, while the CK was on day 32. After 40 days' operation, the daily biogas production in all the reactors decreased from above 200 mL d^{-1} to below 100 mL d^{-1}.

The daily biogas production in the BS-3 reactor exhibited the best performance from day 15 to day 30, and reached greater than 700 mL d^{-1} during day 19-24, while the daily biogas production in the BS-1 and BS-2 reactors also showed better performance than CK, and reached nearly 700 mL d^{-1} on day 20.

The results indicate that biogas slurry inoculum is effective for the improvement of biogas production. After biogas slurry addition, the biogas production process was accelerated with earlier appearance of biogas production peaks.

b) Methane content

Figure 4.6 shows the daily methane content in the reactors of anaerobic co-digestion under different amounts of biogas slurry inoculation. The methane contents in all the reactors gradually increased in the first 10 days, and reached more than 70%. Thereafter, the methane contents kept around 80% until the end of experiment. There was no significant difference among CK, BS-1, BS-2 and BS-3 ($p<0.05$), meaning that biogas slurry inoculation had no obvious influence on methane content during the anaerobic co-digestion of swine manure with rice straw.

c) Cumulative biogas production

Figure 4.7 shows the cumulative biogas production in the reactors of anaerobic co-digestion under different amounts of biogas slurry inoculation. During day 20 to day 40, the cumulative biogas production was higher in the reactors with biogas slurry addition in comparison to the control, and the overall biogas production in all the reactors could reach more than 20 L.

(2) Average performance

Table 4.4 summarized the average performance of anaerobic co-digestion under different amounts of biogas slurry inoculation. The initial pHs in the reactors ranged 7.44-7.68, while the final pHs were 7.97-7.99. After about 60 days' anaerobic digestion, 37.03-38.88% of TS and 42.03-45.05% of VS reduction could be achieved in the reactors. The average biogas yields varied between (278.02-297.62) L/kg-TS loaded or (339.29-367.56) L/kg-VS loaded, while the average biogas productivity were (714.99-773.39) L/kg-TS reduced or (753.09-871.22) L/kg-VS reduced. The average methane yields varied between (209.70-222.96) L/kg-TS loaded or (255.91-275.73) L/kg-VS loaded, while the average biogas productivity were (539.29-584.87) L/kg-TS reduced or (568.03-656.02) L/kg-VS reduced.

Compared to the CK, the biogas and methane yields were increased by 3.00-7.05% and 2.83-6.32% in the reactors after biogas slurry inoculation, with their biogas and methane productivity being improved by 7.48-8.17% and 6.75-8.45%, respectively for per unit of TS. As for per unit of VS, the biogas and methane yields were increased by 5.60-8.33% and 5.95-7.74%, with biogas and methane productivity being improved by 8.67-15.69% and 7.93-15.49%, respectively. Among the reactors with different amounts of biogas slurry inoculum, no significant difference was found on the biogas and methane yields and productivity ($p<0.05$), which indicated that under the tested conditions a large amount of inoculum may have no remarkable effect on the overall biogas or methane yield and productivity, although biogas slurry inoculation could accelerate the progress of the whole anaerobic co-digestion.

According to the previous studies on theoretical methane yield of swine manure, the theoretical methane yield could reach more than 0.5 m^3 kg^{-1} VS (Møller et al., 2004), and the biogas production could be increased by about 10% when crop straw was added (Møller et al., 2004; Wang et al., 2009). Besides, the selection of inoculum ratio was crucial as well as the anaerobic biodegradability of solid wastes. The selected inoculum source is reported to be responsible for achieving a rapid startup of balanced microbial population (Lopes et al., 2004). In case of anaerobic biodegradability of solid wastes, use of highly active anaerobic inoculum would significantly shorten the digestion time (Forster-Carneiro et al., 2007). In this experiment, higher biogas yields and methane contents were obtained than other studies by using different raw materials including animal manures like swine manure, cattle manure and chicken manure, and crop straws like rice straw, wheat straw and switch grass (Lopes et al., 2004; Ye et al., 2013; Liang et al., 2014). The obtained methane yields (568.03-656.02 m^3/kg-VS reduced) were close or equal to the theoretical value. Biogas slurry inoculation did accelerate the biogas production process and shorten the digestion duration, which is in consistent with the results of Motte et al. (2013) and Gu et al. (2014).

4.3.3 Characterization of co-digestion with pretreated rice straw during 60 days' trials

(1) Biogas and methane production evaluation

a) Daily biogas production

Figure 4.8 shows the daily biogas production in the reactors under anaerobic co-digestion of swine manure with different pretreated rice straw. The daily biogas production in the AK and AK+MW reactors rapidly increased from day 2, and reached the first peak on day 5 (1605 mL d^{-1} for AK and 1685 mL d^{-1} for AK+MW), which was followed by a rapidly decreasing tendency. The daily biogas production in the MW reactor gradually increased from day 2, and reached the first peak on day 5 (720 mL d^{-1}), which was followed by the gradually decreasing tendency. The daily biogas production in the CK reactor gradually increased from day 5, and reached the first peak on day 7 (678 mL d^{-1}), which was also followed by a gradually decreasing tendency.

Thereafter, the daily biogas production in the CK, MW, AK and AK+MW reactors could reach the second peaks on day 32, 23, 36 and 30, respectively. After 45 days' operation, the daily biogas production in all the reactors decreased to less than 200 mL d^{-1}.

The AK and AK+MW reactors exhibited better performance for biogas production from day 2 to day 10 and from day 30 to day 45 in comparison to the CK and MW reactors, and reached more than 1200 mL d^{-1} during days 1-7 and more than 500 mL d^{-1} during days 30-37, while no obvious better performance for daily biogas production was detected in the MW reactor than the CK reactor.

The results indicate that, among the tested pretreatment methods, alkaline pretreatment on rice straw is the most effective way to improve the biogas production from anaerobic co-digestion of swine manure with rice straw. The anaerobic co-digestion process was significantly accelerated, with earlier appearance of biogas production peaks when co-digestion with the rice straw pretreated by alkaline method. On the other hand, a slight acceleration of biogas production was observed when co-digestion with the rice straw pretreated by microwave method.

b) Methane content

Figure 4.9 shows the daily methane content in the reactors under anaerobic co-digestion of swine manure with different pretreated rice straw. The methane contents in all the reactors gradually increased in the first 10 days, and reached more than 70%. Thereafter, the methane contents kept around 80% till the end of experiment. There was no significant difference among CK, MW, AK and AK+MW pretreatment methods ($p<0.05$), which implies that the tested pretreatment methods have no obvious influence on methane content under the designed anaerobic co-digestion conditions.

c) Cumulative biogas production

Figure 4.10 shows the cumulative biogas production in the reactors of anaerobic co-digestion of swine manure with different pretreated rice straw. The anaerobic co-digestion in the AK and AK+MW reactors appeared to have two separated stages, with the occurrence of the first stage from day 0 to day 20 and the second stage from day 21 to day 60. In these reactors, the cumulative biogas production during the two stages were higher in comparison to the MW and CK reactors, and their overall biogas production yields could be greater than 25 L.

(2) Average performance

Table 4.5 summarizes the average performance of anaerobic co-digestion of swine manure with different pretreated rice straw. The initial pHs in the reactors were 7.49-8.02, while the final pHs were 7.86-8.01. After about 60-day's anaerobic digestion, 39.20-52.60% of TS and 48.71-60.01% of VS reduction could be achieved in the reactors. The average biogas yields varied between (251.80-355.22) L/kg-TS loaded or (321.98-456.83) L/kg-VS loaded, while the average biogas productivity were (642.29-699.24) L/kg-TS reduced or (679.51-791.04) L/kg-VS reduced. The average methane yields varied between (191.82-261.73) L/kg-TS loaded or (245.28-334.68) L/kg-VS loaded, while the average biogas productivity were (489.29-501.99) L/kg-TS reduced or (517.65-567.90) L/kg -VS reduced.

Compared to the CK, in the AK and MW+AK reactors, the biogas yields had been increased by 25.99-26.71%, with the biogas productivity being improved by 2.85-5.88%, for per unit of TS. The MW reactor didn't achieve better performance. On the contrary, its biogas and methane yields and productivity were significantly lower than CK. The AK and MW+AK reactors achieved similar performance on biogas and methane production, showing no significant difference. The above results indicate that microwave pretreatment is not effective to improve the biogasification of rice straw under the designed pretreatment condition, while alkaline pretreatment could remarkably accelerated the process of anaerobic co-digestion and correspondingly increased the biogas or methane yields and productivity.

Various pretreatment methods have been tried on agricultural residues to improve their biodegradability, including mechanical, thermal, chemical (i.e. alkali, acidic, oxidative) and biological methods (Mussoline et al., 2012; Sapci et al., 2013; Krishania et al., 2013; Liang et al., 2014). Pretreatment can bring about improvements of the enzymatic hydrolysis in the anaerobic digestion. Physical pretreatment like microwave and chemical pretreatment by alkaline can decrease both the degree of polymerization and cellulose crystallinity, disrupt the lignin structure, and break the linkage between lignin and other carbohydrate fractions in lignocellulosic biomass, thus making the carbohydrates in the hetero-matrix more accessible while still maintaining the cellulose concentration (Kumar et al., 2009; Valery et al., 2011). In this experiment, the results show that alkaline pretreatment may be more effective in breaking the ester bonds between lignin, hemicellulose and cellulose as compared to other pretreatments, which is in agreement with previous studies on the pretreatments of other crop straws (Wang et al., 2012; Liang et al., 2014). Microwave pretreatment did not achieve the expected good performance like other studies (Feng et al., 2009; Sapci et al., 2013), probably due to a lower power and shorter time for the microwave pretreatment applied in this study. The biogas and methane productivity in the AK and AK+MW reactors were lower than CK, with the same results with Ai et al. (2010) and Kim et al. (2003), possibly due to the inhabitation matters released during rice straw pretreatment, although the pretreatment could enhance the hydrolysis of rice straw.

4.3.4 Kinetics study

For the purpose of understanding the biogasification process during anaerobic digestion, kinetic parameters are usually utilized to analyze the performance of biogas or methane production in the reactors. In this study, single-stage first order kinetic model was used to evaluate the anaerobic co-digestion of swine manure with rice straw under different amounts of biogas slurry inoculum and different pretreatment methods for rice straw. Moreover, two-stage first order kinetic model was used to evaluate the anaerobic co-digestion of swine manure with different pretreated rice straw, according to the two obvious biogas production peaks in the AK and AK+MW reactors (Fig. 4.10).

Table 4.6 and Figure 4.11 show the characteristics of single-stage first order kinetic model for anaerobic co-digestion of swine manure with rice straw under different amounts of biogas slurry inoculum and different pretreatment methods for rice straw. In the reactors with different amounts of biogas slurry addition, the biogas production rate constants (k=0.0208-0.0314 d^{-1}) obtained from the 66 days' operation indicated that, BS-1, BS-2 and BS-3 exhibited faster in biogasification with their k increased by 39.90%, 42.31% and 50.96% respectively compared to CK. In the reactors with different pretreated rice straw, the biogas production rate constants (k=0.0297-0.0313 d^{-1}) obtained from the 66 days' operation indicated that, MW, AK and AK+MW exhibited faster in biogas with the k further increased by 4.71%, 5.39% and 2.36%, respectively compared to CK, the best condition among the biogas slurry addition tests.

Table 4.7 and Figure 4.12 show the characteristics of two-stage first-order kinetic model for anaerobic co-digestion of swine manure with different pretreated rice straw. The AK and AK+MW appeared two obvious stages during the 66 days' operation, and their biogas production rate constants were 0.1268 and 0.1427 respectively in the first stage, which were 4-6 times of their values (0.0268 and 0.0213, respectively) in the second stage. The two-stage first-order models could increase the accuracy of simulation for the anaerobic co-digestion process occurred in the AK and AK+MW reactors, which can be discerned from the smaller average relative differences of 5.74% and 6.09% in contrast to 7.74% and 9.61% by using the single-stage first order model.

For the single-stage first order kinetics of anaerobic digestion, Liang et al. (2011) and Liang et al. (2014) reported that the biogas production rate constants for dry anaerobic digestion of smooth cordgrass ranged from 0.022-0.052 after being pretreated by lime, hot-water or thermo-lime , which agrees with the single-stage first-order biogas production rate constants obtained in this study. Kafle and Kim (2013) obtained the biogas production rate constants ranging from 0.032-0.077 for anaerobic co-digestion of swine manure with apple waste, greater than the results in this study, most probably due to their lower TS (<5%) and more inoculum applied ($VS_{substrate}/VS_{inoculum}=0.5\text{-}1.0$).

For the single-stage first order kinetics of anaerobic digestion, Lei et al. (2010) achieved the biogas production rate constants in the first and second stages about 0.012-0.015 and 0.045-0.046, respectively for anaerobic digestion of rice straw and anaerobic sludge. Their constants were lower in the first stage and higher in the second stage than the results from this study, which implies that faster biogasification could be realized by using pretreated rice straw.

4.4 Summary

Biogas slurry inoculation increased biogas yield by 3.00-7.05%, and improved biogas productivity by 7.48-8.17%, for per unit of TS. The digestion process fitted the single-stage first-order model well, and the reactors inoculated with biogas slurry exhibited faster in biogas production with the biogas production rate constant (k) increased by 39.90-50.96% compared to the control reactor. Co-digestion with the pretreated rice straw by alkaline and microwave+alkaline pretreatment could increase biogas yield by around 25%, with biogas productivity improved by 2.85-5.88% for per unit of TS. The co-digestion process with alkaline and microwave alkaline pretreated rice straw fitted the two-stage first-order model accurately, which can be discerned from the smaller average relative differences of 5.74% and 6.09% in contrast to 7.74% and 9.61% by using the single-stage first order model.

Table 4.1 Characteristics of the raw materials used in the anaerobic co-digestion.

Parameters	Swine manure	Rice straw	Biogas slurry
45 days' pre-trials			
TS (%)	20.20±0.98	90.90±2.87	-
TOC(%, d.w.)	41.51±0.37	39.71±0.53	-
TN (%, d.w.)	3.14±0.12	0.58±0.05	-
C/N ratio (TOC/TN)	13.22	68.47	-
TP (%, d.w.)	1.15±0.08	0.09±0.03	-
pH	7.16±0.55	N.D.	-
60 days' trials			
TS (%)	13.41±0.54	82.90±3.79	1.78±0.54
TOC(%, d.w.)	40.35±0.28	38.63±0.31	6.27±0.18
TN (%, d.w.)	3.02±0.06	0.55±0.04	2.73±0.05
C/N ratio (TOC/TN)	13.36	70.24	2.30
TP (%, d.w.)	1.03±0.02	0.09±0.01	0.41±0.04
pH	7.29±0.41	N.D.	7.03±0.09

The data are expressed as mean ± standard deviation for triplicate determinations. N.D., no determination.

Table 4.2 Experimental design for 45 days' pre-trials.

Composition (SM:RS)	Theoretical TS (%)	Swine manure (g)	Rice straw (g)	Distilled water (g)	Total weight (g)	Actual TS (%)
2:1	10	80	40	436	556	9.44
2:1	20	150	75	295	520	18.92
2:1	30	240	120	193	553	29.55
1:1	10	50	50	465	565	9.83
1:1	20	100	100	365	565	19.66
1:1	30	150	150	264	564	28.51%
1:2	10	25	50	425	500	10.09
1:2	20	50	100	351	501	20.17
1:2	30	75	150	275	500	30.28

SM:RS, the composition of swine manure and rice straw based on fresh weight.

Table 4.3 Experimental design for 60 days' trials.

Treatment	Inoculum ratio (% TS/TS)	Swine manure (g)	Rice straw (g)	Biogas slurry (mL)	Distilled water (mL)	Total weight (g)
Trial A: different amounts of biogas slurry inoculum						
CK	0	140	60	0	270	470
BS-1	1.2	140	60	34	236	470
BS -2	2.4	140	60	69	201	470
BS-3	4.8	140	60	137	133	470
Trial B: different pretreatments for rice straw						
CK	4.8	140	60	137	133	470
MW	4.8	140	60	137	133	470
AK	4.8	140	60	137	133	470
MW+AK	4.8	140	60	137	133	470

CK, control reactor without inoculum or pretreatment; BS-1, BS-2 and BS-3, reactors inoculated with biogas slurry at the proportions of 1.2%, 2.4% and 4.8% based on the total solids of biogas slurry and raw materials; MW, AK and AK+MW, reactors with the rice straw pretreated by microwave, alkaline and microwave+alkaline.

Table 4.4 Average performance of anaerobic co-digestion with different amounts of biogas slurry inoculum in the 60 days' trials.

Parameters	CK	BS-1	BS-2	BS-3
pH values				
Initial pH	7.62	7.68	7.44	7.47
Final pH	7.97	7.99	7.98	7.97
TS and VS values				
Initial TS (g)	73.79	70.50	71.58	72.38
VS (g)	60.46	57.09	57.29	56.60
VS/TS	0.82	0.81	0.80	0.78
Final TS (g)	45.10	43.20	45.02	45.58
VS (g)	33.22	31.45	32.78	32.81
VS/TS	0.74	0.73	0.73	0.72
TS reduction (%)	38.88	38.72	37.10	37.03
VS reduction (%)	45.05	44.91	42.78	42.03
Biogas production				
Yield (L/kg-TS loaded)	278.02	297.62	286.74	286.37
Yield (L/kg -VS loaded)	339.29	367.56	358.30	366.19
Productivity (L/kg-TS reduced)	714.99	768.50	772.85	773.39
Productivity (L/kg-VS reduced)	753.09	818.38	837.63	871.22
Methane production				
Yield (L/kg-TS loaded)	209.70	222.96	217.00	215.63
Yield (L/kg-VS loaded)	255.91	275.35	271.15	275.73
Productivity (L/kg-TS reduced)	539.29	575.70	584.87	582.35
Productivity (L/kg-VS reduced)	568.03	613.07	633.90	656.02

CK, control without inoculum; BS-1, BS-2 and BS-3, reactors inoculated with biogas slurry at the proportions of 1.2%, 2.4% and 4.8% based on the total solids of biogas slurry and feedstock.

Table 4.5 Average performance of anaerobic co-digestion of swine manure with different pretreated rice straw in the 60 days' trials

Parameters	CK	MW	AK	AK+MW
pH values				
Initial pH	7.49	7.78	7.99	8.02
Final pH	7.95	8.01	7.99	7.86
TS and VS values				
Initial TS (g)	72.85	72.38	71.91	72.85
VS (g)	56.97	56.60	56.24	56.97
VS/TS	0.78	0.78	0.78	0.78
Final TS (g)	41.73	44.00	34.09	35.84
VS (g)	28.12	29.03	22.49	23.65
VS/TS	0.67	0.66	0.66	0.66
TS reduction (%)	42.71	39.20	52.60	50.80
VS reduction (%)	50.64	48.71	60.01	58.49
Biogas production				
Yield (L/kg-TS loaded)	281.95	251.80	357.25	355.22
Yield (L/kg-VS loaded)	360.53	321.98	456.83	454.22
Productivity (L/kg-TS reduced)	660.42	642.29	679.21	699.24
Productivity (L/kg-VS reduced)	712.19	679.51	773.79	791.04
Methane production				
Yield (L/kg-TS loaded)	213.98	191.82	261.73	255.01
Yield (L/kg-VS loaded)	273.62	245.28	334.68	326.09
Productivity (L/kg-TS reduced)	501.21	489.29	497.61	501.99
Productivity (L/kg-VS reduced)	540.50	517.65	566.90	567.90

CK, control without pretreatment; MW, AK and AK+MW, reactors with the rice straw pretreated by microwave, alkaline and microwave+alkaline.

Table 4.6 Characteristics of single-stage first-order kinetic for anaerobic co-digestion of swine manure and rice straw with different amounts of biogas slurry inoculum and different pretreatments for rice straw

Treatment	*k* (d^{-1})	*R²*
Trial A: different amounts of biogas slurry inoculum		
CK	0.0208±0.0012	0.9868
BS-1	0.0291±0.0015	0.9826
BS-2	0.0296±0.0018	0.9763
BS-3	0.0314±0.0019	0.9743
Trial B: different pretreatments for rice straw		
CK	0.0297±0.0019	0.9744
MW	0.0311±0.0019	0.9745
AK	0.0313±0.0017	0.9738
AK+MW	0.0304±0.0020	0.9589

CK, control without inoculum or pretreatment; BS-1, BS-2 and BS-3, reactors inoculated with biogas slurry at the proportions of 1.2%, 2.4% and 4.8% based on the total solids of biogas slurry and raw materials; MW, AK and AK+MW, reactors with rice straw pretreated by microwave, alkaline and microwave+alkaline; G_T, theoretical total biogas yield; k, biogas production rate constant; R^2, coefficient of determination. The data are expressed as mean ± standard deviation *for* triplicate determinations.

Table 4.7 Characteristics of two-stage first-order kinetic for anaerobic co-digestion of swine manure with different pretreated rice straw

Treatment	k (d^{-1})	R^2	Duration (d)
First stage			
AK	0.1268±0.0113	0.9819	20
AK+MW	0.1427±0.0098	0.9814	20
Second stage			
AK	0.0268±0.0014	0.9641	46
AK+MW	0.0213±0.0014	0.9634	46

AK and AK+MW, reactors with rice straw pretreated by alkaline and microwave+alkaline;k, biogas production rate constant; R^2, coefficient of determination. The data are expressed as mean ± standard deviation for triplicate determinations.

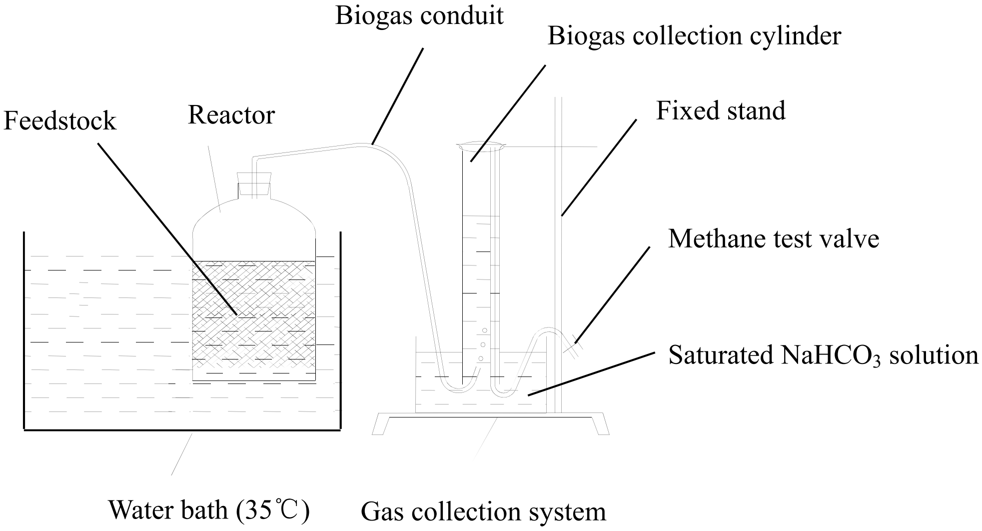

Figure 4.1 Experimental set-up of anaerobic co-digestion.

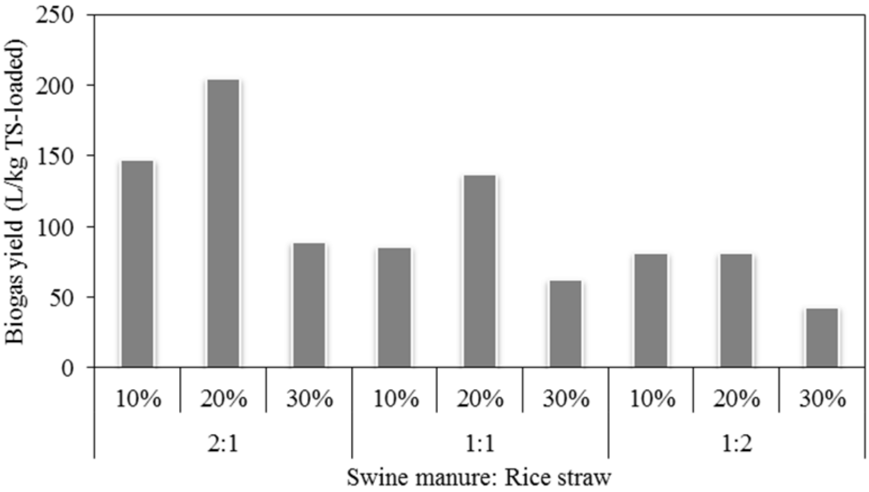

Figure 4.2 Biogas yields in the reactors after 45 days' anaerobic co-digestion under different compositions of swine manure and rice straw.

(10%, 20% and 30% denote the contents of total solid)

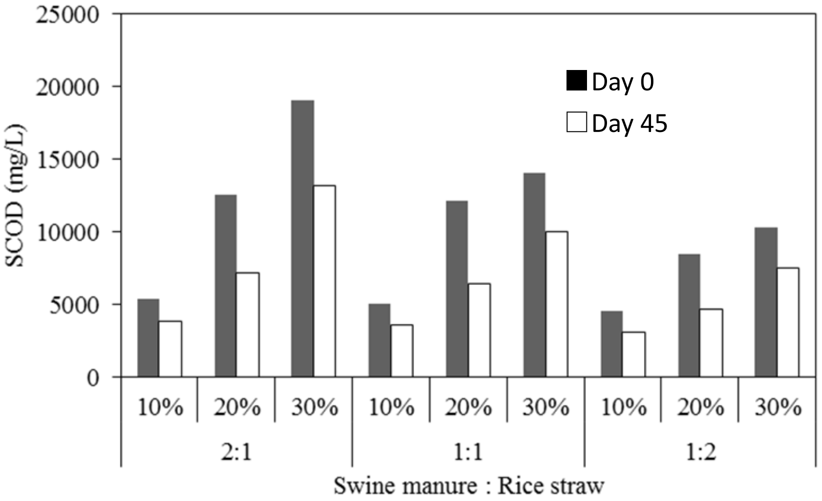

Figure 4.3 SCOD change in the reactors after 45 days' anaerobic co-digestion under different compositions of swine manure and rice straw.

(10%, 20% and 30% denote the contents of total solid)

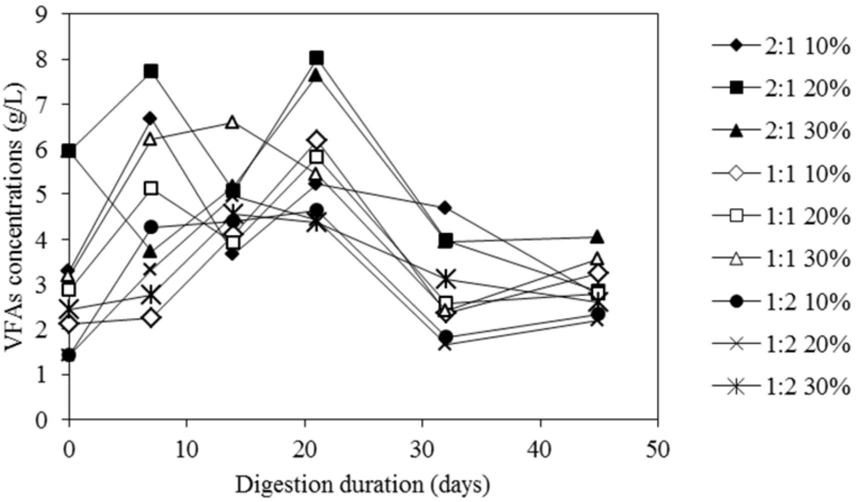

Figure 4.4 VFAs change in the reactors during anaerobic co-digestion under different compositions of swine manure and rice straw.

(2:1, 1:1, and 1:2 indicate the ratio of swine manure to rice straw; 10%, 20% and 30% indicate the TS content in the reactors)

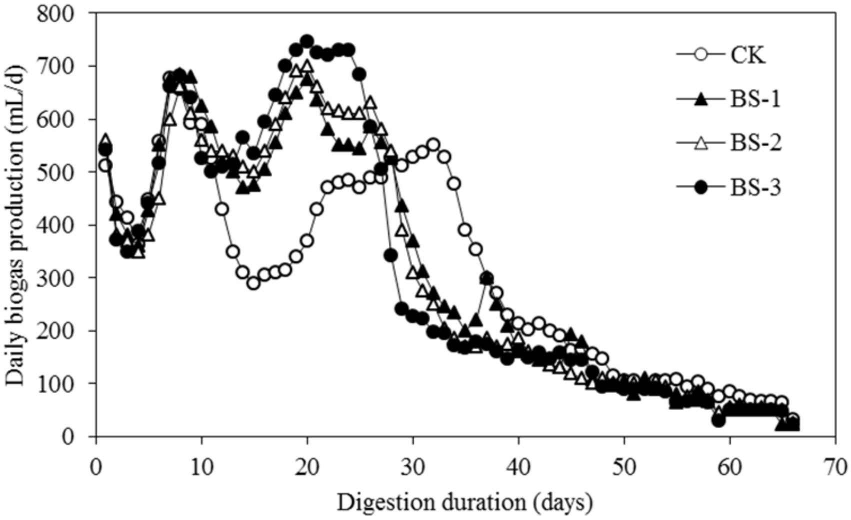

Figure 4.5 Daily biogas production in the reactors during anaerobic co-digestion of swine manure with rice straw under different amounts of inoculum addition.

(CK: control without inoculum; BS-1, BS-2 and BS-3: reactors inoculated with biogas slurry at the proportions of 1.2%, 2.4% and 4.8% based on total solids of biogas slurry and raw materials)

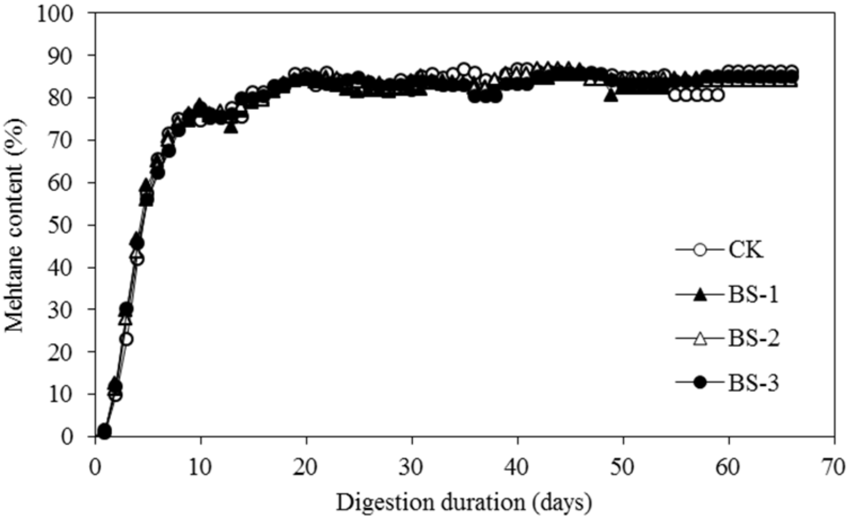

Figure 4.6 Change in methane content in the reactors during anaerobic co-digestion of swine manure with rice straw under different amounts of inoculum addition.

(CK: control without inoculum; BS-1, BS-2 and BS-3: reactors inoculated with biogas slurry at the proportions of 1.2%, 2.4% and 4.8% based on total solids of biogas slurry and raw materials)

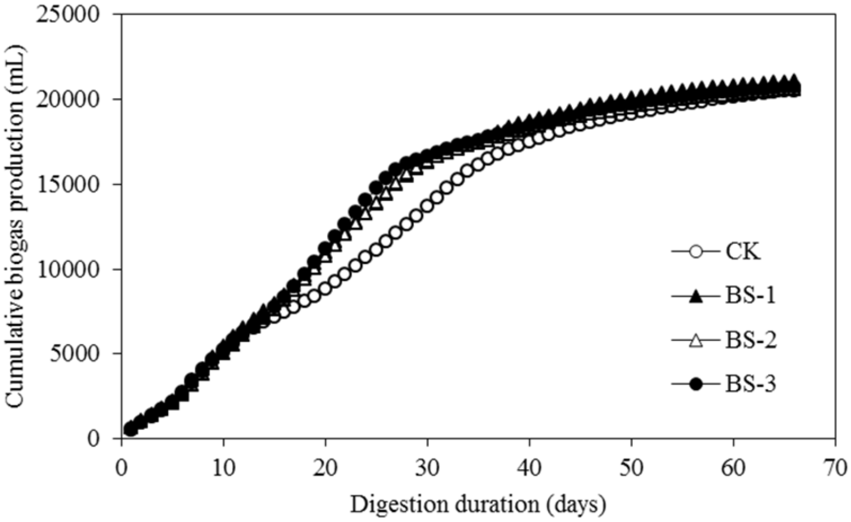

Figure 4.7 Cumulative biogas production in the reactors during anaerobic co-digestion of swine manure with rice straw under different amounts of inoculum addition.

(CK: control without inoculum; BS-1, BS-2 and BS-3: reactors inoculated with biogas slurry at the proportions of 1.2%, 2.4% and 4.8% based on total solids of biogas slurry and raw materials).

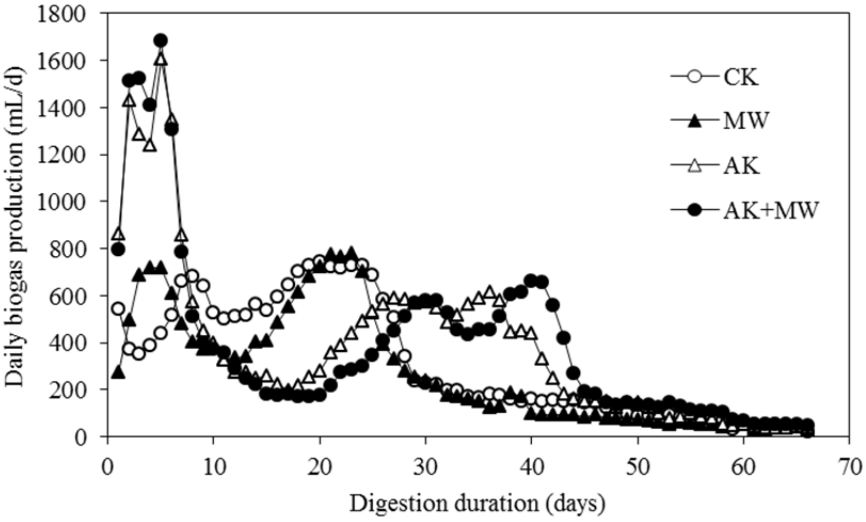

Figure 4.8 Daily biogas production in the reactors during anaerobic co-digestion of swine manure with different pretreated rice straw.

(CK: control with rice straw without pretreatment; MW, AK and AK+MW: reactors with rice straw pretreated by microwave, alkaline and microwave+alkaline, respectively)

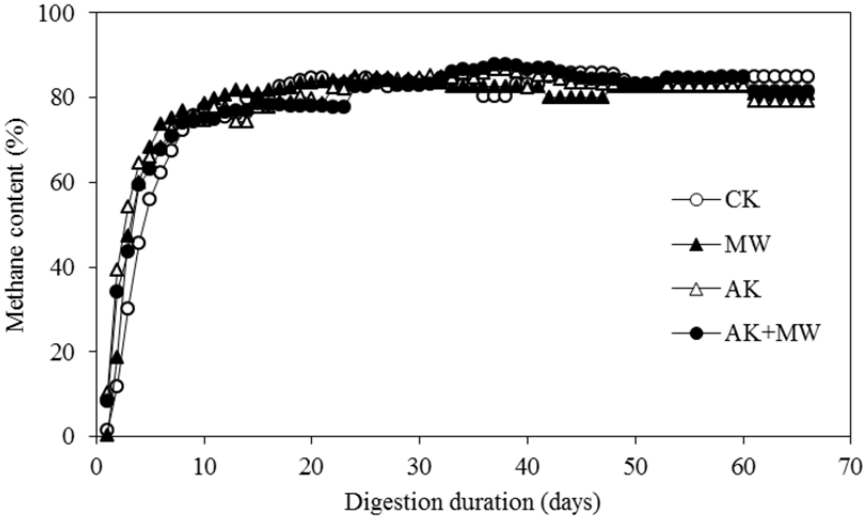

Figure 4.9 Changes in methane content in the reactors of anaerobic co-digestion of swine manure with different pretreated rice straw.

(CK: control with rice straw without pretreatment; MW, AK and AK+MW: reactors with rice straw pretreated by microwave, alkaline and microwave+alkaline, respectively)

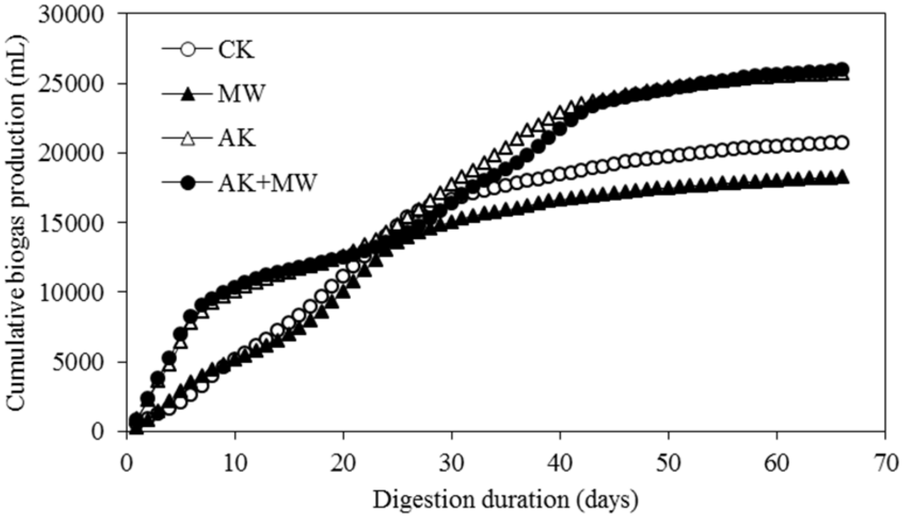

Figure 4.10 Cumulative biogas production in the reactors of anaerobic co-digestion of swine manure with different pretreated rice straw.

(CK: control with rice straw without pretreatment; MW, AK and AK+MW: reactors with rice straw pretreated by microwave, alkaline and microwave+alkaline, respectively)

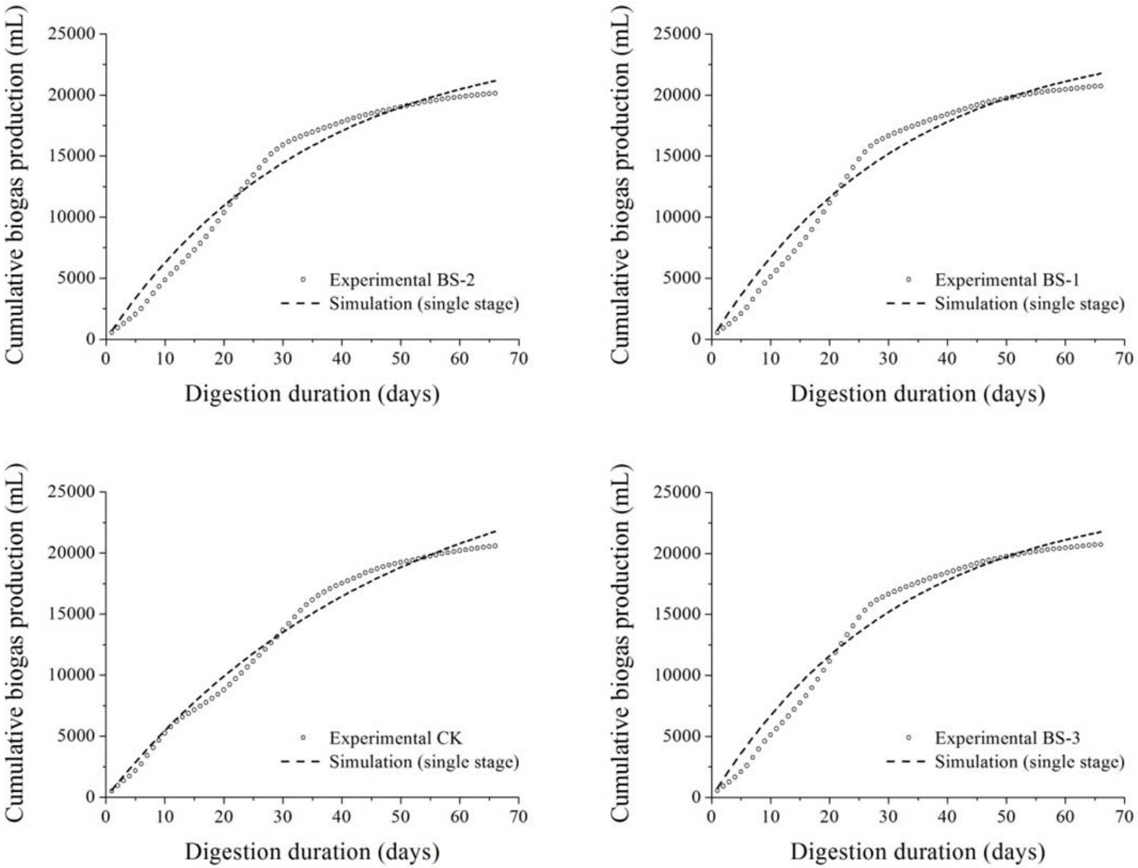

Figure 4.11 Comparison between experimental data and simulated results from the single-stage first-order models for anaerobic co-digestion of swine manure with rice straw under different amounts of inoculum addition.

(CK: control without inoculum; BS-1, BS-2 and BS-3: reactors inoculated with biogas slurry at the proportions of 1.2%, 2.4% and 4.8% based on total solids of biogas slurry and raw materials)

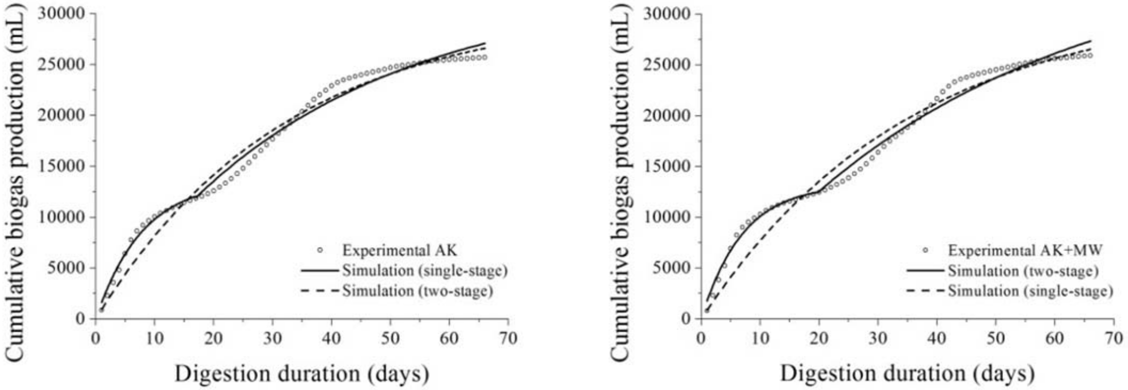

Figure 4.12 Comparison between experimental data and simulated results from the single-stage and two- stage first-order models for anaerobic co-digestion of swine manure with different pretreated rice straw.

(CK: control with rice straw without pretreatment; MW, AK and AK+MW: reactors with rice straw pretreated by microwave, alkaline and microwave+alkaline, respectively)

Chapter 5 Comparison between aerobic co-composting and anaerobic co-digestion of swine manure and rice straw by life cycle assessment

5.1 Introduction

As the two main encouraged methods for the resource utilization of agricultural wastes in Shanghai, dozens of aerobic composting plants and anaerobic digestion projects have been constructed or are under construction in recent years (SMAC, 2008; 2013), which improved the treatment of animal manure and crop straws. It is important not only on how to improve the efficiency of waste treatment and recycling, but also on how to increase the economic and environmental benefits during the whole process. The latter can be actually achieved by the applications of aerobic composting and anaerobic digestion in this context (Evangelisti et al., 2014).

Life cycle assessment (LCA) is an appropriate tool to realize this target. LCA is one of the most developed and widely used environmental assessment tools for comparing alternative technologies when the location of the activity is already defined (Finnveden et al., 2005; Clift, 2013). LCA can quantify the amount of materials and energy used over the whole supply chains (i.e. life cycles) of goods and services and identifies emissions and wastes associated with the life cycles. Moreover, it helps to determine the 'hot spots' in the system, i.e. those parts that have the most significant environmental impact and should be improved in the first instance, thus enabling identification of more environmentally sustainable options (Evangelisti et al., 2014). Many LCA studies have been implemented on waste management systems with anaerobic digestion and composting for animal manure, crop residues and sewage sludge, which focused on the environmental impacts without economic benefits (Mezzullo et al., 2013; Cao and Pawłowski, 2013; Evangelisti et al., 2014). However, few attempts have been tried to compare comprehensively the economic and environmental benefits of aerobic composting and anaerobic digestion systems. Therefore, a life cycle assessment was adopted together with economic studies to systematically assess the environmental impact and economic cost.

5.2 Materials and methods

This study was carried out according to the Life Cycle Assessment Methodologies from ISO 14040 (ISO, 2006), providing a comprehensive analysis of the energy and environmental performance of a production system. The LCA tool is usually accomplished in four phases: (1) goal and scope definition, (2) inventory analysis, (3) impact assessment and (4) interpretation.

5.2.1 Goal and scope definition

The goal of this LCA study was to evaluate the relative environmental and economic impact of aerobic composting and anaerobic digestion to inform decision makers across the industry and to identify any inconsistencies or anomalies in policy. The LCA was based on an aerobic composting plant and an anaerobic digestion project with a treatment capacity of 10 t d^{-1} (raw materials), and the compositions of swine manure and rice straw were 3:2 for composting and 2:1 for digestion. The composting plant used a windrow composting process with mechanical mixing and packing, and the retention time was about 30 days. The digestion project adopted an anaerobic digestion process with mechanical mixing and delivering, and the retention time was about 30 days. The functional unit (FU) for the LCA analysis was 1 ton of feedstock mixture (w.m.) of swine manure and rice straw.

The system boundaries for aerobic composting and anaerobic digestion are illustrated in Figure 5.1. The systems commenced when the swine manure and rice straw were delivered to the aerobic composting plant or anaerobic digestion project, and the aerobic composting system included material pretreatment, feedstock mixing, composting process and compost packing, while the anaerobic digestion system consisted of material pretreatment, feedstock mixing, digestion process (dry or semi-dry), biogas residue production and electricity generation from biogas. The materials of construction for the plant or project were not included, and the same for the transport of swine manure and rice straw, and the spreading of composting products and biogas residues as it was unclear how to distribute the composts or residues. The disposal of the plant or project was also not considered, as the expected operational lifetime was unknown.

The detailed information of main facilities for aerobic composting plant or anaerobic digestion project was listed as follows:

(1)Aerobic composting

- Material pretreatment: straw crushing system (0.5 t h^{-1}, 10 kW)
- Feedstock mixing: feedstock mixing system (1 t h^{-1}, 3 kW)
- Composting process: windrow composting facility, composting mixing system (150 t h^{-1}, 15 kW)

- Composting packing: packing system (3 t h^{-1}, 1.5 kW)

(2)Anaerobic digestion

- Material pretreatment: straw crushing system (0.5 t h^{-1}, 10 kW)
- Feedstock mixing: feedstock mixing system (0.5 t h^{-1}, 3 kW)
- Digestion process: material delivering system (1.67 t h^{-1}, 19 kW), digestion mixing system (150 t h^{-1}, 58 kW), digestate outleting system (1.6 t h^{-1}, 16 kW)
- Digestate drying: drying and packing system (1 t h^{-1}, 30 kW)

5.2.2 Inventory analysis

(1) Aerobic composting

The daily consumption of electric power for rice straw crushing (4 t d^{-1}), feedstock mixing (10 t d^{-1}), composting mixing (2 h per 7 d) and compost packing (6 t d^{-1}) were 80 kWh, 30 kWh, 2 kWh and 3 kWh, respectively, which meant the electricity consumption was 11.5 kWh FU^{-1}. The pollutants emission from electrical production process is listed in Table 5.1 (Jin, 2007).

In the composting process, the coefficients of greenhouse gases (GHGs) emission followed the results of Zhong et al. (2013), Park et al. (2011) and Fukumoto et al. (2003) (Table 5.2).

(2) Anaerobic digestion

The daily consumption of electric power for rice straw crushing (3.33 t d^{-1}), feedstock mixing (10 t d^{-1}), digestion mixing (2 h d^{-1}), materials delivering (10 t d^{-1}), digestate outleting (10 t d^{-1}) and digestate drying (10 t d^{-1}) were 67 kWh, 60 kWh, 116 kWh, 114 kWh, 100 kWh and 300 kWh, respectively, which meant the electricity consumption was 75.7 kWh FU^{-1}.

In the digestion process, the TS was around 15% and the average biogas yield was 0.3 m^3 kg^{-1} TS loaded, which meant the biogas production was 45 m^3 FU^{-1}. The average methane (CH_4) content was about 70%, and carbon dioxide (CO_2) about 20%, which meant the CH_4 and CO_2 yields were 31.5 m^3 FU^{-1} and 17.79 kg FU^{-1}, respectively (the other biogas compositions were neglected).

In the biogas-based electricity generation system, the electricity production was 63 kWh FU^{-1}, as 1 m^3 of CH_4 could produce 2 kWh of power (Zhou et al., 2004), and the concentration of hydrogen sulfide (H_2S) should be lower than 20 mg m^{-3}, which would result in 1.69 g FU^{-1} of sulfur dioxide (SO_2) if meeting the standard by using biogas purification technologies. The CO_2 emission from the biogas burning was 52.76 kg FU^{-1}, according to the calculation method of Wang et al. (1999).

In the digestate drying process, the NH_3 emission was estimated according to the results of Maurer and Müller (2012).

The detailed inventory analysis is presented in Table 5.3.

5.2.3 Impact assessment

This study focused on the environmental impacts of eutrophication potential (EP), global warming potential (GWP) and acidification potential (AP). The GWP was based on the emissions of carbonic oxide (CO), CH_4 and NO_x (NO, NO_2, N_2O, etc) expressed as carbon dioxide (CO_2), and their equivalent factors were 2, 21 and 310, respectively (IPCC, 1996). Evaluation of AP was carried out by means of emissions of

NO_x and ammonia (NH_3) and expressed as sulphur dioxide (SO_2) equivalents (Reinhardt et al., 1997). The EP was calculated on the basis of the emissions of NO_x, nitrate (NO_3^-) and NH_3 expressed as phosphate (PO_4^{3-}) equivalents, and their equivalent factors were 0.10, 0.42 and 0.35, respectively (Brentrup et al., 2004).

The normalizing of GWP, AP and EP was implemented by using the criteria of environmental impacts proposed by Stranddorf et al. (2005), and the world's environmental impact potentials per person for GWP, AP and EP were 8700 kg CO_2 eq a^{-1}, 35 kg SO_2 eq a^{-1} and 59 kg PO_4^{3-} eq a^{-1}.

The weighting of GWP, AP and EP was carried out by following the study of Wang et al. (2006), and the weight coefficients of GWP, AP and EP were 0.32, 0.36 and 0.32, respectively.

The data was processed and analyzed using Microsoft Excel 2010.

5.2.4 Economic evaluation

The economic evaluation focused on the capital expenditure (CapEX), operating expenditure (OpEX), operating income (OpIN) and production profit (ProPR). The CapEx included the expenditures of infrastructure construction, equipment installation and other facilities preparation. The OpEX included the expenditures of materials purchasing, energy consumption, labor cost and daily maintenance. The OpIN covered the incomes from product sale and energy generation, and the ProPR was calculated from OpEX and OpIN.

5.3 Results and discussion

5.3.1 Environmental assessment

Table 5.4 shows the environmental impacts of aerobic co-composting and anaerobic co-digestion. The environmental impacts of GWP, AP and EP were 0.0091, 0.0361 and 0.0038 for aerobic co-composting, and 0.0127, 0.0092 and 0.0006 for anaerobic co-digestion, respectively, which indicated the world's environmental impact potentials per person for GWP, AP and EP were 0.91%, 3.61% and 0.38% for aerobic co-composting, and 1.27%, 0.92% and 0.06% for anaerobic co-digestion, to treat 1 FU of agricultural wastes. The comprehensive impact of aerobic co-composting was more than 2 times of anaerobic co-digestion, implying that anaerobic co-digestion is more environmental friendly. The GWP of anaerobic co-digestion was higher than aerobic co-composting, most probably due to the calculated CO_2 emission included the CO_2 production from CH_4 burning during electricity generation. The AP and EP of aerobic co-composting was higher than anaerobic co-digestion, attributable to the NH_3, PO_4^{3-} and SO_4^{2-} levels originated from the elements of nitrogen, phosphorus and sulfur, and lower H_2S concentration in biogas and more stable nitrogen and phosphorus existing forms in the digestate.

The GWP, AP and EP of aerobic co-composting and anaerobic co-digestion in this study didn't agree with the results of Zhang et al. (2010b), due to no consideration of the treatment of produced wastewater and biogas liquid residues, and different system boundaries and raw materials. Especially, the GWP of anaerobic co-digestion was higher than aerobic co-composting, which could also be attributed to the large amount of electricity consumption by the systems of raw material delivering, digestion mixing, digestate ouleting and digestate drying during the daily operation of the dry or semi-dry anaerobic digestion project in Shanghai suburbs.

5.3.2 Economic evaluation

Tables 5.5, 5.6 and 5.7 show the CapEX, OpEX and OpIN of the aerobic co-composting plant and anaerobic co-digestion project with treatment capacity of 10 ton. The CapEX of the composting plant was 2.52 million, much lower than the 5.63 million of the digestion project, due to more equipments needed and more complicated system. The OpEX of the composting plant was about 0.62 million, lower than 0.79 million of the digestion project, which could be attributed to a large energy consumption and manpower input in the latter. The OpIN of the composting plant was about 0.88 million, similar to the digestion project, and the ProPR of the composting plant was about 0.26 million, much higher than the 0.10 million of the digestion project based on the same plant scale, the unified price of electricity for agricultural production, and the feed-in tariff of electricity from biogas generation facility.

5.3.3 Comprehensive analysis

From the results of environmental life cycle assessment and economic evaluation, aerobic co-composting and anaerobic co-digestion were found to have their own advantages and disadvantages. Aerobic composting had lower CapEX and OpEX and higher ProPR, while exerting higher impacts on the environment. The same scale anaerobic co-digestion, however, had lower environmental impacts with higher CapEX and OpEX and lower ProPR.

Under the circumstances of National Pollution Emission Reduction Plan and

National Climate Change Program in China, both aerobic composting and anaerobic digestion have the prospects for application and extension, based on the characteristics of the agricultural wastes and the requirements of composting products and renewable energy.

5.4 Summary

The world's environmental impact potentials per person for global warming potential, acidification potential and eutrophication potential were 0.91%, 3.61% and 0.38% for aerobic co-composting, and 1.27%, 0.92% and 0.06% for anaerobic co-digestion, to treat 1 functional unit of agricultural wastes. The comprehensive impact of aerobic composting was more than 2 times of anaerobic digestion. The capital expenditures of the composting plant was 2.52 million, much lower than the digestion project (5.63 million); the operating expenditures of the composting plant was about 0.62 million, also lower than the digestion project (0.79 million). Their operating incomes were almost the same, about 0.88 million. The production profits of the composting plant was about 0.26 million, much higher than the 0.10 million of the digestion project.

Table 5.1 Pollutants emission from electricity generation process.

Pollutant	Emission amount (kg kWh^{-1})
CO_2	1.07
SO_2	0.00993
NO_x	0.00646
CO	0.00155
CH_4	0.00260
NMVOC	0.000487

NMVOC, non-methane volatile organic compounds.

Source: Jin et al., 2007.

Table 5.2 Greenhouse gases emission from aerobic composting process.

Pollutant	Emission amount
CO_2	60 g kg^{-1} DM
CH_4	1.9 g kg^{-1} OM
NO_x	6.26 mg kg^{-1} DM
NH_3	626 g kg^{-1} DM

DM, dry matter; OM, organic matter.

Source: Zhong et al., 2013; Park et al., 2011; Fukumoto et al., 2003.

Table 5.3 Inventory analysis of aerobic co-composting and anaerobic co-digestion of swine manure and rice straw.

Pollutant	Aerobic composting	Anaerobic digestion
Pollutant emission (kg FU^{-1})		
CO_2	41.6810	84.1445
SO_2	0.0298	0.1278
NO_x	0.0774	0.0820
CO	0.0047	0.0197
CH_4	0.6521	0.0330
NH_3	0.6238	0.0724
Energy consumption (kWh FU^{-1})		
Electricity	11.5	75.7

Treatment capacity of the plant: 10 t d^{-1}.

Table 5.4 Environmental impacts of aerobic co-composting and anaerobic co-digestion of swine manure with rice straw.

Item	GWP	AP	EP	Weighted sum
Weight coefficient	0.32	0.36	0.32	
Aerobic composting	0.00912	0.03608	0.00383	0.01713
Anaerobic digestion	0.01268	0.00920	0.00057	0.00755

Treatment capacity of the plant: 10 t d^{-1}; GWP, global warming potential; AP, acidification potential; EP, eutrophication potential.

Table 5.5 Capital expenditures of the aerobic composting plant and the anaerobic digestion project.

Item	CapEX (RMB)
Aerobic co-composting plant	
Rice straw pretreatment system	660,000
Material mixing system	300,000
Aerobic windrow composting system	800,000
Composting mixing system	200,000
Compost packing system	160,000
Supporting facilities and equipment	150,000
Electrical control system	100,000
Design and commissioning	150,000
Total	2,520,000
Anaerobic co-digestion project	
Rice straw pretreatment system	650,000
Material mixing system	300,000
Anaerobic digestion system	2,650,000
Biogas purification system	520,000
Digestate drying system	250,000
Electricity generation system	220,000
Supporting facilities and equipments	370,000
Pipeline valves system	210,000
Electrical control system	200,000
Design and commissioning	250,000
Total	5,630,000

Treatment capacity of the plant: 10 t d^{-1}.

Table 5.6 Annual operating expenditures of the aerobic composting plant and the anaerobic digestion project.

Item	Unit	Number	Unit-price (RMB)	OpEX (RMB)
Aerobic co-composting plant				
Swine manure	ton	2,190	50	109,500
Rice straw	ton	1,460	200	292,000
Electricity	kWh	41,975	0.57	23,926
Water	m^3	3,650	4	14,600
Labor	person	5	30,000	150,000
Maintenance			30,000	30,000
Total				620,026
Anaerobic co-digestion project				
Swine manure	ton	2433	50	121,650
Rice straw	ton	1217	200	243,400
Electricity	kWh	276305	0.57	157,494
Water	m^3	3650	4	14,600
Desulfurater	ton	5	2000	10,000
Labor	person	6	30,000	180,000
Maintenance			60,000	60,000
Total				787,144

Treatment capacity of the plant: 10 t d^{-1}.

Table 5.7 Operating incomes of the aerobic composting plant and the anaerobic digestion project.

Item	Unit	Number	Unit-price (RMB)	OpIN (RMB)
Aerobic co-composting plant				
Compost	ton	2,190	400	876,000
Total				876,000
Anaerobic co-digestion project				
Electricity	kWh	229,950	0.67*	154,100
Digestate	ton	1,825	400	730,000
Total				884,100

Treatment capacity of the plant: 10 t d^{-1}.

*The feed-in tariff for electricity generation from biogas production facility was about 0.67 RMB/kWh, while the standard feed-in tariff for electricity generation from coal-fired power plant with desulfurization equipment was around 0.45 RMB/kWh.

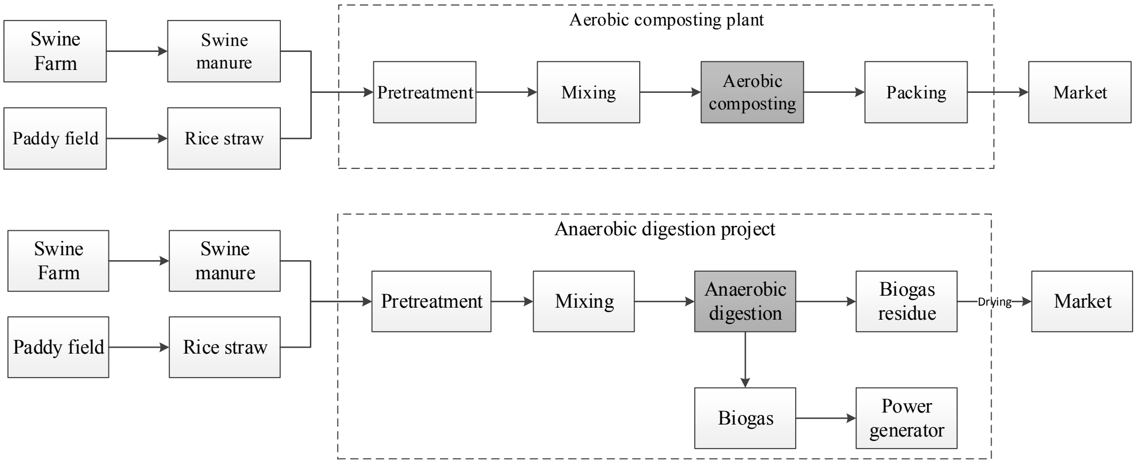

Figure 5.1 System boundaries of LCA for aerobic co-composting and anaerobic co-digestion.

Chapter 6 Conclusions

Swine manure and rice straw, as the primary agricultural wastes in Shanghai, have caused realistic pollution and potential risk to water and atmosphere environment. It is crucial to figure out the pollution profiles and develop practical approaches for the proper treatment of swine manure and rice straw. Under the circumstances of National Pollution Emission Reduction Plan and National Climate Change Program in China, aerobic composting and anaerobic digestion have already been pointed to be the main encouraged approaches for agricultural waste treatment in Shanghai. The investigation on pollution risk and the study on aerobic co-composting and anaerobic co-digestion of swine manure with rice straw can provide the basic information and technical support for the establishment of maturity evaluation index system for aerobic composting and the operation optimization for anaerobic digestion when using swine manure and rice straw as feedstocks.

6.1 Conclusions

(1) More than 80% of all the towns and the whole city were suffering the potential pollution risk of land application of animal manure when the land application of chemical fertilizer was considered. The plentiful amounts of untreated straws under field burning and field discarding could lead to serious air and water pollution when the burning and discarding is conducted and concentrated in the harvest season in the area with dense rice or wheat plantation. Swine manure and rice straw were the two main agricultural wastes in Shanghai.

(2) Mature compost could be achieved after 60 days' aerobic co-composting of

swine manure with rice straw. The fast maturation was signaled by a relatively long thermophilic phase, high OM degradation rate, GI and PGI. A comprehensive maturity evaluation index system consisting of chemical (C/N ratio) and biological (GI or PGI) parameters was established, and the suitable values of GI and PGI were proposed as greater than 120% and 1.00, respectively for mature compost.

(3) Inoculation of biogas slurry into the co-digestion reactors increased the biogas yields by 3.00-7.05%, and improved the biogas productivity by 7.48-8.17% for per unit of TS. The digestion process fitted the single-stage first-order model well. The reactors with biogas slurry inoculation exhibited faster in biogas production with *k* increased by 39.90-50.96% compared with the control. Alkaline and microwave+alkaline pretreatments on rice straw increased the biogas yields from the co-digestion reactors by 25.99-26.71%, and improved the biogas productivity by 2.85-5.88% for per unit of TS. The co-digestion reactors with pretreated rice straw exhibited faster in biogasification with *k* increased by 2.36-5.39% compared with the control. The digestion process with alkaline and microwave alkaline pretreated rice straw fitted the two-stage first-order model more accurately.

(4) The world’s environmental impact potentials per person for global warming potential, acidification potential and eutrophication potential were 0.91%, 3.61% and 0.38% for aerobic co-composting, and 1.27%, 0.92% and 0.06% for anaerobic co-digestion, to treat 1 functional unit of agricultural wastes. The aerobic composting plant had lower capital and operating expenditures and higher production profit than the anaerobic digestion based on the same plant scale, the unified price of electricity

for agricultural production, and the feed-in tariff of electricity from biogas generation facility.

6.2 Future work

From the consideration of practical application and technical guidance in the composting plants and digestion projects, the following directions could be included into the future work.

(1) For the maturity evaluation of aerobic composting, more simple and precise indicators with faster testing methods will be studied, based on the maturity evaluation index system established in this study. After doing so, the quality control for composting process can be practically and quickly implemented in the operation of composting plants in Shanghai suburbs.

(2) In order to obtain stable digestion process with high efficiency in the constructing anaerobic digestion projects, the compositions, pretreatments and inoculums will be further researched on site based on the operation conditions explored in this study. More inoculation will be tested to find the optimal inoculation size for the dry anaerobic co-digestion of swine manure with rice straw.

(3) For the policy making on agricultural waste management, diversified approaches will be encouraged according to the characteristics of agricultural wastes, and subsidy standards for aerobic composting plants and anaerobic digestion projects will be paid more attention, especially for the feed-in tariff of biogas power generation plant.

References

Ahn HK, Smith MC, Kondrad SL, White JW. Evaluation of biogas production potential by dry anaerobic digestion of switchgrass–animal manure mixtures. Applied Biochemistry and Biotechnology 160 (2010) 965-975.

Ai P, Zhang Y, Sheng K, Zhai H, Yan S. Pretreatment for biogas production by anaerobic fermentation of rice straw. Transactions of the Chinese Society of Agricultural Engineering 26 (2010) 266-271. (in Chinese with English abstract)

APHA (American Public Health Association). Standard Methods for the Examination of Water and Wastewater. Washington, DC: American Public Health Association, 1998.

Bernal MP, Alburquerque JA, Moral R. Composting of animal manures and chemical criteria for compost maturity assessment: A review. Bioresource Technology 100 (2009) 5444-5453.

Bollon J, Le-hyaric R, Benbelkacem H, Buffiere P. Development of a kinetic model for anaerobic dry digestion processes: Focus on acetate degradation and moisture content. Biochemical Engineering Journal 56 (2011) 212-218.

Brentrup F, Küsters J, Kuhlmann H, Lammel J. Environmental impact assessment of agricultural production systems using the life cycle assessment (LCA) methodology I: Theoretical concept of a LCA method tailored to crop production. Europe Journal of Agronomy 20 (2004) 247-264.

Buerkert A, Nagieb M, Siebert S, Khan I, Al-Maskri A. Nutrient cycling and field-based partial nutrient balances in two mountain oases of Oman. Field Crops Research 94 (2005) 149-164.

Bustamante MA, Paredes C, Marhuenda-Egea FC, Pérez-Espinosa A, Bernal MP, Moral R. Co-composting of distillery wastes with animal manures: Carbon and nitrogen transformations in the evaluation of compost stability. Chemosphere 72 (2008) 551-557.

Cao Y, Pawłowski A. Life cycle assessment of two emerging sewage sludge-to-energy systems: Evaluating energy and greenhouse gas emissions implications. Bioresource Technology 127 (2013) 81-91.

Chen K-S, Wang H-K, Peng Y-P, Wang W-C, Chen C-H, Lai C-H. Effects of open burning of rice straw on concentrations of atmospheric polycyclic aromatic hydrocarbons in Central Taiwan. Journal of the Air and Waste Management Association 58 (2008) 1318-1327.

Clift R. System Approaches: Life Cycle Assessment and Industrial Ecology. In: Harrison RM (Ed.), Pollution: Causes Effects and Control, 5th ed. Society of Chemistry, London, 2013, Chapter 17.

de Guardia A, Mallard P, Teglia C, Marin A, Le Pape C, Launay M, Benoist JC, Petiot C. Comparison of five organic wastes regarding their behaviour during composting: Part 1, biodegradability, stabilization kinetics and temperature rise. Waste Management 30 (2010) 402-414.

Dias BO, Silva CA, Higashikawa FS, Roig A, Sánchez-Monedero MA. Use of biochar as bulking agent for the composting of poultry manure: Effect on organic matter degradation and humification. Bioresource Technology 101 (2010) 1239-1246.

Duan G, Zhang H, Liu Y, Jia Y, Hu Y, Cheng W. Long-term fertilization with pig-biogas residues results in heavy metal accumulation in paddy field and rice grains in Jiaxing of China. Soil Science and Plant Nutrition 58 (2012) 637-646.

Dusek U, Frank GP, Hildebrandt L, Curtius J, Schneider J, Walter S, Chand D, Drewnick F, Hing S, Jung D, Borrmann S, Andreae MO. Size matters more than chemistry for cloud-nucleating ability of aerosol particles. Science 312 (2006) 1375-1378.

Estrellan CR, Iino F. Toxic emissions from open burning. Chemosphere 80 (2010) 193-207.

Evangelisti S, Lettieri P, Borello D, Clift R. Life cycle assessment of energy from waste via anaerobic digestion: A UK case study. Waste Management 34 (2014) 226-237.

Feng L, Li R, Raninger B, Gehring MJ. Efficiency of anaerobic digestion of straw pretreated with microwave energy. Chinese Journal of Environmental Engineering 3(No.8) (2009) 1503-1508. (in Chinese with English abstract)

Fernández J, Pérez M, Romero LI. Kinetics of mesophilic anaerobic digestion of the organic fraction of municipal solid waste: Influence of initial total solid concentration. Bioresource Technology 101 (2010) 6322-6328.

Finnveden G, Johansson J, Lind P, Moberg Å. Life cycle assessment of energy from solid waste - part 1: general methodology and results. Journal of Cleaner Production 13 (2005) 213-229.

Forster-Carneiro T, Pérez M, Romero LI, Sales D. Dry-thermophilic anaerobic digestion of organic fraction of the municipal solid waste: Focusing on the inoculum sources. Bioresource Technology 98 (2007) 3195-3203.

Fukumoto Y, Osada T, Hanajima D, Haga K. Patterns and quantities of NH_3, N_2O and CH_4 emissions during swine manure composting without forced aeration - effect of compost pile scale. Bioresource Technology 89 (2003) 109-114.

Gao M, Liang F, Yu A, Li B, Yang L. Evaluation of stability and maturity during forced-aeration composting of chicken manure and sawdust at different C/N ratios. Chemosphere 78 (2010) 614-619.

Gigliotti G, Proietti P, Said-Pullicino D, Nasini L, Pezzolla D, Rosati L, Porceddu PR. Co-composting of olive husks with high moisture contents: Organic matter dynamics and compost quality. International Biodeterioration and Biodegradation 67 (2012) 8-14.

Gómez-Brandón M, Lazcano C, Domínguez J. The evaluation of stability and maturity during the composting of cattle manure. Chemosphere 70 (2008) 436-444.

Grube M, Lin JG, Lee PH, Kokorevicha S. Evaluation of sewage sludge-based compost by FT-IR spectroscopy. Geoderma 130 (2006) 324-333.

Gu Y, Chen X, Liu Z, Zhou X, Zhang Y. Effect of inoculum sources on the anaerobic digestion of rice straw. Bioresource Technology 158 (2014) 149-155.

He HR, Zhang LX, Li Q. Rational fertilization and reduction of large-scale farmland pollution by rationalized fertilizer usage. Journal of Agrotechnical Economics 6 (2006) 2-10. (in Chinese with English abstract)

He M, Li W, Liang X, Wu D, Tian G. Effect of composting process on phytotoxicity and speciation of copper, zinc and lead in sewage sludge and swine manure. Waste Management 29 (2009) 590-597.

He X-S, Xi B-D, Jiang Y-H, He L-S, Li D, Pan H-W, Bai S-G. Structural transformation study of water-extractable organic matter during the industrial composting of cattle manure. Microchemical Journal 106 (2013) 160-166.

Himanen M, Hänninen M. Composting of bio-waste, aerobic and anaerobic sludges - Effect of feedstock on the process and quality of compost. Bioresource Technology 102 (2011) 2842-2852.

Huang GF, Wong JWC, Wu QT, Nagar BB. Effect of C/N on composting of pig manure with sawdust. Waste Management 24 (2004) 805-813.

IPCC (Intergovernmental Panel on Climate Change). Climate change 1995 - the science of climate change. University Press, Cambridge, UK, 1996.

ISO (International Organization for Standardization). ISO 14040: Environmental management-life cycle assessment-principles and framework. Geneva, 2006.

Ito A, Penner JE. Global estimates of biomass burning emissions based on satellite imagery for the Year 2000. Journal of Geophysical Research 109 (2004) 1-18.

Jin J. Analysis on environmental impact and application prospect of the comprehensive utilization ways of FGD gypsum. Master Thesis of University of Science and Technology Beijing, 2007. (in Chinese with English abstract).

Juanga JP. Optimizing dry anaerobic digestion of organic fraction of municipal solid waste. Master Thesis of Asian Institute of Technology, Thailand, 2005.

Kafle GK, Kim SH. Anaerobic treatment of apple waste with swine manure for biogas production: Batch and continuous operation. Applied Energy 103 (2013) 61-72.

Kim M-K, Kwon S-I, Chun H-C, Jung G-B, Kang K-K. Impacts of pig manure-based liquid fertilizer agricultural application on the water quality of agricultural catchment. Journal of Environmental Protection 4 (2013) 195-200.

Kim J, Park C, Kim TH, Lee M, Kim S, Kim SW, Lee J. Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. Journal of Bioscience and Bioengineering 95 (2003) 271-275.

Ko HJ, Kim KY, Kim HT, Kim CN, Umeda M. Evaluation of maturity parameters and heavy metal contents in composts made from animal manure. Waste Management 28 (2008) 813-820.

Krishania M, Vijay VK, Chandra R. Methane fermentation and kinetics of wheat straw pretreated substrates co-digested with cattle manure in batch assay. Energy 57 (2013) 359-367.

Kumar P, Barrett DM, Delwiche MJ, Stroeve P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Industrial & Engineering Chemistry Research 48 (2009) 3713-3729.

Lai CH. Chen KS, Wang HK. Influence of rice straw burning on the levels of polycyclic aromatic hydrocarbons in agricultural county of Taiwan. Journal of Environmental Science (China) 21 (2009) 1200-1207.

Laumbach RJ, Kipen HM. Respiratory health effects of air pollution: Update on biomass smoke and traffic pollution. Journal of Allergy and Clinical Immunology 129 (2012) 3-11.

Lei Z, Chen J, Zhang Z, Sugiura N. Methane production from rice straw with acclimated anaerobic sludge: Effect of phosphate supplementation, Bioresource Technology 101 (2010) 4343-4348.

Li Y, Li W, Liu B, Wang K, Su C, Wu C. Ammonia emissions and biodegradation of organic carbon during sewage sludge composting with different extra carbon sources. International Biodeterioration & Biodegradation 85 (2013a) 624-630.

Li H, Su B. Estimation methods of agricultural non-point source pollution in plain river network area: a review. Journal of Beijing Normal Universtiy (Natural Science) 45 (2009) 662-666. (in Chinese with English abstract)

Li X, Zhang R, Pang Y. Characteristics of dairy manure composting with rice straw. Bioresource Technology 99 (2008) 359-367.

Li Y, Zhang W, Ma L, Huang G, Oenema O, Zhang F, Dou Z. An analysis of China’s fertilizer policies: Impacts on the industry, food security, and the environment. Journal of Environmental Quality 42 (2013b) 972-981.

Liang Y, Zheng Z, Huang R, Luo X. A preliminary study of simultaneous lime treatment and dry digestion of smooth cordgrass for biogas production. Chemical Engineering Journal 174 (2011) 175-181.

Liang Y, Yin S, Si Y, Zheng Z, Yuan S, Nie E, Luo X. Effect of pretreatment and total solid content on thermophilic dry anaerobic digestion of Spartina alterniflora. Chemical Engineering Journal 237 (2014) 209-216.

Lopes WS, Leite VD, Prasad S. Influence of inoculum on performance of anaerobic reactors for treating municipal solid waste. Bioresource Technology 94 (2004) 261-266.

Ma J, Cai X. Farmers' willingness and impact factors of reducing application amount of nitrogen fertilizer. China Rural Economy 9 (2007) 9-16. (in Chinese with English abstract)

Maruf Hossain AMM, Park K. Exploiting potentials from interdisciplinary perspectives with reference to global atmosphere and biomass burning management. Aerosol and Air Quality Research 12 (2012) 123–132.

Matsi T. Liquid cattle manure application to soil and its effect on crop growth, yield, composition, and on soil properties. In: Whalen JK (Ed.), Soil Fertility Improvement and Integrated Nutrient Management – A Global Perspective, InTech, Rijeka, Croatia, 2012, 97-118.

Maurer C, Müller J. Ammonia (NH_3) emissions during drying of untreated and dewatered biogas digestate in a hybrid waste-heat/solar dryer. Engineering in Life Sciences 12 (2012) 321-326.

Meng F, Liu M, Shi TG. Evaluation on environmental quality of heavy metals in agricultural soils of Shanghai. Environmental Sciences 29 (2008) 428-433. (in Chinese with English abstract)

Mezzullo WG, McManus MC, Hammond GP. Life cycle assessment of a small-scale anaerobic digestion plant from cattle waste. Applied Energy 102 (2013) 657-664.

MEP China (Ministry of Environmental Protection of China). Notifications on the deration of pollution charge of livestock and poultry breeding. http://www.mep.gov.cn/gkml/zj/wj/200910/t20091022_172271.htm, 2004.

Møller HB, Sommer SG, Ahring B. Methane productivity of manure, straw and solid fractions of manure. Biomass and Bioenergy 26 (2004) 485-495.

Motte JC, Escudié R, Bernet N, Delgenes JP, Steyer JP, Dumas C. Dynamic effect of total solid content, low substrate/inoculum ratio and particle size on solid-state anaerobic digestion. Bioresource Technology 144 (2013) 141-148.

Mussoline W, Esposito G, Lens P, Garuti G, Giordano, A. Design considerations for a farm-scale biogas plant based on pilot-scale anaerobic digesters loaded with rice straw and piggery wastewater. Biomass and Bioenergy 46 (2012) 469-478.

NBSC (National Bureau of Statistics of China). China Statistical Yearbook. China Statistics Press, Beijing, 2011, 461-462; 482-483.

Niu MF, Pang XP, Chen SR. The study of influencing factors to corn straw mixed with pig effluent anaerobic fermentation. Procedia Environmental Sciences 8 (2011) 54-60.

Nolan T, Troy SM, Healy MG, Kwapinski W, Leahy JJ, Lawlor PG. Characterization of compost produced from separated pig manure and a variety of bulking agents at low initial C/N ratios. Bioresource Technology 102 (2011) 7131-7138.

Orr Jr. DE, Shen YR. World pig production, opportunity or threat? Midwest Swine Nutrition Conference Proceedings, Indianapolis, September 2006, 3-8.

Ouyang W, Hao F, Wei X, Huang H. Spatial and temporal trend of Chinese manure nutrient pollution and assimilation capacity of cropland and grassland. Environmental Science and Pollution Research 20 (2013) 5036-5046.

Park KH, Jeon JH, Jeon KH, Kwag JH, Choi DY. Low greenhouse gas emissions during composting of solid swine manure. Animal Feed Science and Technology 166-167 (2011) 550-556.

Rao MS, Singh SP. Bioenergy conversion studies of organic fraction of MSW: kinetics studies and gas yield-organic loading relationships for process optimization. Bioresource Technology 95 (2004) 173-185.

Raposo F, De la Rubia MA, Fernández-Cegrí V, Borja R. Anaerobic digestion of solid organic substrates in batch mode: An overview relating to methane yields and experimental procedures. Renewable and Sustainable Energy Reviews 16 (2011) 861-877.

Reinhardt GA. Bilanzenüber die gesamten Lebenswege. Kaltschmitt M, Reinhardt GA, Nachwachsende Energieträger - Grundlagen, Verfahren, ökologische Bilanzierung. Verlag Vieweg, Braunschweig, Wiesbaden, Germany, 1997, 84-95.

Sapci Z, Morken J, Linfjordet R. An investigation of the enhancement of biogas yields using two pretreatment methods: microwave irradiation and steam explosion. Bioresources 8 (2013) 1976-1985.

Sinpaisansomboon N, Intanon P, Rakwichian W, Kongsricharoern N. Development of two-stage anaerobic digesters for biogas production from biodegradable waste of Phitsanulok Municipal, Thailand. International Journal of Renewable Energy 2 (2007) 63-70.

Shen G, Qian X, Yao Z, Xu Z, Huang S, Yan Z, Evaluation of livestock and poultry breeding carrying capacity of arable lands in Shanghai suburbs. Livestock Environment VII - Proceedings of the Seventh International Symposium, Beijing, May 2005, 452-457.

Shen G, Xie Z, Qian X, Huang L, Guo C, Wang M, Shan Z. Investigation and analysis of heavy metal accumulation in the soil of vegetable cropland in Shanghai. Journal of Agro-Environment Science 25 (2006) 37-40. (in Chinese with English abstract)

Shih S-I, Lee W-J, Lin L-F, Huang J-Y, Su J-W, Chang-Chien G-P. Significance of biomass open burning on the levels of polychlorinated dibenzo-p-dioxinsand dibenzofurans in the ambient air. Journal of Hazardous Materials 153 (2008) 276-284.

SMAC (Shanghai Municipal Agricultural Commission). Announcement on project construction of animal manure treatment centers in Shanghai suburbs. http://www.shagri.gov.cn/xwkd/zwxw/xumuye/200805/t20080527_749615.htm, 2008. (in Chinese)

SMAC (Shanghai Municipal Agricultural Commission). Approval for the 2nd batch of pollution reduction projects of scale livestock and poultry farms in Shanghai. http://e-nw.shac.gov.cn/zfxxgk/mulu/yewu/xumu/qita/201307/t20130726_1348201.htm, 2013. (in Chinese)

SMDRC (Shanghai Municipal Development and Reform Commission). Plan of Shanghai Municipality on the Comprehensive Utilization of Crop Straws. http://fgw.sh.gov.cn/main?main_colid=380&top_id=312&main_artid=15783, 2009. (in Chinese)

SMPG (Shanghai Municipal People's Government). Regulations of Shanghai Municipality on the Management of Livestock and Poultry Breeding. http://www.shanghai.gov.cn/shanghai/node2314/node3124/node3141/node3147/u6ai1265.html, 2004. (in Chinese)

SMPG (Shanghai Municipal People's Government). Suggestion on the forbidding of open field burning of crop straws and the subsiding of returning to field of crop straws. http://www.shanghai.gov.cn/shanghai/node2314/node2315/node4411/u21ai820640.html, 2013. (in Chinese)

SSB (Shanghai Statistical Bureau). Statistical Yearbook of Shanghai Suburbs 2009. State Statistics Press, Beijing, 2009. (in Chinese)

Stranddorf HK, Hoffmann L, Schmidt A. Update on impact categories, normalization and weighting in LCA. Environmental Project No. 995, Danish Environmental Protection Agency, 2005.

Sun C, Wu H. Pollution from animal husbandry in China: a case study of the Han River Basin. Water Science and Technology 66 (2012) 872-878.

Sun J, Yu X, Zhang M, Lu S, Wu W, WU J, Xu J. Potential risks of copper, zinc, and cadmium pollution due to pig manure application in a soil–rice system under intensive farming: a case study of Nanhu, China. Journal of Environmental Quality 40 (2011) 1695-1704.

Tipayarom D, Oanh NTK. Effects from open rice straw burning emission on air quality in the Bangkok metropolitan region. Science Asia 33 (2007) 339-345.

Troy SM, Nolan T, Kwapinski W, Leahy JJ, Healy MG. Effect of sawdust addition on composting of separated raw and anaerobically digested pig manure. Journal of Environmental Management 111 (2012) 70-77.

Valery BA, Nazim C, Richard S, Alex B, David BL. Biomass pretreatment: fundamentals toward application. Biotechnology Advances 29 (2011) 675-685.

Viana M, López JM, Querol X, Alastuey A, García-Gacio D, Blanco-Heras G, López-Mahía P, Piñeiro-Iglesias M, Sanz MJ, Sanz F, Chi X, Maenhaut W. Tracers and impact of open burning of rice straw residues on PM in Eastern Spain. Atmospheric Environment 42 (2008) 1941-1957.

Wang G, Gavala HN, Skiadas IV, Ahring BK. Wet explosion of wheat straw and codigestion with swine manure: effect on the methane productivity. Waste Management 29 (2009) 2830-2835.

Wang H, Qin Y, Yu K. Utilization, distribution and exploitation tactics of crop stalk resources in China. Territory and Natural Resources Study 2 (2008) 92-93. (in Chinese with English abstract)

Wang G. Analysis method on reducing emission of SO_2 and CO_2 by rural energy construction. Transactions of the Chinese Society of Agricultural Engineering 15 (1999) 169-172. (in Chinese with English abstract)

Wang M, Bao Y, Wu W, Liu W. Life cycle environmental impact assessment of winter wheat in North China plain. Journal of Ago-Environment Science 25 (2006) 1127-1132. (in Chinese with English abstract)

Wang X, Yang G, Feng Y, Ren G, Han X. Optimizing feeding composition and carbon–nitrogen ratios for improved methane yield during anaerobic co-digestion of dairy, chicken manure and wheat straw. Bioresource Technology 120 (2012) 78-83.

Woods End Research. Guide to Solvita testing for compost maturity index. Compost New Manual 11 (2002) 1-8.

Xiong X, Li Y, Li W, Lin C, Han W, Yang M. Copper content in animal manures and potential risk of soil copper pollution with animal manure use in agriculture. Resources, Conservation and Recycling 54 (2010) 985-990.

Ye J, Li D, Sun Y, Wang G, Yuan Z, Zhen F, Wang Y. Improved biogas production from rice straw by co-digestion with kitchen waste and pig manure. Waste Management 33 (2013) 2653–2658.

Yuan B, Liu Y, Shao M, Lu S, Streets DG. Biomass burning contributions to ambient VOCs species at a receptor site in the Pearl River Delta (PRD), China. Environmental Science and Technology 44 (2010) 4577-4582.

Zhang H, Ye X, Chen T, Chen J, Yang X, Wang L, Zhang R. A laboratory study of agricultural crop residue combustion in China: emission factors and emission inventory. Atmospheric Environment 42 (2008) 8432-8441.

Zhang H, Hu D, Chen J, Ye X, Wang S, Hao J, Wang L, Zhang R, An Z. Particle size distribution and polycyclic aromatic hydrocarbons emissions from agricultural crop residue burning. Environmental Science and Technology 45 (2011) 5477-5482.

Zhang Z, Engling G, Lin C-Y, Chou C C-K, Lung S-C C, Chang S-Y, Fan S, Chan C-Y, Zhang Y-H. Chemical speciation, transport and contribution of biomass burning smoke to ambient aerosol in Guangzhou, a mega city of China. Atmospheric Environment 44 (2010a) 3187-3195.

Zhang Y, Xia X, Li Z, Wang M, Yang T, Xi B. Life cycle assessment of manure treatment in scaled cattle farms. Journal of Agro-Environment Science 29 (2010b) 1423-1427.

Zhang F, Hu H. Pollution effect of fertilizer application and regional differences in China. Journal of Hunan Agricultural University (Social Sciences) 12 (2013) 33-38. (in Chinese with English abstract)

Zhong J, Wei Y, Wan H, Wu Y, Zheng J, Han S, Zheng B. Greenhouse gas emission from the total process of swine manure composting and land application of compost. Atmospheric Environment 81 (2013) 348-355.

Zhong W, Zhang Z, Luo Y, Sun S, Qiao W, Xiao M. Effect of biological pretreatments in enhancing corn straw biogas production. Bioresource Technology 102 (2011) 11177–11182.

Zhou M, Zhang R, Lin J. The operative technology and engineering of biogas. Chemical Industry Press, Beijing, 2004, 5-23. (in Chinese with English abstract)

Zhu N. Effect of low initial C/N ratio on aerobic composting of swine manure with rice straw. Bioresource Technology 98 (2007) 9-13.

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