BIOGAS PRODUCTION FROM SHRIMP FARMING WASTE

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การผลิตก๊าซชีวภาพจากของเสียที่ได้จากการทำฟาร์มกุ้ง

นางสาวธาริณี ฤทธิรณ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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THE BIOGAS PRODUCTION FROM SHRIMP FARMING WASTE

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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ธาริณี ฤทธิรณ : การผลิตก๊าซชีวภาพจากของเสียที่ได้จากการทำฟาร์มกุ้ง (BIOGAS PRODUCTION FROM SHRIMP FARMING WASTE) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.อัฆพรรค์ วรรณโกมล, 64 หน้า.

งานวิจัยนี้มีวัตถุประสงค์เพื่อประเมินศักยภาพการผลิตก๊าซชีวภาพจากของเสียที่ได้จากการทำฟาร์มกุ้งและวัสดุหมักร่วมต่างๆ ด้วยกระบวนการย่อยสลายแบบไม่ใช้ออกซิเจนแบบแบตซ์ เป็นระยะเวลา 30 วัน ภายใต้การทดลองที่อุณหภูมิห้องและใช้ปริมาณสัดส่วนของเชื้อจุลินทรีย์และสารตั้งต้นที่แตกต่างกัน 3 2 และ 1 ต่อ 1 ตามลำดับ จากการทดลองแสดงให้เห็นว่าการย่อยสลายของเสียที่ได้จากการทำฟาร์มกุ้งเพียงอย่างเดียวนั้นให้ปริมาณผลผลิตของก๊าซชีวภาพ 0.21 0.34 และ 0.00 mL/g VS การย่อยสลายของเสียที่ได้จากการทำฟาร์มกุ้งร่วมกับฟางข้าวซึ่งเป็นวัสดุหมักร่วมให้ปริมาณผลผลิตของก๊าซชีวภาพ 0.29 0.67 และ 1.11 mL/g VS และการย่อยสลายของเสียที่ได้จากการทำฟาร์มกุ้งร่วมกับเศษอาหารซึ่งเป็นวัสดุหมักร่วมมีค่า 0.31 1.01 และ 0.69 mL/g VS ตามลำดับ การย่อยสลายของเสียที่ได้จากการทำฟาร์มกุ้งเพียงและใช้วัสดุหมักร่วมเป็นฟางข้าวแสดงปริมาณการผลิตก๊าซมีเทนมากที่สุด คือ 53.71 mL CH_4/g VS ผลที่ได้ยังบ่งชี้ให้เห็นอีกด้วยว่าการเพิ่มปริมาณสัดส่วนของเชื้อจุลินทรีย์และสารตั้งต้นมีผลกระทบโดยตรงต่อปริมาณผลผลิตของก๊าซมีเทนที่มีสารตั้งต้นแตกต่างกัน

สาขาวิชา เทคโนโลยีธรณี ลายมือชื่อนักศึกษา ____________________

ปีการศึกษา 2557 ลายมือชื่ออาจารย์ที่ปรึกษา________________

TARINEE RITTIRON : THE BIOGAS PRODUCTION FROM SHRIMP FARMING WASTE. THESIS ADVISOR : ASSOC. PROF. AKKHAPUN WANNAKOMOL, Ph.D., 64 PP.

SHRIMP FARMING WASTE/ANAEROBIC DIGESTION/ BIOCHEMICAL METHANATION POTENTIAL /BIOGAS PRODUCTION

The objective of this study was to evaluate the potential of biogas production from shrimp farming waste and from the different co-digesting under batch anaerobic digestion. The batch test was conducted for 30 days under room temperature condition at different inoculum to substrate ratios of 3, 2 and 1:1, respectively. The results showed the determined biogas yield was 0.21, 0.34 and 0.00 mL/g VS for shrimp farming waste, 0.29, 0.67 and 1.11 mL/g VS for co-digesting substrate of shrimp farming waste and rice straw, and 0.31, 1.01 and 0.69 mL/g VS for co-digesting substrate of shrimp waste and food waste, respectively. The shrimp farming waste and rice straw as co-digesting substrate displayed the maximum methanogenic activity 53.71 mL CH_4/g VS. Results also indicated that the higher inoculum to substrate ratio indicated a significant impact on methane yield from different substrate.

School of Geotechnology Student's Signature_________________

Academic Year 2014 Advisor's Signature_________________

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Tarinee Rittiron

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SYMBOLS AND ABBREVIATIONS

ROMAN ABBREVIATIONS:

BMP	=	Biochemical Methane Potential
C/N	=	Carbon to nitrogen ratio
CO_2	=	Carbon dioxide gas
CH_4	=	Methane gas
FW	=	Food waste
ISR	=	Inoculum to Substrate Ratio
I/F	=	Inoculum to Feed ratio
MW	=	Mixed Waste
SW	=	Shrimp farming waste
g	=	Gram
l	=	Liter
m^3	=	Cubic meter
MJ	=	Mega Joule
N_2	=	Nitrogen gas
TS	=	Total Solids
VS	=	Volatile Solids
W	=	Inoculum
°C	=	Degree Celsius (Standard Temperature unit)

SYMBOLS AND ABBREVIATIONS (Continued)

GREEK ABBREVIATIONS:

ρ_{sw}	=	Density of shrimp farming waste at the time of measurement
ρ_{mw}	=	Density of rice straw at the time of measurement
ρ_{fw}	=	Density of food waste at the time of measurement

CHAPTER I

INTRODUCTION

1.1 Background and rationale

Due to insufficiency of petroleum and coal throughout the world, mankind is seeking for a new source of energy for living in the future which is friendly to the environment. The marsh gas methane was discovered by Volta in 1776 and appears to be an alternative to petroleum based energy. This gas occurs naturally in some soils, lake and oceanic basin sediments referred as anaerobic digestion. Since that time, anaerobic digestion has then been studied. The process is fermentation from disposal in an absence of oxygen and mainly converted to methane and carbon dioxide gas by products. The methane gas from this reaction has been studied for many years and proofed can be used as renewable energy. This renewable energy is distinct from others because it is simple to use and apply in household or industry factories and much of the world. Electricity and heating system is converted from biogas and using in many industries (S. Dechrugsa et al., 2013). Since 1991, Thailand has been the leader of shrimp manufacturer and frozen exporter which is more than hundred thousand million baht per year (T. Sitipokkaporn., 2011). Nevertheless, problems have been found out through the environment nearby shrimp pond and the sea. Due to shrimp culture, most shrimpers still using an opened water system; discharged inlet – outlet water in drained water pond and replace by natural water. The procedure causes many vast problems as result of lacking of shrimpers' responsibility before drain water out back through source of natural water. The effects on the environment are pH value consistence, salinity, shrimp disposals, nitrogen chemical compound, hydrogen sulfide, and even methane gas were left over from shrimp feeding. According to the biogas occurrence, one was found out from disposal soils. Therefore, this study is carried out shrimp farming wastes as substrate to produce a biogas.

Most of anaerobic digestions were also made by energy crops such as sugar crane, maize and rice straw. Those crops are easy to find, clean, low capital cost and also give high percentage of methane gas in anaerobic digestion. In Thailand, rice straw is easy to find in every region after end of rice harvesting. So in this study, rice straw was used as co-substrate. Anaerobic digester has been widely used to treat waste water and waste product then produced biogas by-product. The feasibility of co-digesting of shrimp manure and rice straw is to approach biogas manufacturing. Due to carbon to nitrogen ratio of shrimp disposal was too low, the carbon to nitrogen ratio of rice straw was mixed to carry out the optimum carbon to nitrogen ratio. Owing to the different characteristics of both substrates, the consequence of this rice straw needs to be known.

Rice straw, waste agricultural straw, cannot be digested by itself according to the complex structure which difficult to digest for bacteria (Himmel et al., 2007). To start the digestive process, it needs to address the active microbial. The biochemical methane potential (BMP) assay has been using to achieve the utmost biodegradability and methane yield (I. Angelidaki et al., 2009). Therefore, the purpose of this study was to evaluate the feasibility to biogas production in anaerobic digestion from shrimp farming waste on mesophilic in batch mode using BMP assay with different inoculum to substrate ratio (ISR).

1.2 Research objectives

The specific objectives of this study can be defined as follows:

1. To evaluate the potential of biogas production from shrimp farming wastes under anaerobic digestion by biochemical methane potential method.

2. To assess and analyze the physical and chemical properties of biogas produced from shrimp farming wastes.

1.3 Research methodology

1.3.1 Research place

1. Shrimp farming waste was collected only from Bangkrajed Sub-district, Bangkla District, Chachengsao, Thailand.

2. Inoculum was collected and supported from Sanguan Wongse Industries, Nakorn Ratchasima, Thailand.

3. Experiments were performed at Environment engineering laboratory, Suranaree University of Technology.

4. Food waste was collect from Suranaree University of Technology canteen.

1.3.2 Assessment and analysis the physical and chemical properties of shrimp farming waste

1. The experiments were conducted in the laboratory under anaerobic digestion by BMP method under room temperature 28±3°C for 30 days, and the using supplement medium was followed the experiment of F. Raposo et al. (2006).

2. The anaerobic digestion was carried out in 300 ml working volume, liquid volume 250 ml with maintained pH around 6-8 only before digestion.

1.4 Research plan

This study was conducted following the step as depicted in Figure 1.1, including 1) literature reviewed, 2) sampling area designed and selected, 3) samples collecting and analyzing to characterized their physical and chemical composition, 4) conduction of anaerobic digestion by BMP method in laboratory, 5) results analytical and comparisons, 6) results of the experiment conclusions and discussion, and 7) thesis and report writing, respectively.

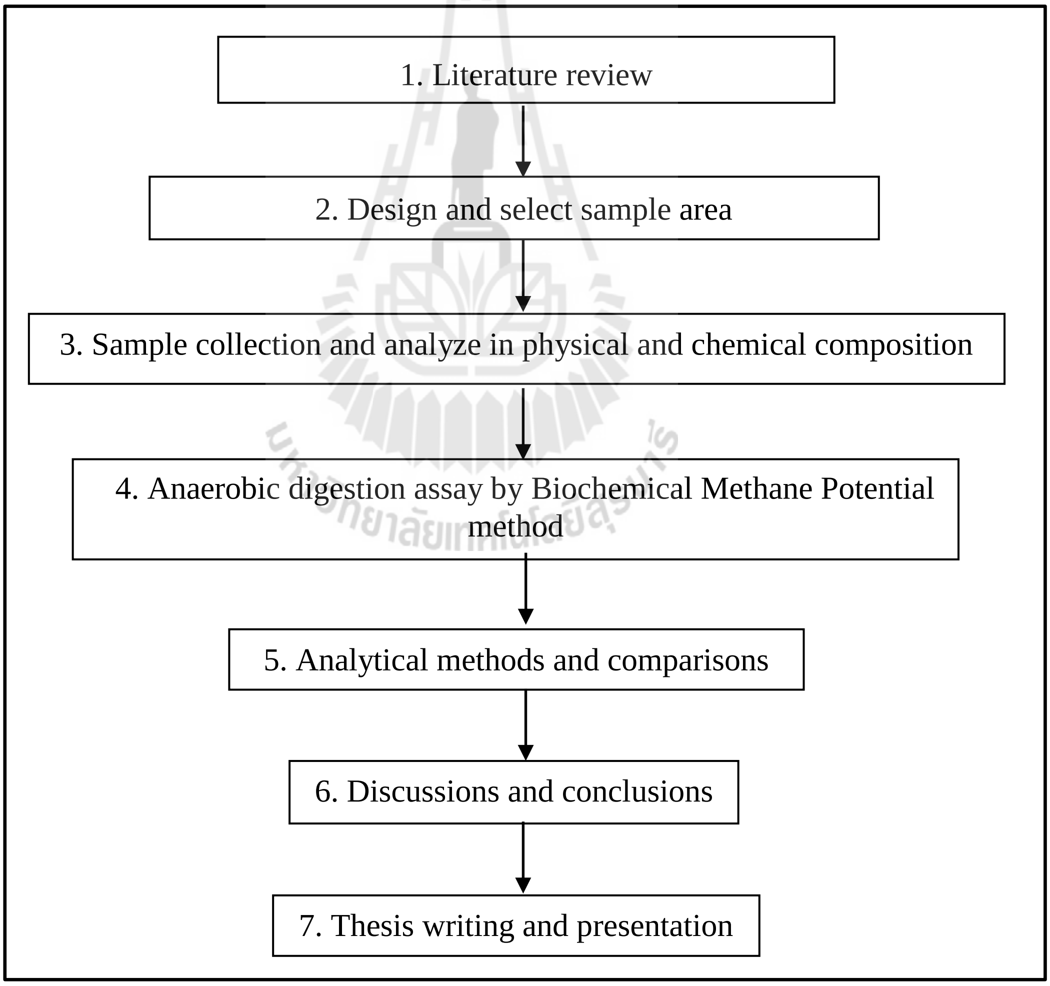


Figure 1.1 Research plan

1.5 Thesis contents

Chapter I introduces the thesis by briefly describing the background and rationale of the study, the study objectives, methodology, scope and limitations of the study. Chapter II summarizes the results of the literature review. Chapter III describes the sample and mixture preparations. Chapter IV describes the results from the laboratory experiments which are separated by different substrate, including 1) shrimp farming waste 2) shrimp farming waste and rice straw as co-digesting 3) shrimp farming waste and food waste as co-digesting. Chapter V discusses and concludes the research results and provides recommendations for future research studies, respectively.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction

Oil price, finite resource, is increasing and will be run out in the future. As we can see on human energy demand is raising vary on world population. World energy demand is expected as it is showed in Figure 2.1

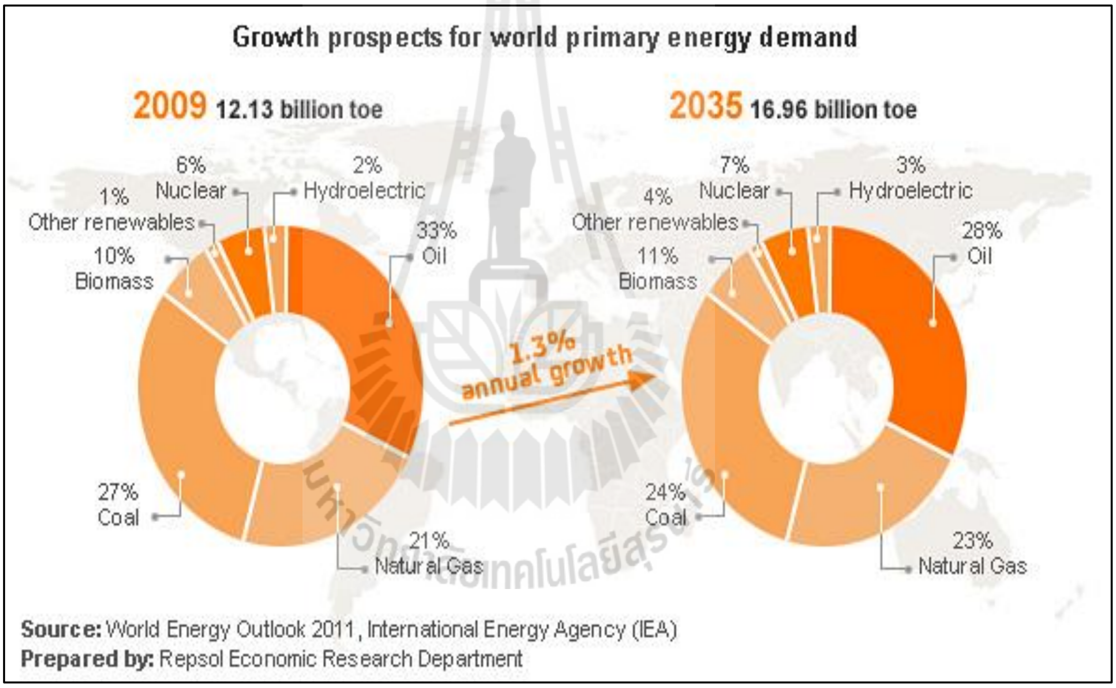


Figure 2.1 Growth Prospects for World Energy Demand (after World energy Outlook, 2011)

A finite resource, fossil fuel, is not a sustain energy supply and produce CO_2 which is cause greenhouse gas emissions. To minimize the emission of greenhouse and find a new source of sustain energy supply is called biofuel. Biofuel or biomass resources now can be an alternative energy which gives (i) produced from renewable resources, (ii) does not add any greenhouse gases in the atmosphere, (iii) produced locally without any dependency on foreign oil or natural gas supplies, (iv) to reducing the pollution produced by organic wastes, and (v) slow down wastes management problems (R. Chandra et al., 2012). The biomass in general use such as synthesis of chemicals and pharmaceuticals, production of animal feeds or food, fuels and construction materials. The energy utilization can be derivative from various processes such as anaerobic digestion, ethanol fermentation gasification or combustion as depicted in Figure 2.2 and Figure 2.3 below (Omolola, 2007).

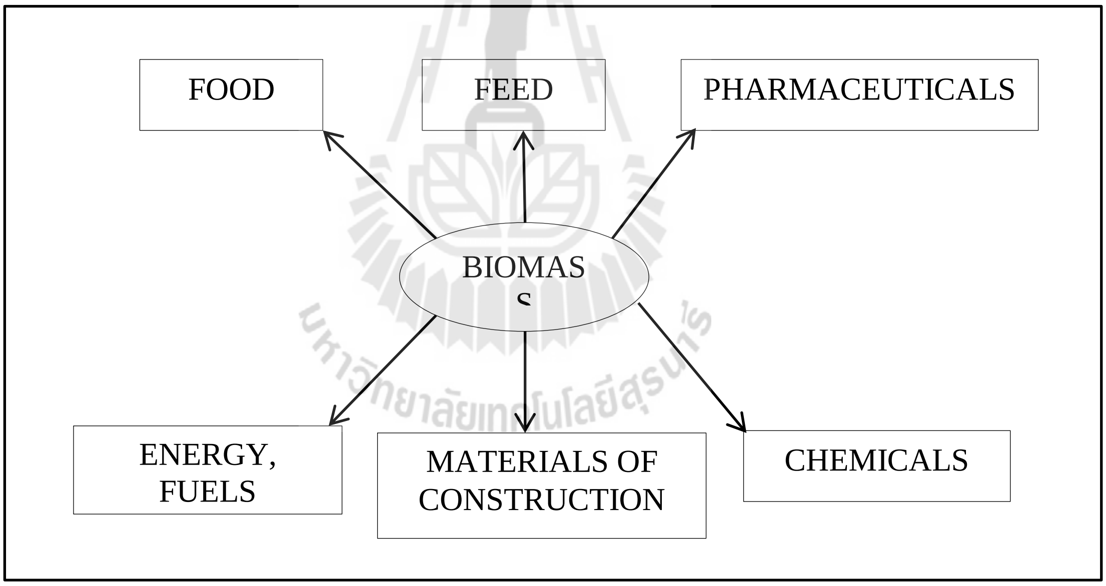


Figure 2.2 Biomass utilization (after Omolola, 2007)

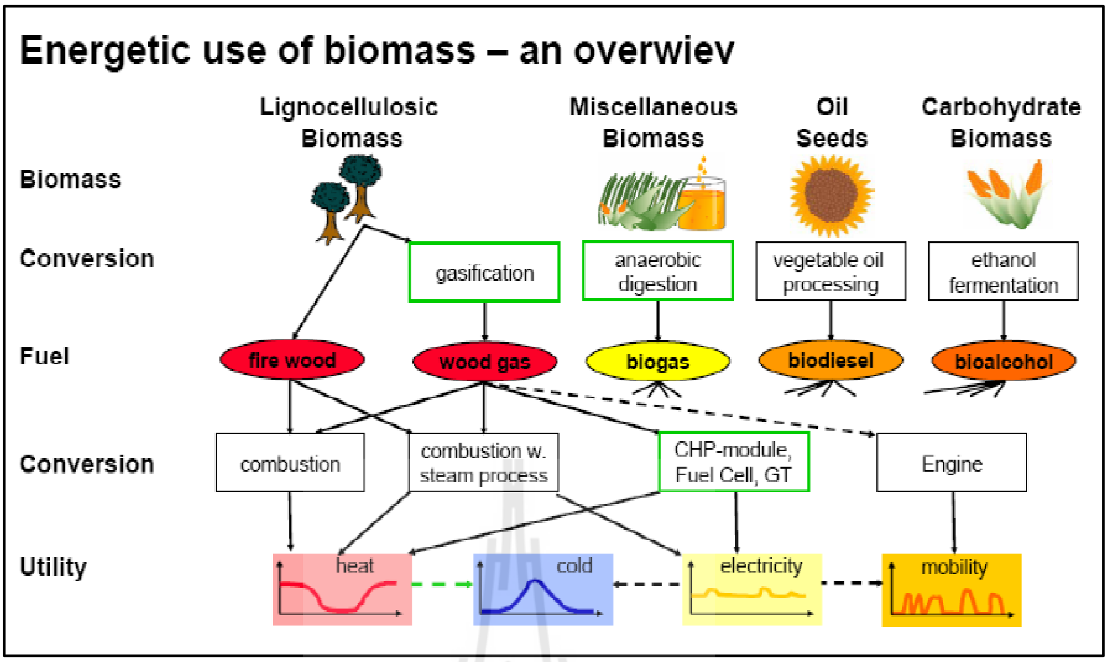


Figure 2.3 Biomass and energy used (after Omolola, 2007)

2.2 Biomass resource and biomass from agriculture

Biomass or biofuels are derivatives of food crops, agricultural residues, waste from municipalities, animal wastes, wood and wood wastes, and aquatic plants and algae. These original sources are considered as a new source of energy due to infinite fuels. The source of biogas has been widely used to treat the wastes and produces biogas by-product (Omolola, 2007 and R. Chandra et al., 2012). Most of biogas source is from agricultural.

The largest agricultural is from energy crop such as crops straw, rice husk, bagasse, maize cobs, coconut husk, nutshells and saw dust as showed in Table 2.1. All of these residue has been dumping many million tons in annual. Top four major agricultural crops grown in global are maize, wheat, rice and sugarcane, respectively, in term of total cultivated area and production. The residue from agriculture process could be the starter of biogas production for fuels or chemicals. This obviously decrease overall global warming and new way for alternative fuel.

Table 2.1 Category of biomass resources (after R. Chandra et al., 2012)

SI. No.	Feedstock type	Definitions	Resources
1	Sugars/starches	Traditional agricultural crops suitable for fermentation using first generation technologies, some food processing residues are sugar and starch materials	Agricultural crops (sugars/starches), food processing residues containing residual sugars
2	Lignocellulosic biomass	Clean woody and herbaceous materials from a variety of source includes clean urban biomass that is generally collected separately from the municipal waste stream (wood from the urban forest, yard waste, used pallets)	Agricultural residues, cellulosic energy crops, food processing residues, forest residues, mill residues, urban wood wastes, yard wastes
3	Bio-oils	Traditional edible and non-edible oil crops and waste oils suitable for conversion to bio-diesel	Agricultural and forestry oil bearing crops and trees, waste oils/fats/grease

Table 2.1 Category of biomass resources cont. (after R. Chandra et al., 2012)

SI. No.	Feedstock type	Definitions	Resources
4	Solid wastes	Primarily lignocellulosic biomass, but that maybe contaminates (e.g., construction and demolition woods) or co-mingled with other biomass types	Municipal solid waste, construction and demolition wood, food wastes, non-recycled paper, recycled materials
5	Other wastes	Other biomass wastes that are generally separate from the solid waste stream which include biogas and landfill gas	Animal waste, waste from wastewater treatment Biogas and landfill gas

2.3 The biomethanation operation

According to the work of M.H. Gerardi, 2003 and R. Chandra et al., 2012, it is found that the biomethanation or methane fermentation or anaerobic digestion is a complex process which combined four steps of biomass and digestion; hydrolysis, acidogenic, acetogenic and methanogenic. All four steps are described as follows:

2.3.1 The hydrolysis

Complex organic matter like carbohydrates, proteins and fats are cracked down into smaller molecule or monomer of facultative and obligatorily anaerobic bacteria. The hydrolysis of carbohydrates takes place within few hours, while hydrolysis of proteins and lipids may take few days. The facultative anaerobic micro-organisms take the oxygen dissolved in the water and thus cause the low redox potential necessary for obligatorily anaerobic micro-organisms. The carbohydrates turn into simple sugar, while lipids turns into fatty acids and protein turns into amino acids.

2.3.2 The acidogenic

The monomers from the hydrolysis step are converted into short chain organic acids, C_1-C_5 molecules (e.g. butyric acid, propionic acid, acetate, and acetic acid), hydrogen, carbon dioxide and alcohols.

2.3.3 The acetogenic

The products from previous phase serve as substrate for other bacteria, in the third place. In this phase, homoacetogenic micro-organisms constantly reduce exergonic H_2 and CO_2 to acetic acid. Acetogenic bacteria grow in a symbiotic relationship with methane-forming bacteria. During acetogenic phase, organic acids and alcohols are converted into acetate. Acetate serves as a substrate for methane-forming bacteria.

2.3.4 The methanogenic

The methane fermentation in this stage takes place under strict anaerobic condition. This reaction is categorically exergonic. As follows from the description of the methanogenic micro-organisms, not all methanogenic species demote all substrates. One can divide substrates acceptable for methanogenesis into the following three groups (R. Chandra et al., 2012);

(I) Acetoclastic methanogenesis

$$\text{Acetate} \rightarrow CH_4 + CO_2 \qquad (2.1)$$

(II) Hydogenotrophic methanogenesis

$$4H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O \qquad (2.2)$$

(III) Methyltrophic methanogenesis

$$\text{Methanol} \rightarrow CH_4 + CO_2 \qquad (2.3)$$

Two biochemical components that seems unique to methanogens, is that they have mechanism of hydrogen oxidation and carbon dioxide reduction. Methanogenic bacteria utilize H_2 with CO_2, formate, methanol, and acetate as substrates for methanogenesis. The methanogenic bacteria use carbon dioxide as the terminal electron acceptor and produces methane. The optimal environment requirements are showed in Table 2.2 in different stages of biomethanation process (R. Chandra et al., 2012). The biomethanation process can be summarized as showed in Figure 2.4.

Table 2.2 The optimal environment requirements (after R. Chandra et al., 2012)

Parameter	Hydrolysis/Acidogenesis	Methane formation
Temperature	25-35°C	Mesophilic:32-42°C Thermophilic:50-58°C
pH value	5.2-6.3	6.7-7.5
C:N ratio	10:1-45:1	20:1-30:1
DM content	<40% DM	<30% DM
Redox potential	+400 to -300 mV	<-250 mV

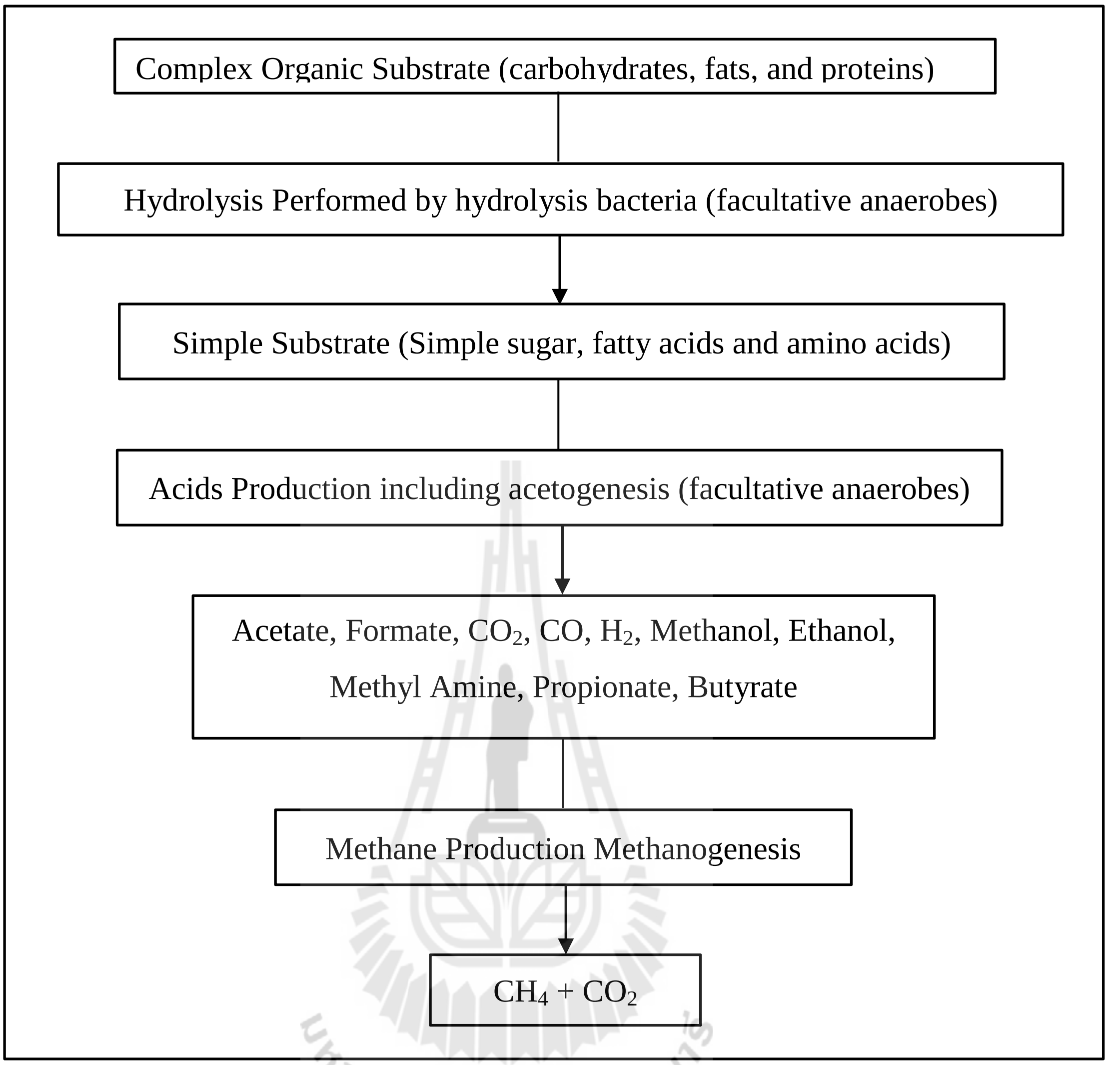


Figure 2.4 Biomethanation process (after R. Chandra et al., 2012)

2.4 The basic parameter requirements

There are some basic factors which should be knew before starting anaerobic digestion and converted to efficiency gas product including:

2.4.1 Hydraulic Retention time

The retention time is possibly the most important functional condition influences volatile solids to gaseous products. To avoid the terminate gas production, hydraulic retention time must be at least 10-15 days in reactor. Moreover, retention time was considered as to reduce the biogas capital cost according to R. Chandra et al., 2012 and M.H. Gerardi., 2003.

2.4.2 Process temperature

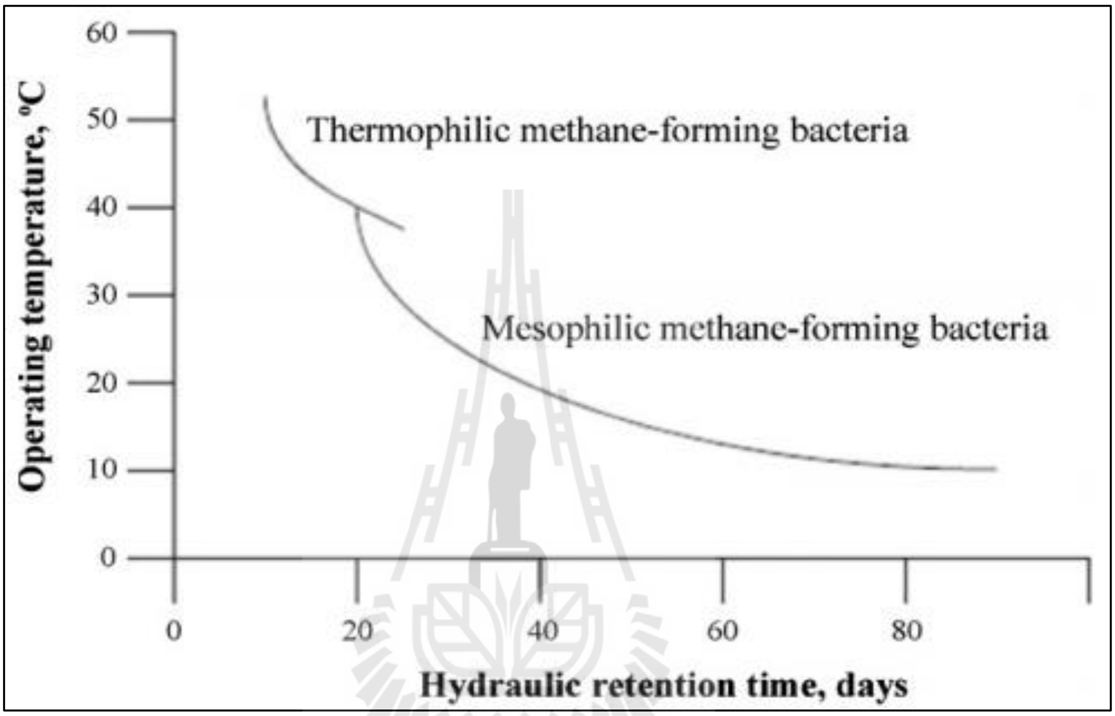


Figure 2.5 Operating temperature of methanogenic bacteria in relation to digestion time (after R. Chandra et al., 2012)

K.M. Mital (1996) indicates that there are three temperature range that suitable to convert organic substrate to methane; psychrophilic, mesophilic and thermophilic, respectively as in Figure 2.5. The psychrophilic produces methane when the temperature is up to 20 °C, gives very low amount of biogas as a result. The mesophilic, 20–45 °C, biogas has been produced maximum rate when the temperature maintain 35 °C. Above 50 °C is called thermophilic which gives a short degradation, high gas production rate but difficult to control. In addition, for tropical zone, the thermophilic increases the capital cost (R. Chandra et al., 2012).

2.4.3 pH value

There are two groups of bacteria occurs during the biomethanation with difference pH value preference. The acid-forming bacteria occurs when pH value is above 5.0. On the other hand, the methane-forming bacteria preferred pH value above 6.2. Most anaerobic bacteria performs well in pH range of 6.8-7.2. The methane-forming bacteria starts to digests the volatile acid after the hydraulic retention times is more than 5 days (R. Chandra et al., 2012). In pH range of 6.8-7.2 in process operation, volatile acids are converted to methane and carbon dioxide which effects essentially to the carbon oxide percentage in biogas (M.H. Gerardi., 2003). The decreasing of pH value effects directly to the increasing of percentage of carbon dioxide in anaerobic digestion because the incomplete of methane-forming bacteria process (Ruth et al., 1997). The pH range of 6.7-7.5 is the optimum for microbial to produces methane in methane-forming stage (R. Chandra et al., 2012).

2.4.4 Substrate composition and consistency of feed material

All types of biomass which can be degraded can be used as a substrate for biomethanation process. There is some preferred biomass for production process that composed of carbohydrate, proteins, fats as main components (K.M. Mital, 1996). Mostly anaerobic production has been using the waste products to produce the material for biomethanation due to the low cost, easy to find and friendly with the environment. Water is also used as one of substrate and could be about 90% of total volume. Too much water trends to reduce gas production rate. On the contrary, too low water, the accumulation of acetic acid is occurred which inhibit anaerobic digestion and the thick scum formed on the surface as a result (Mazumdar, 1982).

2.4.5 Organic loading rate

The amount of volatile solids (VS) and the chemical oxygen demand (COD) has been defined as organic loading rate, feed per day per unit digester volume which is proper to the retention time to crack down the organic materials and convert to gas then (Keri et al., 2008). The most ideal of total solids (TS) has been found at 13.0%-15.0% as feedstock for fresh diary manure (Hill and Mehlschau, 1984).

2.4.6 C/N ratio

Carbon to nitrogen ratio is the metabolism of the micro-organism to produce methane. If the carbon to nitrogen is too high, lacking of nitrogen, the micro-organism will rapidly consume the nitrogen to meet their protein and no longer to react with the leftover of carbon component hence low gas production. In contrast, carbon to nitrogen is too low, the excess of ammonium ion will happened. If pH value is over 8.5, toxic to population of methanogens. The optimum of C/N ratio for anaerobic process is 20-30 (K.M. Mital, 1996 and Anonymous, 1977). The C/N ratio of some common organic wastes is presented in Table 2.3.

Table 2.3 C/N ratio of some organic wastes (after Deublein, 2008)

Waste	**DM content, %**	**Organic substance % of DM**	**C/N**
Straw	70	90	90
Waste from saw mill	20-80	95	511
Paper	85-95	75	173
Waste from household	40-60	40	18
Sewage sludge	0.5-5	60	6

However, the anaerobic digestion is dependent on various parameters. So many parameters must be considered and controlled to an optimum process (R. Chandra et al., 2012).

2.5 Biogas

Methane production can be affected by system pH, temperature, and the presence of a number of potentially toxic materials such as salts, heavy metals and ammonia (Figure 2.6). The optimum pH for anaerobic digestion is between 6.8 and 7.5.

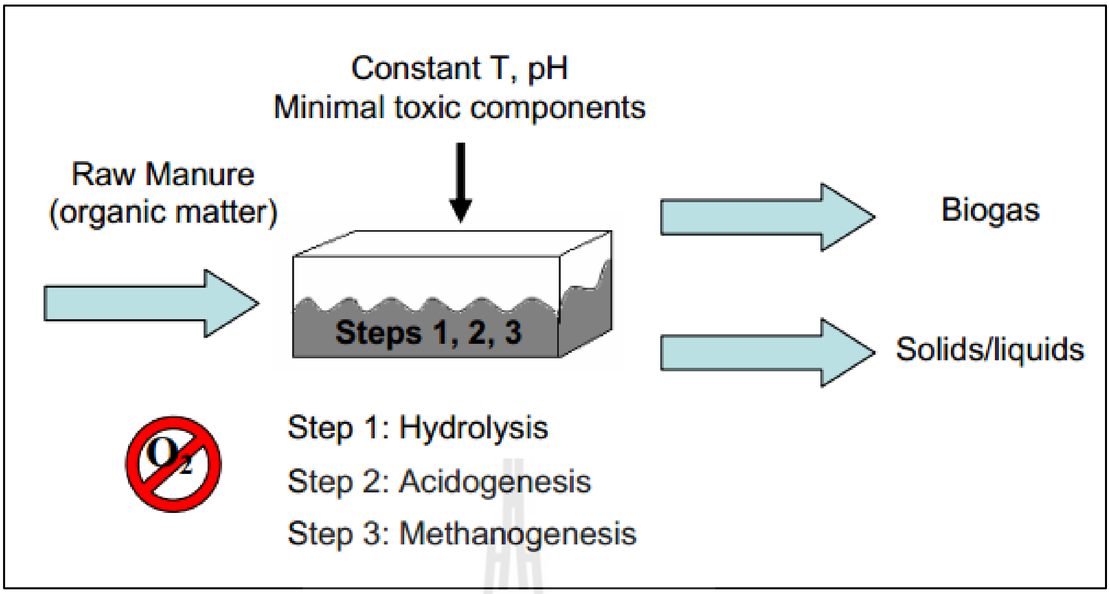


Figure 2.6 Microbial process of anaerobic digestion (after Bothi, 2007)

An increase in acidity can be happened when acetogenic bacteria grow rapidly at times of high organic matter loading. This can be controlled by simply buffering the system with an alkali at the time during start-up or high-loading periods. Temperature is also an impact on microbial productivity. For the optimum biogas production and increased methane content, loading rates and each of these factors must be controlled. The biogas can be processed and utilized in a more efficient, cost-effective way as shown in Table 2.4. Biogas contains primarily CH_4 with the balance being mostly CO_2 and a small amount of trace components. Biogas has around two-thirds the energy potential of refined natural gas due to the significant amount of CO_2 and lower CH_4 content, lowering the energy value relative to that of natural gas (Bothi, 2007).

Table 2.4 Biogas Composition (after N. Sorkratok, 2013)

Composition	**%**
Methane	50-75
CO_2	25-45
H_2	<1
H_2S	<1

Even though biogas consists mainly of methane and carbon dioxide, it has specific properties which are listed in Table 2.5. Biogas with methane content higher than 45% is flammable (Audra and Vincensia, 2010)

Table 2.5 General Features of Biogas (after Audra and Vincensia, 2010)

Properties	**General Features**
Energy content	6.0-6.5 kWh/m^3
Fuel equivalent	0.60-0.65 L oil/m^3 biogas
Critical pressure	75-89 bar
Critical temperature	-82.5°C
Normal density	1.2 kg/m^3
Smell	Bad eggs (the smell of desulfurized biogas is hardly noticeable)
Molar Mass	16.043 kg/kmol

2.6 Biogas utilization

Biogas is generated from organic wastes under anaerobic digestion by mixed population of microorganisms. The organic wastes including domestic, industry and agriculture wastes can produce methane which is a valuable fuel. Methane is more attractive which is a valuable fuel can be called alternative energy (W, Anunputtikul, 2004). There are various of the usage of methane gas from anaerobic digestion such as W. Haiyan et al. (2012) studied the effect of biogas production by anaerobic fermentation with single component waste via fat powder, cellulose powder and protein powder. All assays were run in a constant temperature bath. The highest cumulative methane production is cellulose powder around 25 mL/g.

Biogas can be used in many ways; either raw or upgraded. As a minimum, biogas has to be cooled, drained and dried immediately after production. It has to be cleaned for the hydrogen sulphide (H_2S) which is below 100 ppm. There are various biogas utilization as listed below (J.B. Holm-Nielsen et al., 2009).

1. Production of heat and/or steam (the lowest value chain utilization).
2. Electricity production with combined heat and power production (CHP).
3. Industrial energy source for heat, steam and/or electricity and cooling.
4. Upgraded and utilization as vehicle fuel.
5. Production of chemicals and/or proteins.
6. Upgrading and injection in the natural gas grids.
7. Fuel for fuel cells.

2.7 Previous works

Some of previous works and literature reviews for this study can be listed as follows:

R. Singh et al. (2010) completed a biogas operation in batch reactor in laboratory scale by using a difference mixed inoculums to determine the best ability on the respect of methane production and methane content in different mixed inoculums from various source. Cow dung slurry was used as substrate. The average yield of methane was obtained in range 0.245-0.323 $Lg^{-1}VS$ in 41 days of digestion. The maximum methane content in biogas is 68% during day 27-30.

Y. Zhou et al. (2011) observed a higher production rate of methane and shorten the start-up time by using high total solid without dilution with water under mesophilic (36 °C) and anaerobic conditions. The characteristics of substrates, the proportions are also greatly influence the rate of anaerobic digestion. Methane production at different substrate-to-inoculum (S/I) ratios can provide important information about how to initialize a new batch digester. The maximum methane yields was S/I ratios between 0.6 and 0.9, produced methane yield about 478 - 495 mL CH_4gVS^{-1} in 19 days.

P. Gupta and A. Gupta (2014) investigated anaerobic fermentation with mixed inoculums from cow dung, paddy field soil, termites and mine waters. The different parameters solid-liquid ratio1:20-1:10, pH, temperature and particle size were optimized for maximum production rate of methane. The maximum methane produced was 479.3 cc/100 g with percentage (92.6%) in biogas.

The Defining the Biochemical Methane Potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays was carried out by

I .Angelidaki et al. (2009). Anaerobic digestion was observed for several years to provide important experimentation guidelines and advices for the reliable and reproducible assessment of the anaerobic biodegradability of any compound or undefined material to methane and carbon dioxide, with particular emphasis for solid organic substrates such as biowaste, energy crops, agro waste, manure, sludge and other substrates. To measure the biogas production from methane potential test, Esposito et al. (2012) was created the device by using the water displacement.

F. Raposo et al. (2006) determined the inoculum to substrate ratio as one of the most important factor to influence the result of biochemical methane potential test. The inoculum to substrate ratio was varied of 3, 2, 1.5 and 1. The overall temperature was controlled at 35˚C for 30 days. The working volume in each reactor was 5 L and stirred at 40 rpm. The concentrations of inoculum and substrate for the inoculum to substrate ratio 3, 2, 1.5 and 1 were: 15 and 5 g VS l^{-1}, 15 and 7.5 g VS l^{-1}, 15 and 10 g VS l^{-1}, 15 and 15 g VS l^{-1}, respectively. The maximum values of specific methane production rate for the ratios of 3, 2, 1.5 and 1 were 10, 14, 16 and 23 ml CH_4 (STP) g VSS day^{-1}, respectively.

G. Liu et al. (2009) determined the effect of feed to inoculum ratio using anaerobic of food and green wastes at mesophilic and thermophilic temperature. At thermophilic digestion test were performed at feed to inoculum ratios of 1.6, 3.1, 4.0 and 5.0. The duration of anaerobic test was controlled 25 days. The biogas production was obtained during the first 10 days of digestion. The results showed that the thermophilic produced biogas more than mesophilic and the maximum methane production from feed to inoculum ratio was 1.6 in food wastes, green waste and the mixture. The biogas yield at ratio 1.6 of food wastes, green waste and the mixture was 778 mL/g VS, 631 mL/g VS, 716 mL/g VS, respectively.

G.K. Kafle et al. (2014) investigated effect of feed to microbe ratios on anaerobic digestion of Chinese cabbage waste between mesophilic and thermophilic conditions. The feed to microbe (F/M) ratios was 0.5, 1.0 and 2.0 in batch test for 96 days. The maximum production from both mesophilic and thermophilic conditions was 2.0 at 677 mL/g VS and 639 mL/g VS, respectively. In this study, the mesophilic condition can produced biogas more than thermophilic condition.

Since Thailand has million tons of shrimp farming waste that could be used as a main substrate for biogas production. This study aims to evaluate the potential of this waste plus some agricultural wastes e.g. rice straw for biogas production under anaerobic digestion by BMP method and to analyze the physical and chemical properties of this produced biogas. Moreover, the quantity of the produced gas is also considered in term of economics return if it would be produced in an industrial scale.

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

3.1.1 Substrate

Raw shrimp farming wastes which were used as the main substrate for biogas production in this study were originated and collected from Chachengsao province, Thailand (Figure 3.1). Biochemical methane potential assays were set-up within 2 days of sampling.

Figure 3.1 Selected Shrimp farm at Bangkla district and samples collecting

A course-cut folder rice straw has been used as co-substrate. This was delicately cut and dried at 105°C before being ground until it passed a 2 mm sieve and stored in room temperature in zip locked bag until it was used for biogas production (Figure 3.2).

Figure 3.2 Rice straw samples

Another co-substrate was used in this study, food waste. It was collected from canteen in Suranaree University of Technology, Nakhon Ratchasima province, Thailand. The non-biodegradable contaminants in the food wastes, such as the bone, plastic bags, egg shell, and tissue paper, were removed by hand, after which the food wastes was crushed using an electrical kitchen blender and stored at 4˚C until it was used for biogas production (Q. Wei et al., 2014).

3.1.2 Inoculum

Inoculum was obtained from the effluent of the open-anaerobic pond of cassava starch production factory, Sanguan Wongse Industries Co., Ltd. in Nakhon Ratchasima province, Thailand, kept at 4°C within 24 hour before they were used.

Figure 3.3 Inoculum

3.2 Study methodology

According to the study of W. Anunttikul, (2004)**,** moisture, total solids (TS), ash, volatile solids (VS), total carbon, and total nitrogen contents of the samples had been determined as follows:

3.2.1 Moisture and total solids (TS) contents

Moisture and TS contents of this study were evaluated using standard method of Association of Official Analytical Chemists (1990). The empty porcelain dishes in duplicate were dried at 105°C for 1 hour or until weight becomes constant. The empty porcelain dishes were allowed to cool to room temperature in desiccator. Then, the empty porcelain dishes were weighed and recorded in the unit of g. About 10 g of raw materials were placed in each porcelain dish. The porcelain dishes were weighed again and recorded. The dishes containing samples were heated in hot air oven at 105°C for 1 hour, then weighed until the constant weight was obtained. The different in weight of the material after drying was the moisture content of the raw materials and the weight of dry material was TS and total solid (TS) which were calculated by using equation 3.1 and 3.2 respectively.

$$\text{Moisture content (\%)} = \frac{(A-B) \times 100}{\text{Sample weight (g)}} \qquad (3.1)$$

$$\text{Total solids (\%)} = 100 - \text{moisture content (\%)} \qquad (3.2)$$

Where: A = Sample weight before heating and porcelain dish weight (g)

B = Sample weight after heating and porcelain dish weight (g)

C = Initial sample weight (g)

3.2.2 Ash and volatile solids (VS)

Ash and VS of sample of this study were determined by standard methods of Association of Official Analytical Chemists (1990). Ten grams of dried samples were placed in porcelain dishes in duplicate, weighted, and heated in muffle furnace at 550°C for 30 min. The organic solids burnt off on ignition were VS (or organic matter) which the residue contributed to the ash content. Ash and volatile solids (VS) were then determined by using following equation 3.3 and 3.4.

$$\text{Ash (\%)} = \frac{\text{Sample weight after burnt + porcelain dish x 100}}{\text{Sample weight}} \qquad (3.3)$$

$$\text{Volatile solids (\%)} = 100 - \text{ash (\%)} \qquad (3.4)$$

Where: A = Sample weight after burning and porcelain dish weight (g)

B = Sample weight before burning

3.2.3 Total carbon and total nitrogen contents

Total carbon and total nitrogen contents were obtained using CHN-628 Element Analyzer (Leco Corporation, U.S.A.). Dry sample (0.2 g) were put into ceramic boats, and loaded into the CHN-628 Element Analyzer, where they were combusted with the pure oxygen of the furnace. Combustion gases were collected in 4.5 L ballast after being pulled through anhydrone to scrub out water. Individual Infrared (IR) cell detected carbon and a thermal conductivity cell detected nitrogen. Results of the analysis were reported as % of C and % of N using computer software. A summary of the characteristics of substrate used in the experiments is given in Table 3.1.

Table 3.1 Characteristics of the substrates used

Parameter	Shrimp farming wastes (SW)	Rice straw (MW)	Food wastes (FW)	Inoculum
TS (g VS/l)	234	887	330	33.51
VS (gVS/l)	27	671	312	19.756
VS/TS (%)	11.53	76	94.5	59
pH	7.5	6.7	5.1	6.77
C/N ratio	8	57.8	15	-

3.3 Experimental set-up

The BMP was conducted according to F. Raposo et al., 2006. A total of 20 batch bottles including duplicates and controls were run in a room temperature (28±3°C). Serum bottles (300 mL) with butyl rubber stoppers were used as batch digesters. Each bottle was partially fulfilled with inoculum and substrate, according to their VS content in table 3.2; tap water was added up to a 250 mL of working volume.

Table 3.2 Experimental design for the tests

I/F* Ratio (g VS/L)	Substrate loading (g)				No. of replications
	Shrimp wastes only (SW)	Shrimp wastes (SW) and Rice straw (MW)	Shrimp wastes (SW) and Food wastes (FW)	Inoculum loading (g)	
15:15	139	70:2.8	70:6	190	2
15:7.5	70	35:1.4	35:3	190	2
15:5	46.3	23.2:0.93	23.2:2	190	2

I/F* ratio: Inoculum to Feed ratio (g VS substrate added/g VS inoculums added).

The inoculum to substrate mixtures were supplemented with 20% (v/v) of a medium containing macro- and micro- elements (F. Raposo et al., 2006). The composition of this nutrient and trace element solution was as follows:

-Stock nutrient solution: NH_4Cl, 1.4 g/l; K_2HPO_4, 1.25 g/l; $MgSO_4 \cdot H_2O$, 0.5 g/l; $CaCl_2 \cdot 2H_2O$, 0.05 g/l; yeast extract, 0.5 g/l; trace element solution, 5 ml/l.

- Trace element solution: $FeCl_2 \cdot 4H_2O$, 2000 mg/l; H_3BO_3, 50 mg/l; $ZnCl_2$, 50 mg/l; $CuCl_2 \cdot 2H_2O$, 38 mg/l; $MnCl_2 \cdot 4H_2O$, 500 mg/l, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 50 mg/l; $AlCl_3 \cdot 6H_2O$, 90 mg/l; $CoCl_2 \cdot 6H_2O$, 2000 mg/l.

Each bottle was connected by a capillary tube to an inverted 1000 ml plastic bottle containing an alkaline solution (2% NaOH) which to removed CO_2, NH_3 and H_2O produced. To enable gas transfer through the two connected bottles, the capillary tube was equipped on both ends with a needle, sharp enough to pierce the silicone disc (G. Esposito et al., 2012). The methane produced displaced a measurable volume of NaOH solution from the gas-collecting in bottle, which equivalent to the methane volume. So the volume of methane from each digester could be determined by a measuring cylinder (Y. Lin et al., 2013). All digesters were flushed with N_2 for 3 minutes to remove oxygen from the headspace and maintained anaerobic condition. All digesters were shook by hand one minute per day to assure the sufficient mixing of substrate.

All digesters were conducted under the room temperature 28±3°C which in the mesophilic condition for 30 days. The experiment was carried out in duplicate. The total biogas production was measured daily by water displacement technique. The pH was measured daily without pH adjustment. The equipment components to measure the total biogas were fabricated as depicted in Figure 3.4.

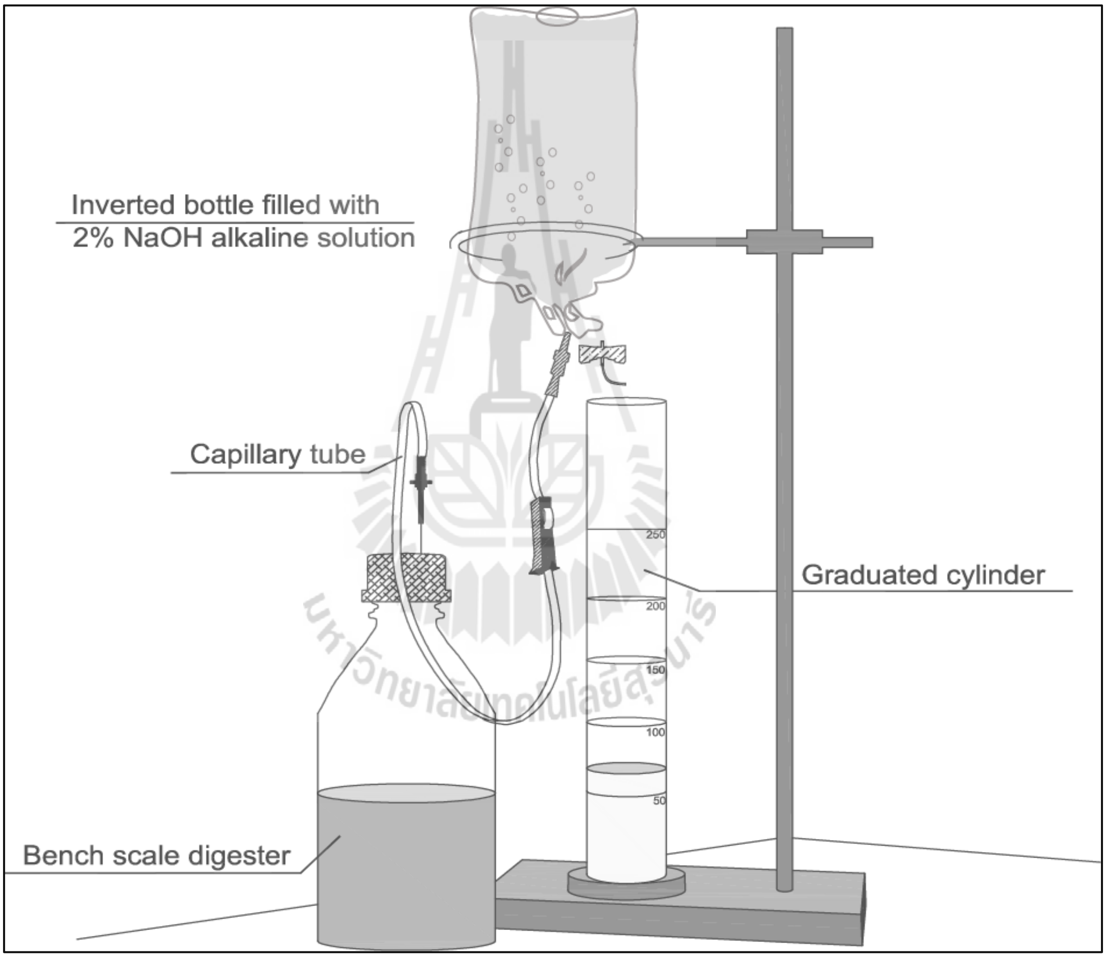


Figure 3.4 Experimental equipment used to measure the daily biogas (ml)

(modified after G. Esposito et al., 2012)

3.4 Analytical methods and calculation

The parameters during the biogas production from shrimp farming wastes were monitored as follows:

3.4.1 Biogas yield and gas composition analysis

Biogas production was measured daily from the water displacement technique. The total biogas yields were calculated from the total biogas production of the digester divided by the total amount of TS initially. Biogas composition was analyzed by using gas analyzer (Gas Chromatography, 7890A, Agilent Technology, USA) equipped with a thermal conductivity detector (TCD) and the packed column (Shincarbon Restek 19808). Helium was used as a carrier gas at flow rate of 20 mL/min. The oven, injection inlet and detector temperature were 100, 200, 250°C, respectively. Gas sample (0.1 mL) was taken from head space of the gas collector through the gas-sampling port with syringe. The syringe was redrawn and the sample was injected directly into a gas analyzer where the mass of methane, carbon dioxide and other traces gas was detected by comparing to the standard gas mixture of methane and nitrogen.

3.4.2 Total solids (TS) and volatile solids (VS) contents

Total solids and volatile solids contents of shrimp wastes slurry before and after fermentation were calculated using standard methods (American Public Health Association, 2005). The procedure was described in section 3.2.1 and 3.2.2.

3.4.3 pH

The measurement of pH value was performed and recorded daily using a Mettler Toledo Thornton M 300 (Mettler-Toledo LTD, England).

3.4.4 Temperature

Samples were measured and recorded daily by thermometer.

3.4.5 Volume of produced methane

The volume produced of methane was recorded by water displacement equipment and calculated as follows:

The Volatile Solid removed

$$VS_{in}\ (mg/l) - VS_{out}\ (mg/l) = VS_{removed}\ (mg/l) \qquad (3.5)$$

The Removal Efficiency

$$\text{VS removal Efficiency}\ (\%) = \frac{VS_{in}\ (mg/l)\ -\ VS_{out}\ (mg/l)}{VS_{in}\ (mg/l)}\ x100 \qquad (3.6)$$

Specific Methane Yield

$$\text{Methane yield}\left(\frac{l\,CH_4}{g\,VS_{removal}}\right) = \frac{\text{Cummulative methane (l)}}{TVS_{input}\ -\ TVS_{output}}\ x(\%\ CH_4) \qquad (3.7)$$

% Biochemical Methane Potential, BMP

$$BMP(\%) = \frac{\text{Methane production rate}}{\text{Methane production in theory}}\ x100 \qquad (3.8)$$

Where VS_{in} = Input Volatile Solids (mg/L)

VS_{out} = Output Volatile Solids (mg/L)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Physical and chemical composition of the fermented materials

4.1.1 The shrimp farming waste

Shrimp farming waste was collected from Bangkla sub-district of Chachengsao province, Thailand. The dry shrimp wastes material contained average 7.5 of pH, 234 g/L of TS, 27 g/L of VS, VS/TS = 11.53%. The average carbon-to-nitrogen was 8, which was very low ration compared to the optimum 20-30:1 for the maximum biogas production suggested by R. Chandra et al., 2012 and N. Saokratok., 2013. The very low ratio of carbon-to-nitrogen can be caused inhibition of methane production. Therefore, it needs some additives or co-substrate for better biogas production.

4.1.2 Rice straw

For this study, the rice straw was assembled from Suranaree University of Technology farm. The dry rice straw was used as co-substrate in anaerobic digestion which composed of average 6.7-7.0 of pH, 887 g/L of TS, 671 g/L of VS, VS/TS was 75.64%, and average carbon-to-nitrogen ratio 57.8. The carbon-to-nitrogen ratio is very high according to average of carbon-to-nitrogen ratio compared to the maximum biogas generation, 20-30:1 which was suggested by R. Chandra et al., 2012. If the carbon-to-nitrogen ratio is too high, gas production could be low due to rapidly consume the nitrogen for meeting their protein and left over carbon of the material referred to R. Chandra et al., 2012.

4.1.3 Food waste

The food waste was used as another co-substrate for comparing to rice straw. It contains 15 of carbon-to-nitrogen ratio, 330 of TS, 312 g/L of VS and 94.5 % of VS/TS. The ratio of carbon-to-nitrogen is lower than the optimum biogas production which is 20-30: 1 due to R. Chandra et al., 2012.

4.1.4 Inoculum

In this assay, the inoculum was used for start-up of the laboratory-scale reactor. The inoculum constitutes 6.77 of pH, 231 g/L of TS, 211 g/L of VS and 91.33 g/L of VS/TS.

From this study, the carbon-to-nitrogen ratios of shrimp farming and food wastes are lower than the optimum ratios of 20-30:1 for maximum biogas production suggested by R. Chandra et al., 2012 except the dry rice straw sample. Therefore, the mixing of substrate and co-substrate was needed for optimizing carbon to nitrogen ratio for biogas production. In this experiment, the nutrients and trace element were supplemented and no adjust of pH all duration time.

4.2 Determination of biogas production

The shrimp farming waste was used as the main substrate for biogas production which was determined in BMP analysis according to the protocol described by F. Raposo et al., 2006. The BMP assay was run in order to analyze the methane potential of shrimp farming waste. The samples were analyzed duplicate with mean values and recorded. The amount of biogas and methane produced was directly measured on the gas chromatography as depicted in Figure 4.1 to Figure 4.6.

4.2.1 pH value

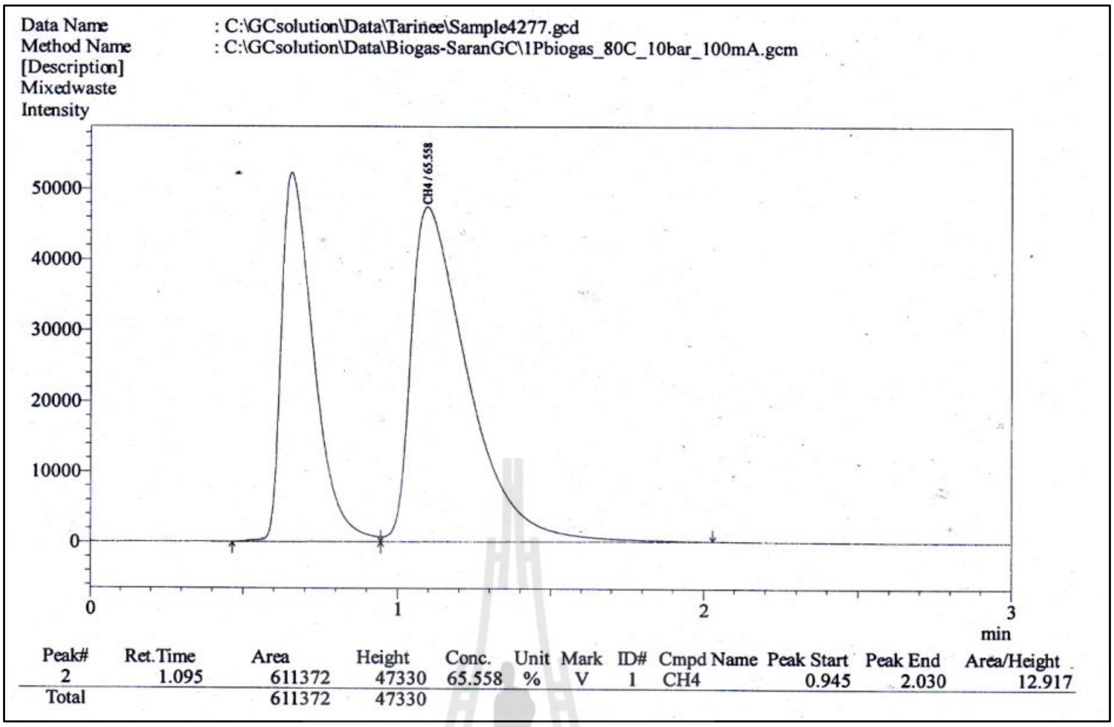
The optimum pH of anaerobic digestion for activated microorganism or inoculum is 6.6-7.6 according to R. Chandra et al., 2012. The sample pH in this study was maintained nearly neutral pH (7) for optimum operation and unadjusted pH after anaerobic digestion started for 30 days of operation time. During 10 days of operation time, the acid-forming bacteria proceeded quickly to digest the organic materials and the pH was increased after 10 days for the methanogenic bacteria population. The methanogenic bacteria population might not be adequate to consume the acids produced and maintained a neutral pH resulting declining pH below the neutral pH due to W. Anunputtikul., 2004. After 30 days of operation time, some ratio still maintained nearly neutral, some ratio was inclined to high pH which was not adequate for methane microorganism to produce biogas (Table 4.1 to Table 4.6).

4.2.2 Temperature

For this study, the temperature was in room temperature, maintained around 28±3°C which was under mesophilic condition.

4.2.3 Gas Chromatography

A gas standard consisting of 65% (v/v) of methane gas (CH4) and 35% of nitrogen (N2) was used for GC calibration. Biogas composition of each digester was measured in duplicate. The measured wet biogas and methane volumes were adjusted to the volumes at standard temperature (0 ˚C) and pressure (1 atm). According to Figure 4.1 - 4.6 were showed the chromatograms of standard gas and biogas in this study which was analyzed by the gas analyzer (Agilent Technology, USA) equipped with a Thermal Conductivity Detector (TCD).



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name	Peak Start	Peak End	Area/Height
2	1.095	611372	47330	65.558	%	V	1	CH4	0.945	2.030	12.917
Total		611372	47330								

Figure 4.1 Chromatogram and report of standard methane and standard nitrogen analyzed by the gas analyzer

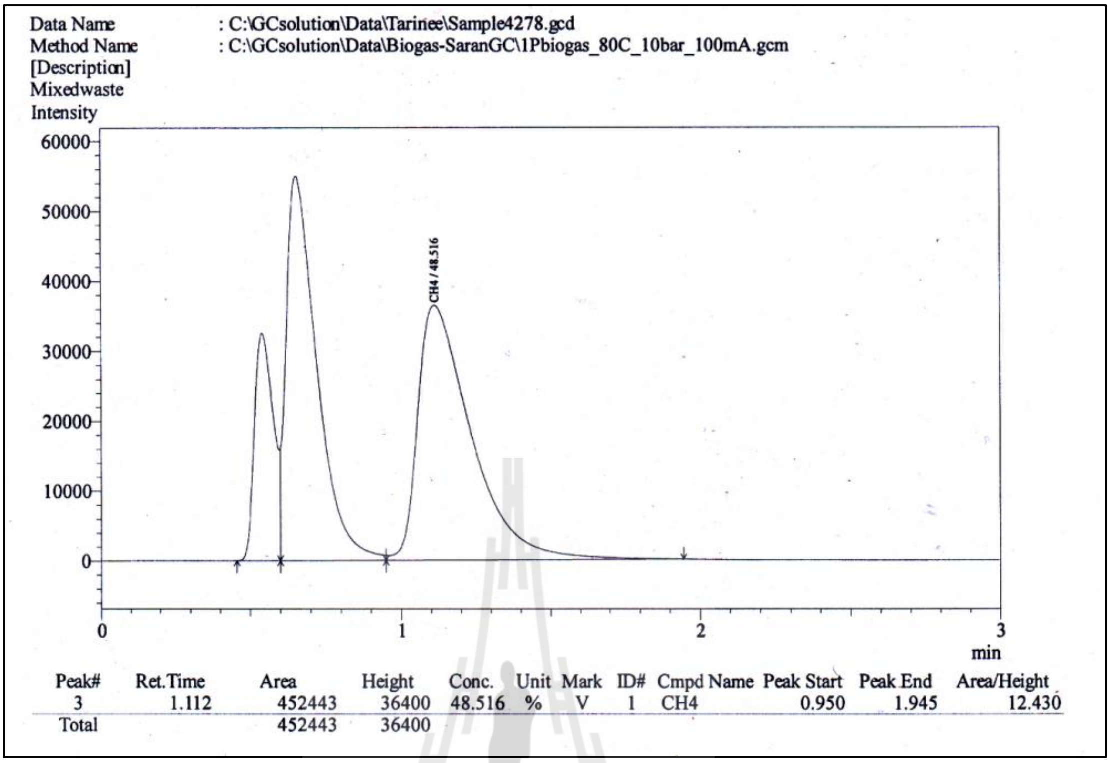


Figure 4.2 Chromatogram and report of methane and nitrogen analyzed by the gas analyzer at inoculum to feed ratio of 15W:15MS

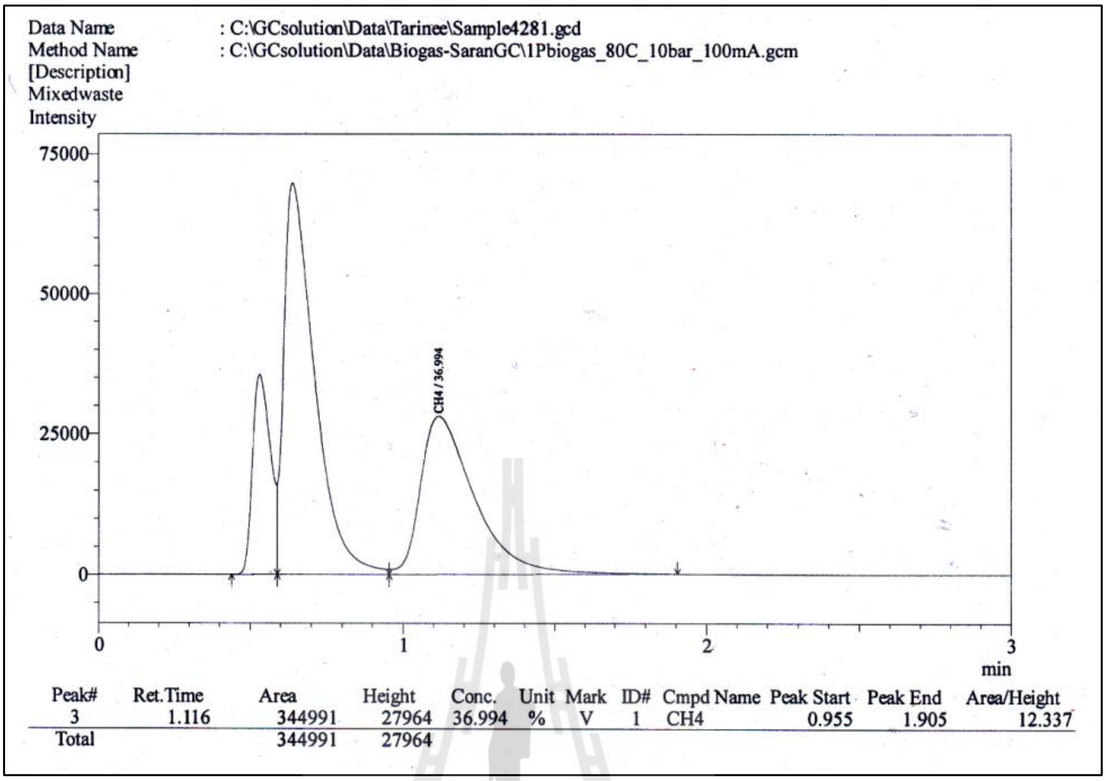


Figure 4.3 Chromatogram and report of methane and nitrogen analyzed by the gas analyzer at inoculum to feed ratio of 15W:7.5MS

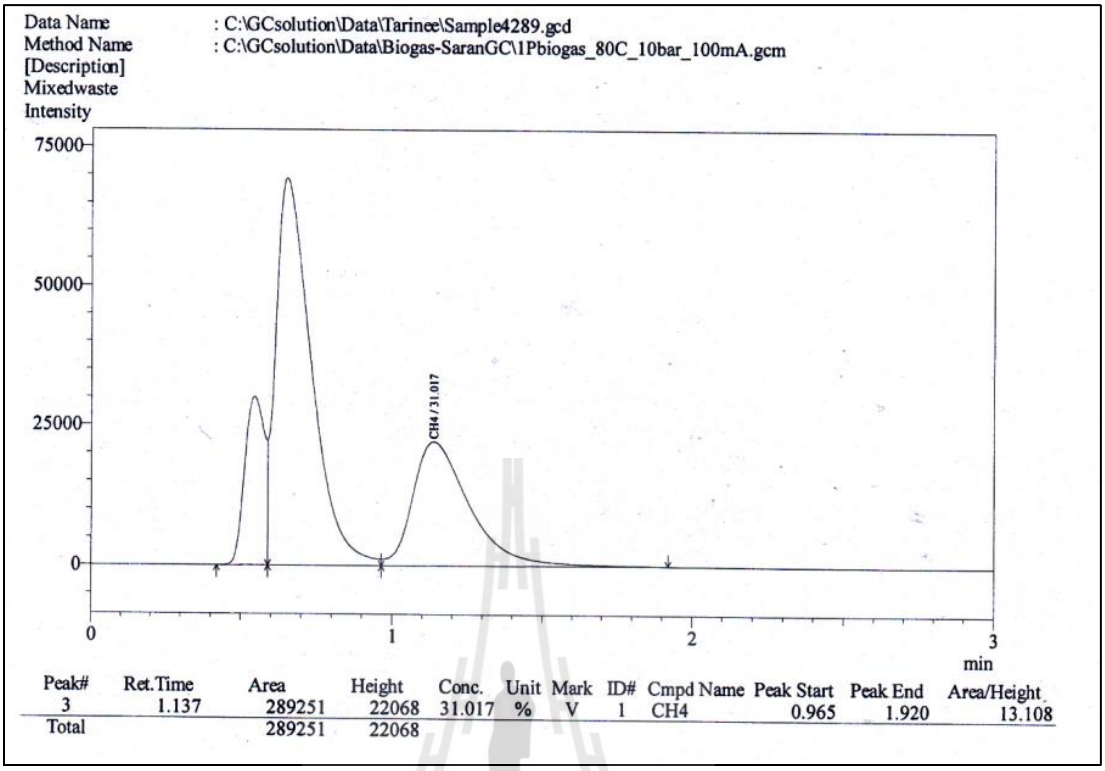
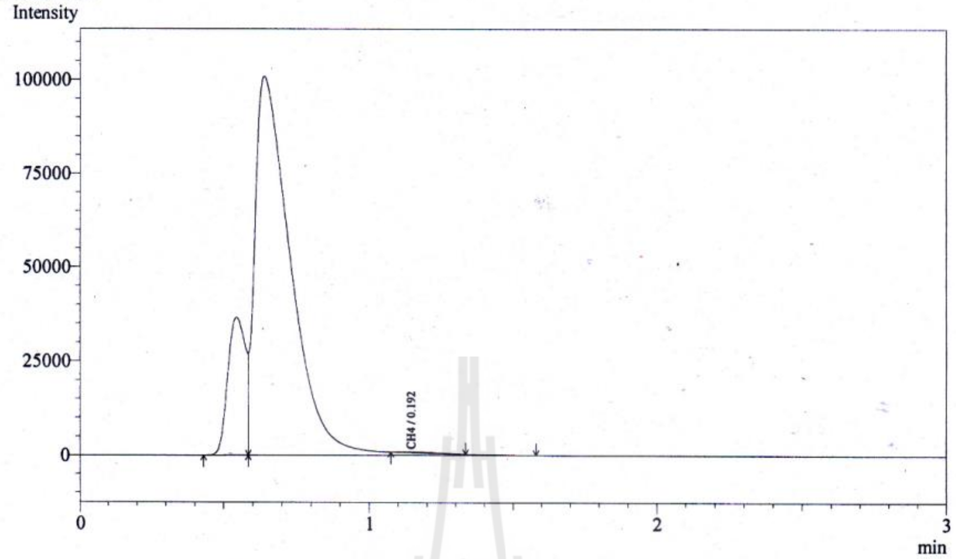


Figure 4.4 Chromatogram and report of methane and nitrogen analyzed by the gas analyzer at inoculum to feed ratio of 15W:5MS

Data Name : C:\GCsolution\Data\Tarinee\Sample4290.gcd
Method Name : C:\GCsolution\Data\Biogas-SaranGC\1Pbiogas_80C_10bar_100mA.gcm
[Description]
Mixedwaste



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name	Peak Start	Peak End	Area/Height
3	1.145	1789	199	0.192	%	T	1	CH4	1.075	1.335	9.009
Total		1789	199								

Figure 4.5 Chromatogram and report of methane and nitrogen analyzed by the gas analyzer at inoculum to feed ratio of 15W:15SW

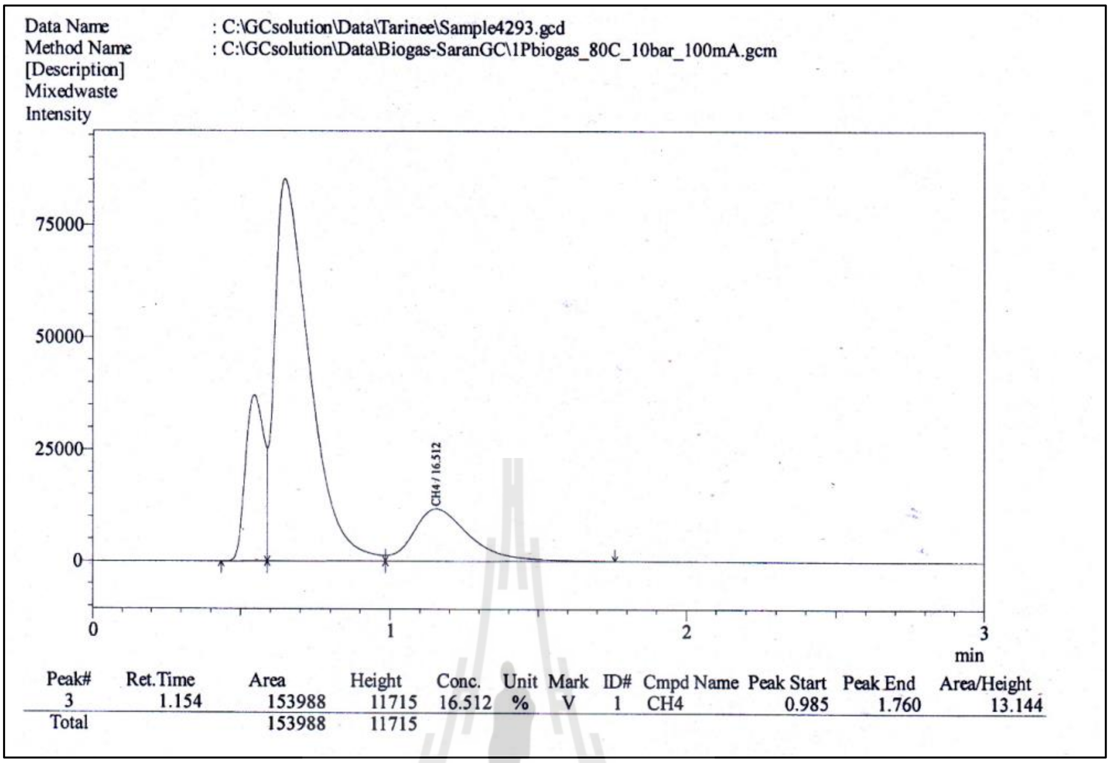


Figure 4.6 Chromatogram and report of methane and nitrogen analyzed by the gas analyzer at inoculum to feed ratio of 15W:7.5SW

4.2.4 Biogas production rate and yield

The cumulative biogas production rate (mL/g VS d) and biogas yield (mL/g VS) from shrimp farming waste at different ISRs are displayed in Figure 4.7 - 4.8. Biogas production started since the first day. The peak volumes of daily biogas production rates were calculated to be 17 and 14 mL/g VS after 2 and 8 days of digestion at inoculum to substrate ratios of 15W:5SW and 15W:7.5SW, respectively. The specific biogas yield increased until about days 6 and 9, respectively at ISRs of 15W:5SW and 15W:7.5SW, and gradually leveled off. At ratio of 15W:7.5SW, after days 20, the biogas still produced, however less than previous days. On the other hand, at ratio 15W:15SW was inhibited for biogas production. This might be due to the ratio composition even though the shrimp farming waste samples were taken from the same place.

The average biogas yields from the digesters performed at ISRs of 15W:5SW and 15W:7.5SW were calculated to be 124.25 and 88 mL/g VS, respectively. The maximum and the lower biogas yields were obtained at inoculum to substrate ratios of 15W:5SW and 15SW:15SW, respectively. The biogas yields obtained from this study similar to the earlier study of F. Raposo et al., 2006.

Based on the final methane content values after 30 days of digestion time were 14.19%, 16.51% and 0% at the ISRs of 3.0, 2.0 and 1.0, respectively. The results were shown that shrimp waste as a substrate was inhibited to produce biogas. This was due to the concentration of methane gas less than 45% to produce biogas (F. Raposo et al., 2006; G. Lui et al., 2009; R. Chandra et al., 2012 and G.K. Kafle et al., 2014).

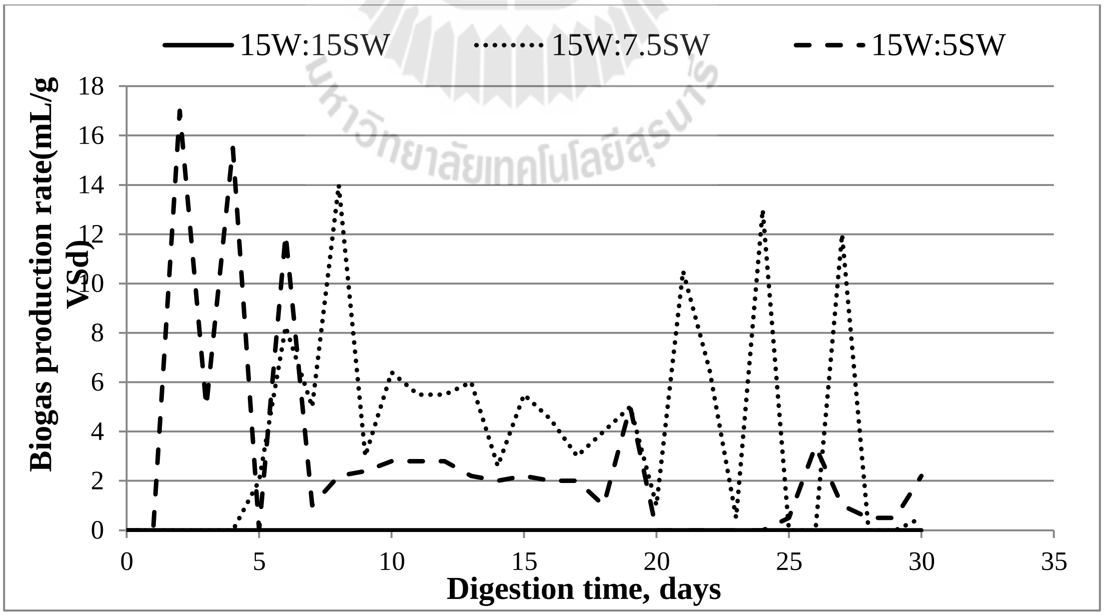


Figure 4.7 The biogas production rate (mL/g VS d) from shrimp farming waste at different ISRs

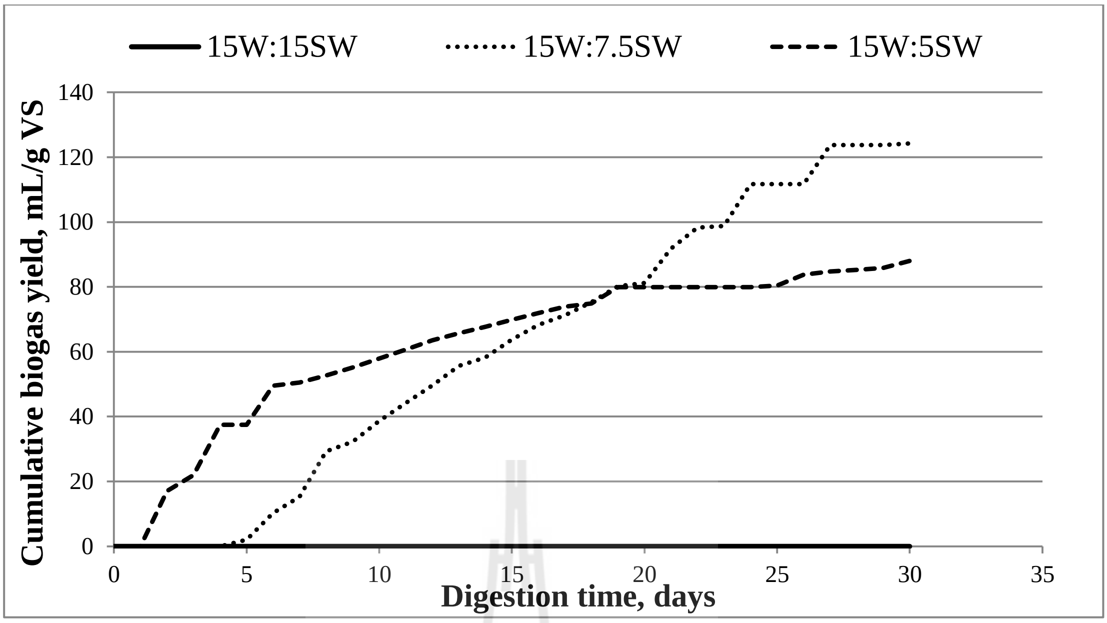


Figure 4.8 Cumulative biogas yield (mL/g VS) from shrimp farming waste at ISRs

The daily biogas production rate and cumulative biogas yield during the digestion of shrimp farming waste and rice straw as co-digesting substrate are shown in Figure 4.9-4.10. Similar to shrimp waste, biogas production started from the first day. The biogas production rates at ISRs at 15W:5MS, 15W:7.5MS and 15W:15MS reached their peak values of 54, 33.5 and 48 mL/g VS day on the third, fourth and seventh day, respectively.

After 30 days of digestion, the average biogas yields were calculated to be 359, 389.7 and 599.5 mL/g VS at the ISRs at 15W:5MS, 15W:7.5MS and 15W:15MS, respectively. The maximum and the lower biogas yields were obtained at ISRs of 15W:15MS and 15SW:5SW, respectively. The biogas yields obtained from this study similar to the earlier studies of G. Lui et al., 2009 and G.K. Kafle et al., 2014. Biogas was still producing in shrimp waste unlike substrate mixture of shrimp waste and rice straw. This might be due the differences in physical structure and/or in chemical compositions between the two substrates.

The final methane concentration values of ISRs at 1.0, 2.0 and 3.0 were 31.01%, 37% and 48.52%, respectively. The results were showed that the methane yields increased significantly when the ISRs increased. Similarly, F. Raposo et al., 2006 also reported a significant increase in methane yield with an increase in the ISRs during anaerobic digestion of maize. Also at ISRs of 3.0 was shown the highest methane concentration from all digesters.

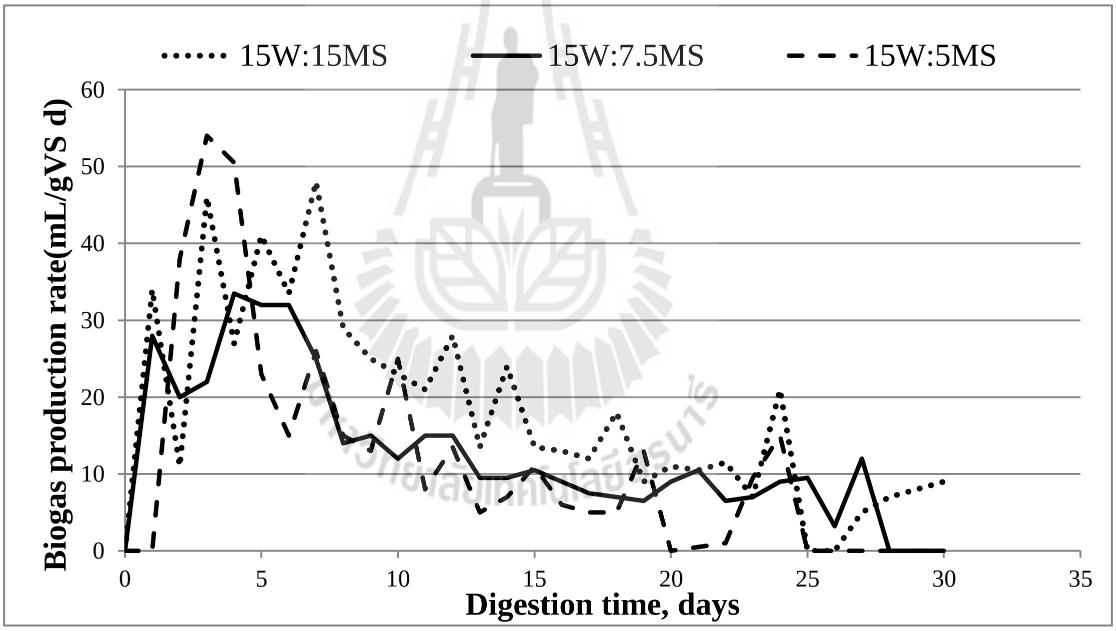


Figure 4.9 The biogas production rate (mL/g VS d) from shrimp farming waste and rice straw as co-digesting substrate at different ISRs

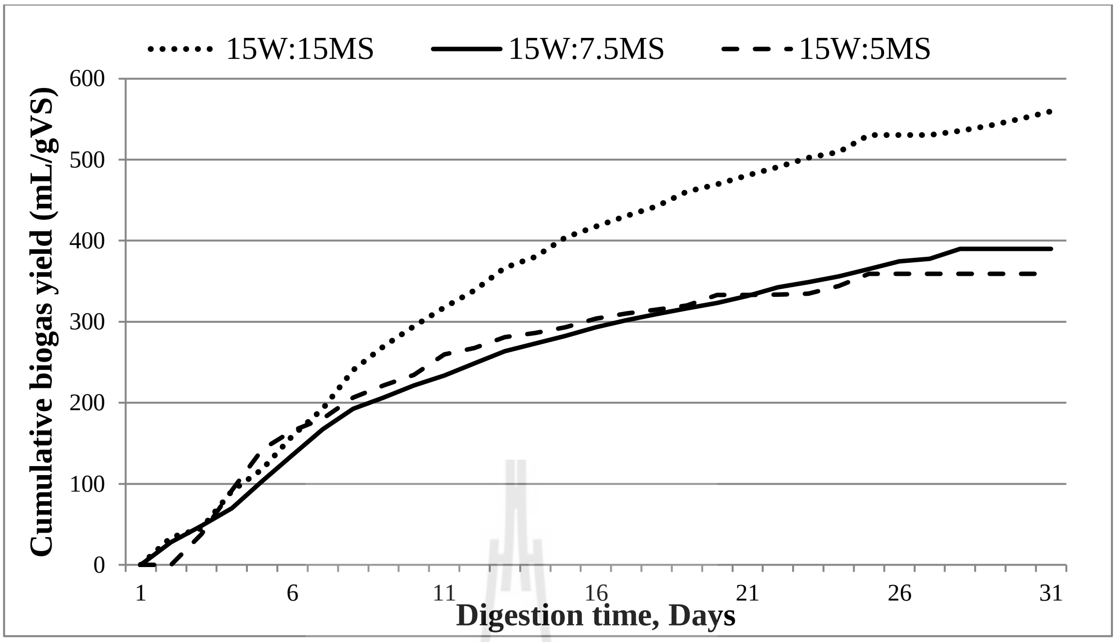


Figure 4.10 Cumulative biogas yield (mL/g VS) from shrimp waste and rice straw as co-digesting substrate at different ISRs

The daily biogas production yields and cumulative biogas yield rates during the digestion of shrimp farming waste and food waste mixture at different ISRs are shown in Figure 4.11and Figure 4.12.

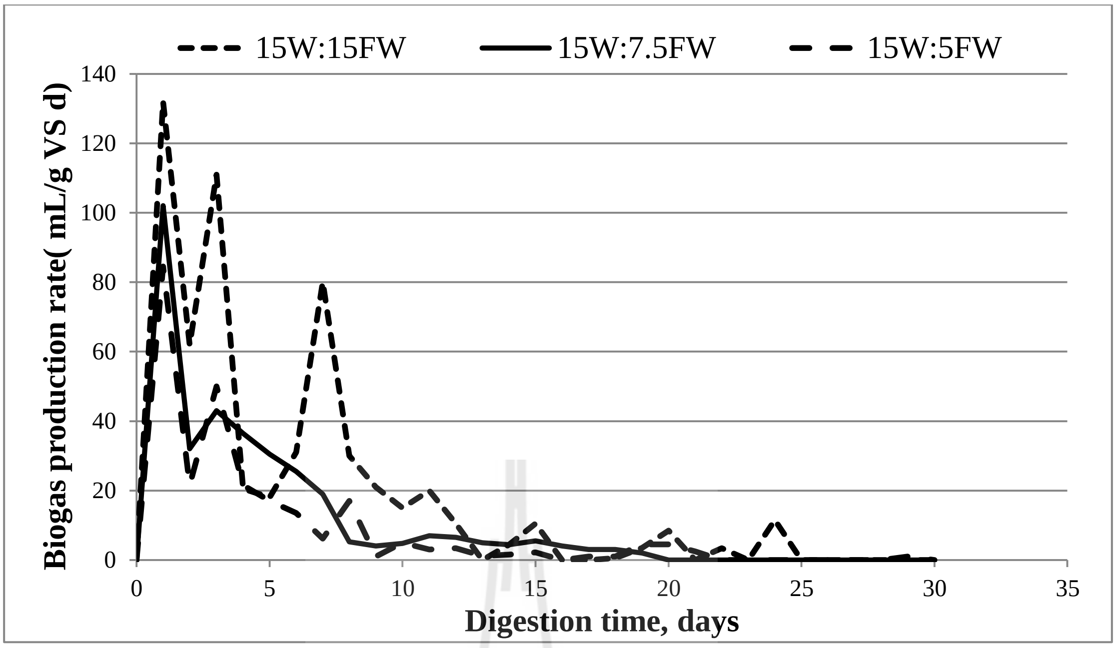


Figure 4.11 The biogas production rate (mL/g VS d) from shrimp farming waste and food waste as co-digesting substrate at different ISRs

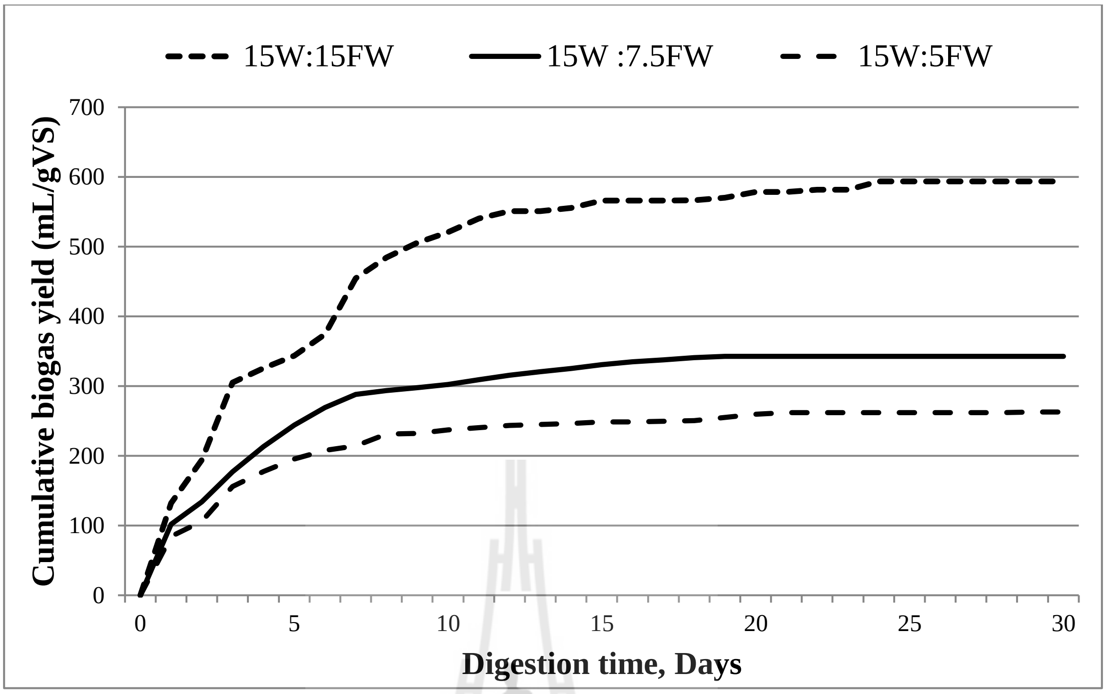


Figure 4.12 Cumulative biogas yield (mL/g VS) from shrimp farming waste and food waste as co-digesting substrate at different ISRs

The daily biogas production rates at ISRs of 15W:5FW, 15W:7.5FW and 15W:15FW reached their peak values of 84.5, 102, and 132 mL/g VS day, respectively, all on the first day of digestion. After added food waste as co-substrate, the digestion was higher than other substrates. After 30 days of fermentation, the average biogas yields were calculated to be 263.1, 342.7 and 593.3 mL/g VS at ISRs of 15W:5FW, 15W:7.5FW and 15W:15FW, respectively.

The final methane concentration values of ISRs at 1.0, 2.0 and 3.0 were 30.65%, 35.67% and 39.18%, respectively. The results were showed that the methane yields increased significantly when the ISRs increased. The cumulative biogas production of mixture substrate of shrimp waste and food waste produced maximum values, however, the final methane concentration less than the methane production from mixture of shrimp waste and rice straw. To determine the optimum limit of the ISRs, further studies need to be performed at increase in substrate to inoculum ratio or inoculum to substrate ratios exceeds 3.0.

4.2.5 Relationship between TS and VS removal

At the beginning of anaerobic digestion, the biogas rate was very high due to the decomposition of organic matter which called hydrolysis. After day 11 until day 30, all substrate ratios still produced biogas rate but lower than the first ten day until no biogas production. The biogas rate was high at the beginning caused by the formation of shorter chain carbon (Audra and Vincensia, 2010). The shorter chains are easier decomposed by bacteria for hydrolysis stage. In hydrolysis phase, acidogenic bacteria produced acid from organic matter and served acid to methanogenic bacteria as substrate methane gas. After hydrolysis phase occurred, the substrate was used and produced methane gas in the optimum condition. According to the substrate completely hydrolyzed and no fresh feeding into the biodigester, biogas will be finished. If the substrate in biodigester do not hydrolyzed completely, the biogas will be produced for long lasting.

The calculated TS and VS removal at the end of all digesters were displayed in Table 4.1. The highest VS destruction was from the mixture of shrimp farming waste and rice straw due to the highest methane concentration. In contrast, the lowest methane concentration was from the shrimp farming waste as substrate. This different were consequence of different substrate and co-substrate ratio due to the composition rate of acidogenic bacteria. The low biogas productivity derived from the complicated decomposition of the main materials and the microorganisms. The acidogenic bacteria decomposed a short chain of organic matter and used acid from the decomposition as substrate of methanogenic bacteria to produced biogas.

Table 4.1 Results of 30-day BMP anaerobic digestion of shrimp farming waste (SW), rice straw (MS) and food waste (FW)

Ratio	**Initial loading (g VS/L)**	**VS reduction (%)**	**CH_4 content (%)**	**Biogas yield (mL/g VS)**	**CH_4 yield (mL/g VS)**
15W:5SW	20	77.18	14.19	0.21	2.92
15W:5MS	20	98.48	31.01	0.29	8.95
15W:5FW	20	97.41	30.65	0.31	9.59
15W:7.5SW	22.5	69.05	16.51	0.34	5.54
15W:7.5MS	22.5	96.29	37	0.67	24.95
15W:7.5FW	22.5	93.70	35.67	1.01	36.12
15W:15SW	30	99.62	0	0.00	0.00
15W:15MS	30	97.17	48.52	1.09	53.71
15W:15FW	30	99.67	39.18	0.69	27.01

4.2.6 Discussion

The biogas productivity in this study was obtained for conditional tested, not ultimate yields or biogas production potential. The results demonstrate the biogas yield after 30 days of anaerobic digestion time are influence by the IRS: the higher ISR, the higher biogas yield. The outstanding biogas production was from the substrate of shrimp farming waste. This might be caused from inhibition to methanogenesis. The volatile fatty acid concentrations were not measured in this study.

All results showed the biogas production started after fermentation. This may indicated the fast adaptation of microorganisms to feedstock (G. Lui et al., 2009). The results of this study are not only important for lab scale but also when sizing large scale of mixing for waste organic matter substrate. It is also important to point out the certain ratio for shrimp waste and maximum biogas potential.

4.3 Assessment of the energy and utilization from produced biogas

To evaluate and compare the energy from shrimp farming waste as main substrate and shrimp farming waste with co-substrate can preliminary determined as the following step and assumptions:

1. The amount of waste from shrimp farm in Thailand

In general, the average size of shrimp pond could be 1 – 5 hectares per pond which is 25x50 m^2 and 1 meter depth (http://www.fisheries.go.th). The pond should be dredged every 2-3 months for one cycle of shrimp crop. The amount of shrimp farming waste could be 1/3 of pond size which has approximately 417 kg/year/pond.

2. The amount of waste from rice straw in Thailand

According to the studied of Sripongpunkul K. (2008), one acre of rice farming gave 800 kg of straw each year and he has also found that rice straw and rice stubble at least 50 million tons per year.

3. The amount of food waste in Thailand

Thinakul S. 2013 revealed the municipal solid waste has around 26 million tons a year in 2013.

4. The maximum ratio for biogas productivity in this research can be calculated as follows:

The amount of waste from shrimp farm in Thailand per pond

417 kg/year (If ρ_{SW} = 2.5 g/l from this study)

The total amount waste would be 166.8 m^3 /year

The amount of waste from rice straw in Thailand per acre 800 kg/year

(If ρ_{MW} = 0.463 g/l from this study)

The total amount waste would be 1.72 m^3 /year

The amount of food waste in Thailand 26 million tons per year

(If ρ_{FW} = 180-420 g/l from United Nations Environment Program) The total amount of waste would be 1.44x106 m^3 /year

5. One cubic meter of methane gas from biogas is equivalent to 0.46 kg of Liquefied Petroleum Gas (LPG) or 1.2 kwh of electricity or diesel 0.6 liter or 39.4 MJ/m^3 of heating value (Department of Alternative Energy Development and Efficiency, Ministry of Energy).

According to this studied of biogas from anaerobic digestion, the best methane yield was from the ratio of 15W:15MS which the biogas yields were 53.75 mL/g VS and 48.52% of methane concentration. The 250 mL working volume of digester can produce biogas from priceless substrate and materials. In house scale, the shrimp farming waste, rice straw and food waste, are free due to waste product. The methane production can be calculated as shown in Table 4.1 and the biogas produced can be converted to its heating value as shown in Table 4.2 for the maximum ratio.

Table 4.2 The biogas production converted to its heating value at 250 mL working volume of digester

Ratio	**CH_4 concentration (%)**	**CH_4 yield (mL/g VS)**	**Biogas productivity (m^3 /year)**
15W:5SW	14.19	2.93	7,722.84
15W:5MS	31.01	8.95	3,871.36
15W:5FW	30.65	9.91	3,872.64
15W:7.5SW	16.51	5.54	11,676
15W:7.5MS	37	24.95	5,840.41
15W:7.5FW	35.67	36.12	5,842.32
15W:15SW	0	0.00	23,185.2
15W:15MS	48.52	53.75	11,680.82
15W:15FW	39.18	27.01	11,684.64

Calculation example:

$$1.\ CH_4 \text{ yield (mL/g VS)} = \frac{\text{Cummulative methane (ml)}}{TVS_{input} - TVS_{output}} \text{ x } (\%\ CH_4)$$

$$\text{At ratio 15W:5SW} = \frac{44}{(554.81-126.61)} \text{ x } (14.19) = 2.93 \text{ mL/g VS}$$

2. Biogas productivity (m^3 /year) = (Waste Substrate Quantity per year, m^3) x ratio based on g VS

At ratio 15W:5SW = 166.8 m^3/ year x 46.3 (based on I/F ratios) = 7,722.84 m^3/ year

At ratio 15W:15FW = [(70 x 166.8) + (6 x 1.44)] = 11,684.64 m^3/ year

3. Heating Value (MJ/year) = Biogas productivity (m^3/year) x 39.4 MJ/m^3; (Biogas 1 m^3 equal to heating value of 39.4 MJ/m^3)

Therefore at ratio of 15W:15MS which the highest biogas yields were 53.75 mL/g VS and 48.52% of methane concentration can be produced 11,680.82 m^3/year. According to the study of P. Chungchaichana and S. Vivanpatarakij (2012), one meter of biogas from ratio of 15W:15MS can be replaced other energy fuel as shown in Table 4.3.

Table 4.3 A cubic meter of biogas at ratio of 15W:15MS converted to renewable energy

Energy Fuel	Equivalent volume	Energy replacement	Price per unit	Price replacing (Baht/year)
LPG	0.46 kg	5,373.18 kg/year	15 Baht/kg*	80,597.7
Diesel	0.67 L	7,826.15 L/year	26.09Baht/L**	204,184.26
Electricity	1.2 kwh	14,017 kwh/year	3.2315 Baht/Unit***	45,295.94

*, ** price in January 14, 2015

*** price based on household less than 250 unit/month

Calculation example:

- Energy replacement = Biogas productivity (m^3 /year) x 0.46 kg of LPG

  = 11,680.82 x 0.46 = 5373.18 kg/year

- Price replacing (Baht per year) = Energy replacement x Price per unit

The results from this study showed that the energy from biogas production can be used and diminished the expenses in household or pig farm due to the close system. Moreover anaerobic digestion can be managed waste and wastewater from animal efficiently and sustainably.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

5.1 Conclusions

This research was focused on the production of biogas as an energy source from raw shrimp farming waste which inexpensive and abundant agricultural by product in Thailand. The potential biogas production from raw shrimp farming waste could be evaluated as mentioned above. Data involved biogas quantity and quality, biogas production process from raw shrimp farming waste were obtained. Concisely, the utilization and economic value of raw shrimp farming waste could be increased.

The results from this study showed that the shrimp farming waste can be anaerobically during the digestion for different inoculum to feed ratios under BMP condition. The biogas production volumetric from shrimp farming waste as co-substrate, rice straw, food waste linearly increased with increase in inoculum to feed ratios from 1.0 to 3.0. Similarly, the specific biogas yield (mL/g VS) increased significantly when the inoculum to feed ratios increased from 1.0 to 3.0. The best methane yield was from the ratio of 15W:15MS which the biogas yields were 53.75 mL/g VS and 48.52% of methane concentration. The exception of shrimp farming waste as substrate showed the different results. This might be inhibited condition for microorganisms to be digested during incubation. The data obtained from this study could be useful in designing field scale anaerobic digesters for treatment of shrimp farming waste.

5.2 Recommendations for future studies

For future study based on the obtainable results of this study, the carbon-to-nitrogen ratio of shrimp farming waste was too low, increasing the higher the carbon-to-nitrogen ratio could support the maximum biogas yield. Using the semi-continuous or two state digesters could be used to increase the productivity of biogas. Higher substrate to inoculum ratios is recommended to determine the optimum limit of the substrate to inoculum ratios for other type anaerobic digestion of shrimp waste.

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APPENDIX A

DAILY AND CUMULATIVE BIOGAS PRODUCTION

Table A.1 Daily biogas production in each I/F ratios

Day	15W:15SW	15W:15MS	15W:15FW	15W:7.5SW	15W:7.5MS	15W:7.5FW	15W:5SW	15W:5MS	15W:5FW
0	0	0	0	0	0	0	0	0	0
1	0	0	0	34	28	0	132	102	84.5
2	0	0	17	11	20	38	62	32	21.5
3	0	0	5	46	22	54	111	43	50
4	0	0	15.5	27	33.5	50.5	20.5	36.5	21.5
5	0	2	0	41	32	23	18	30.5	17
6	0	8.25	12	33.5	32	15	31	25.5	13.5
7	0	5	1	48	25	26	80	19	6.2
8	0	14	2.2	29	14	15	30	5.2	17
9	0	3	2.4	25	15	13	21	4	1
10	0	6.4	2.8	23	12	25	15	4.8	5
11	0	5.5	2.8	21	15	8	20	7	3
12	0	5.5	2.8	28	15	13.5	10.5	6.5	3.4
13	0	6	2.2	13.5	9.5	5	0	5	1.2
14	0	2.6	2	24	9.5	7	4.4	4.4	1.6
15	0	5.5	2.2	13.5	10.5	11	10.5	5.5	2.2
16	0	4.5	2	13	9	6	0	4	0
17	0	3	2	12	7.5	5	0	3	1
18	0	4	1	18	7	5	0.5	3	1
19	0	5	5	9	6.5	13	3.5	2	4.5
20	0	1	0	11	9	0	8.5	0	4.5
21	0	10.5	0	10.5	10.5	0.5	0	0	2.5
22	0	6.5	0	11.5	6.5	1	3.4	0	0
23	0	0.5	0	7	7	9.5	0	0	0
24	0	13	0	21	9	15	11.5	0	0
25	0	0	0.5	0	9.5	0	0	0	0
26	0	0	3.4	0	3.2	0	0	0	0
27	0	12	1	5	12	0	0	0	0
28	0	0	0.5	7	0	0	0	0	0
29	0	0	0.5	8	0	0	0	0	1
30	0	0.5	2.2	9	0	0	0	0	0
31	0	0	0	0	0	0	0	0	0

Table A.2 Cumulative biogas production in each I/F ratios

Day	15W:15SW	15W:15MS	15W:15FW	15W:7.5SW	15W:7.5MS	15W:7.5FW	15W:5SW	15W:5MS	15W:5FW
0	0	0	0	0	0	0	0	0	0
1	0	34	132	0	28	102	0	0	84.5
2	0	45	194	0	48	134	17	38	106
3	0	91	305	0	70	177	22	92	156
4	0	118	325.5	0	103.5	213.5	37.5	142.5	177.5
5	0	159	343.5	2	135.5	244	37.5	165.5	195.5
6	0	192.5	374.5	10.25	167.5	269.3	49.5	180.5	208
7	0	240.5	454.5	15.25	192.5	288.3	50.5	206.5	214.2
8	0	269.5	484.5	29.25	206.5	293.5	52.7	221.5	231.2
9	0	294.5	505.5	32.25	221.5	297.5	55.1	234.5	232.2
10	0	317.5	520.5	38.65	233.5	302.3	57.9	259.5	237.2
11	0	338.5	540.5	44.15	248.5	309.3	60.7	267.5	240.2
12	0	366.5	551	49.65	263.5	315.8	63.5	281	243.6
13	0	380	551	55.65	273	320.8	65.7	286	244.8
14	0	404	555.4	58.25	282.5	325.2	67.7	293	246.4
15	0	417.5	565.9	63.75	293	330.7	69.9	304	248.6
16	0	430.5	565.9	68.25	302	334.7	71.9	310	248.6
17	0	442.5	565.9	71.25	309.5	337.7	73.9	315	249.6
18	0	460.5	566.4	75.25	316.5	340.7	74.9	320	250.6
19	0	469.5	569.9	80.25	323	342.7	79.9	333	255.1
20	0	480.5	578.4	81.25	332	342.7	79.9	333	259.6
21	0	491	578.4	91.75	342.5	342.7	79.9	333.5	262.1
22	0	502.5	581.8	98.25	349	342.7	79.9	334.5	262.1
23	0	509.5	581.8	98.75	356	342.7	79.9	344	262.1
24	0	530.5	593.3	111.75	365	342.7	79.9	359	262.1
25	0	530.5	593.3	111.75	374.5	342.7	80.4	359	262.1
26	0	530.5	593.3	111.75	377.7	342.7	83.8	359	262.1
27	0	535.5	593.3	123.75	389.7	342.7	84.8	359	262.1
28	0	542.2	593.3	123.75	389.7	342.7	85.3	359	262.1
29	0	550.5	593.3	123.75	389.7	342.7	85.8	359	263.1
30	0	559.5	593.3	124.25	389.7	342.7	88	359	263.1
31	0	570.5	593.3	125.45	389.7	342.7	88.5	359	271.9

BIOGRAPHY

Miss Tarinee Rittiron was born on 24th of July 1988 in Surin province. She earned her Bachelor's Degree in Chemical Engineering in 2010 from King Mongkut's University of Technology North Bangkok (KMUTNB). She continued with her Master Degree in Geotechnology, Institute of Engineering at Suranaree University of Technology (SUT) with the major in Geological Engineering. Here, her responsibility is on the waste disposal and treatment.