Upgrading Biomethane from Biogas using Microbubble Technique in Absorption System

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ชื่อวิทยานิพนธ์	การปรับปรุงไบโอมีเทนจากก๊าซชีวภาพด้วยเทคนิคไมโครบับเบิลร่วมกับการดูดซึม
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บทคัดย่อ

ไบโอมีเทน (Biomethane) เป็นพลังงานทางเลือกที่น่าสนใจที่ผลิตได้จากการปรับปรุงก๊าซชีวภาพ (Biogas upgrading) ให้มีความเข้มข้นของก๊าซมีเทน (Methane) ที่เพิ่มขึ้น สามารถนำไบโอมีเทนมาใช้เป็นแหล่งพลังงานหมุนเวียนได้หลากหลายทั้งในด้านความร้อน ผลิตพลังงานไฟฟ้าและเป็นเชื้อเพลิงสำหรับยานพาหนะ การปรับปรุงก๊าซชีวภาพทำได้โดยการกำจัดองค์ประกอบก๊าซคาร์บอนไดออกไซด์ (CO_2) และก๊าซไฮโดรเจนซัลไฟด์ (H_2S) ออกจากก๊าซชีวภาพจนเหลือก๊าซมีเทนที่ความเข้มข้นมากกว่า 90% ซึ่งการปรับปรุงก๊าซชีวภาพมีหลายวิธี เช่น การดูดซับ (Adsorption) การดูดซึมทางเคมี (Chemical absorption) การดูดซับสลับความดัน (PSA) และการแยกด้วยเทคนิคเมแบรน (Membrane separation) เป็นต้น กระบวนการดูดซึมด้วยน้ำร่วมกับเทคนิคอื่นๆ เป็นหนึ่งในกระบวนการที่น่าสนใจ

โครงการวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการผลิตไบโอมีเทนโดยการใช้กระบวนการดูดซึม (Absorption) ด้วยสารดูดซึมชนิดน้ำร่วมกับเทคนิคการสร้างไมโครบับเบิลด้วยการใช้หัวฉีดเวนจูรี (Venturi ejector) ขนาด 0.25 และ 0.5 นิ้ว ที่ทำหน้าที่การสร้างฟองก๊าซขนาด 20-30 ไมครอน หรือเรียกอีกอย่างหนึ่งว่าไมโครบับเบิลให้ผสมแทรกตัวอยู่ในน้ำเพื่อให้เกิดการดูดซึมของก๊าซ CO_2 เมื่อผ่านคอลัมน์ดูดซึม โดยการใช้ก๊าซชีวภาพจำลอง (Simulated biogas) ที่เกิดจากการผสมของก๊าซ CO_2 และก๊าซ N_2 ที่ความเข้มข้นของก๊าซ CO_2 20-40% และก๊าซชีวภาพจากการหมักแบบไร้อากาศในการศึกษา

การผลิตไบโอมีเทนในโครงการวิจัยนี้ดำเนินด้วยการออกแบบและพัฒนาชุดอุปกรณ์การทดลองใน 3 ขั้นตอน คือ

1) ทำการออกแบบและติดตั้งชุดทดลองและทำการทดลองด้วยชุดสร้างฟองขนาดเล็กและคอลัมน์ดูดซึมที่มีขนาดเส้นผ่านศูนย์กลาง 0.18 เมตร และมีความสูง 1 เมตร โดยการใช้ก๊าซชีวภาพจำลอง (Simulated biogas) โดยการศึกษาผลของความเข้มข้นของก๊าซ N_2 ทางขาออก เพื่อยืนยันว่าระบบสามารถล้างก๊าซ CO_2 ออกจากกระแสก๊าซชีวภาพจำลองได้

2) ทำการศึกษาชุดอุปกรณ์ต้นแบบ (Prototype) ที่ผ่านการพัฒนาปรับปรุงเทคนิคและอุปกรณ์สำหรับการศึกษาการผลิตไบโอมีเทนเพื่อลดความต่างของความความดัน (Pressure drop)

ด้วยอุปกรณ์หลักที่ประกอบด้วยชุดสร้างฟองก๊าซขนาดไมครอนแบบหัวฉีดเวนจูรีขนาด 0.25 และ 0.5 นิ้ว คอลัมน์ดูดซึมแบบในท่อที่มีขนาดเส้นผ่านศูนย์กลาง 0.016 เมตร และมีความยาว 10 เมตร คอลัมน์แยกไบโอมีเทนต่ออนุกรมกันจำนวน 2 คอลัมน์ ด้วยการใช้หัวสเปรย์ชนิดเกลียวเดือยหมู (Spiral nozzle) ที่ทำให้สารดูดซึมกระจายตัวเป็นหยดขนาดเล็กส่งผลให้ไบโอมีเทนแยกตัวออก

3) ทำการศึกษาชุดฟื้นฟูสภาพสารดูดซึมด้วยการใช้คอลัมน์ที่ทำให้เกิดการไหลสวนทางระหว่างหยดของสารดูดซึมกับอากาศ ทำให้สามารถนำน้ำกลับมาวนซ้ำกลับมาใช้ใหม่ในระบบได้

ตัวแปรที่ศึกษาในการผลิตไบโอมีเทนประกอบด้วยขนาดของฟองก๊าซที่ผลิตได้จากหัวฉีดแบบเวนจูรี อัตราการไหลของก๊าซ อัตราการไหลของน้ำ ค่า L/G Ratio ความเข้มข้นของก๊าซ CO_2 ในกระแสก๊าซชีวภาพจำลองตั้งต้น และอัตราการไหลของอากาศสำหรับการฟื้นฟูสภาพสารดูดซึม จากการศึกษา พบว่าขนาดของฟองก๊าซขึ้นอยู่กับอัตราการไหลของก๊าซ ซึ่งอัตราการไหลของก๊าซต่ำส่งผลให้ฟองก๊าซมีขนาดที่เล็กลง และหัวฉีดเวนจูรีขนาด 0.5 นิ้ว สามารถผลิตฟองก๊าซขนาด 20 -30 ไมครอน ที่ช่วยเพิ่มประสิทธิภาพการดูดซึมก๊าซ CO_2 ในน้ำ ซึ่งสภาวะที่เหมาะสมในการดำเนินการ คือ อัตราการไหลก๊าซ 4 L/min อัตราการไหลน้ำ 15 L/min และ ค่า L/G Ratio เท่ากับ 3.75 ซึ่งสามารถดักจับก๊าซคาร์บอนไดออกไซด์ได้ประสิทธิภาพมากว่า 80% จากก๊าซชีวภาพจำลองที่ความเข้มข้นตั้งต้น 35-50% เมื่อนำก๊าซชีวภาพไปทดลองการดูดซึมก๊าซ CO_2 ด้วยชุดต้นแบบ พบว่า ได้ความเข้มข้นของก๊าซมีเทนสูงถึง 96% โดยปริมาตร ซึ่งตรงกับข้อกำหนดความบริสุทธิ์สำหรับไบโอมีเทน

นอกจากนี้ยังพบว่ามีปริมาณการสูญเสียมีเทน (Methane loss) ในระบบ 0.013% จากการวิเคราะห์ทางเศรษฐศาสตร์เบื้องต้น พบว่า ค่าใช้จ่ายในการดำเนินการ (Operating cost) ของระบบการผลิตไบโอมีเทนด้วยระบบคอลัมน์ดูดซึมร่วมกับไมโครบับเบิล เท่ากับ 10.63 บาท/1 ลบ.ม. ก๊าซชีวภาพ และมีผลของแนวทางการออกแบบระบบที่จะสามารถนำไปประยุกต์ใช้งานจริงในการผลิตไบโอมีเทนจากก๊าซชีวภาพในระดับอุตสาหกรรม

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ABSTRACT

Biomethane is an interesting alternative energy produced from biogas upgrading. Concentration of methane (CH_4) in the biogas is increased more than 90% and can be used as a renewable energy. Biogas improvement can be done by eliminating carbon dioxide (CO_2) and hydrogen sulfide (H_2S) from biogas until meeting biomethane specifications. There are many ways to clean biogas for producing biomethane, such as adsorption, chemical absorption, pressure swing adsorption (PSA), cryogenic separation, biological methane enrichment, and membrane separation. Absorption using water as an absorbent is one of interesting processes which is able to combine with other techniques.

The aim of this research project was to study the production of biomethane by using the absorption process with water based absorbent. The absorption was combined with a technique of microbubbles generated by using a venturi ejector, A size 0.25 and 0.5 inches, as a tiny bubble generator can create the bubble size range of 20-30 µm which can be called microbubble gas. The bubbles were mixed with the water before sending through the absorption unit. The treated gas is separated and released out from the water absorbent while CO_2 still remains in the water. The simulated biogas was a mixure of CO_2 and N_2 gas at 20-40% CO_2 concentration and biogas from the anaerobic fermentation were finally used as a feed gas in this study.

The production of biomethane in this research project was carried out by designing and developing equipment set, as follows;

1) The first step was to design and a gas bubble generation set and equipped with construct a CO_2 absorption column with a diameter of 0.18 meters and height 1.0 meters. The simulated biogas was applied to confirm that the CO_2 can be removed from the system. Observing the N_2 concentration in outlet treated gas stream was monitored and proved the upgrading of biogas to biomethane.

2) Step 2, the experimental prototype was developed to reduce pressure drop. A tube absorber of 0.016 meters in dia. 10 meters long was designed for CO_2 absorption in water instead of the absorption column. Treated gas was separated from water absorbent in a series of 2 columns. A spiral nozzle was fixed at top of column to spray the tiny absorbent dropets.

3) The CO_2-rich water stream from the gas separator was sent to a column of regeneration unit. The water was sprayed through spray nozzle to make small droplet of water. The counter current flow between the water droplets and air in regeneration column allows the CO_2 desorbing from the water which is readity to reuse.

The process variables ware studied to produce bio-methane consist of venturi ejector size, gas flow rate, water flow rate, L/G ratio, CO_2 concentration in the initial simulated biogas feed. The air flow rate feeding to the regeneration unit was monitored for the effect on the system efficiency. Based on the study, it was found that size of bubble is decreased with decreasing the gas flow rate to the venturi ejector. The 0.5-inch venturi nozzle can produce microbubble size of 20-30 µm that helps to increase CO_2 absorption in water. The operating condition for the absorption unit with microbubble of 4 L/min gas flow rate, 15 L/min water flow rate, and L/G ratio of 3.75 can effectively capture CO_2 for more than 80% from the simulated biogas at 35-50% CO_2. The CO_2 absorption from real biogas by the prototype experimental was effectively performed with high concentration of methane to 96% by volume, which corresponds to the purity requirements for biomethane.

In addition, it was found that the amount of methane loss in the system was only about 0.013%. The economic analysis for the biomethane production system with the absorption column system together with microbubble was found the operating cost of 10.63 baht /1 m^3 biogas. The system design approach in this research can be possibly be applied in the production of biomethane from industrial biogas.

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CHAPTER 1

INTRODUCTION

1.1 Background and Rationale

In the current stage over 85% of world energy demand is supplied by fossil fuels. With increasing concerns in environmental pollution and global energy crisis, development of renewable energy has been a strategic issue for environmental protection (Chu., 2009). An alternative source of energy like biogas has become of interest as it is environmentally friendly in additional to other several advantages. Biogas, which consists mainly of methane (CH_4) about 50-70% and carbon dioxide (CO_2) about 30-50% with some other gases about 2%, such as hydrogen sulfide (H_2S), ammonia (NH_3), hydrogen (H_2), nitrogen (N_2), and humidity. Biogas has CO_2 at concentration of 30-50% which will result in lower heating value of the gas. Then the concentration of methane is not fixed causing incomplete combustion, unstable flame, and the performance of the system decreases and causes corrosion within the pipeline with gas. Therefore, it is necessary to upgrading biogas by reducing the proportion of CO_2 to produce biomethane with component of about 95% methane. The biomethane can be used instead of LPG for household and industrial, which faced the problem of the price and are likely to be lacking in the future.

Nowadays, various techniques are used to remove CO_2 contaminants in biogas for producing biomethane. Among the most commonly used technologies are adsorption, chemical absorption, pressure swing adsorption (PSA), cryogenic separation, biological methane enrichment and membrane separation. However, above methods have expensive investment, high operating cost, and environmental pollution. One interesting method is water absorption that is directly related to solubility and efficiency of the surface area between gas phase and liquid phase. The ability of CO_2 and CH_4 dissolving in water at 30^oC are 1.25 and 0.0175 g CO_2/ g H_2O, respectively. CO_2 gas has likely be dissolved in water 70 times higher than CH_4 gas. CO_2 also have different electronegativity, hence surrounded by polar water molecule forming cage structure this leads to a high solubility. The regeneration of water recirculation in the system by pulling the substances absorbed from water also need to be considered.

A technique involving apply microbubble using venturi ejector to bubbling of the gas spread throughout the liquid will enhance the absorption capacity. Microbubble with 50-200 µm bubbles size can increase surface area of the gas bubble in water absorption process. Among the physicochemical characteristics of microbubble, there is a large specific area and high pressurization of gas inside the bubble. Moreover, the microbubble has a low buoyant force, it floats to the water surface slower, and efficiency of gas dissolved in water is higher than that conventional gas bubbles. A venturi ejector that is to create a microbubble due to the shear forces encountered in the low-pressure zone. The surface of the microbubble is surrounded by anions helping to prevent forming into large bubbles. The combining technique can possible be used to absorb CO_2 into the water.

The desorption of CO_2 from water have to study for regenerate the absorbed water. Countercurrent flow between air flow and CO_2-rich water creates a contacting and releasing the CO_2 gases. This contact of O_2 from air to CO_2 dissolved in water has a resulting in deformation of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) to form CO_2 gas, which the CO_2 gas can separate from water. It causes the water to be continuously recirculated and re-absorbed CO_2 in the process, which can reduce costs and waste from the system.

Therefore, the aims of this research are to produce biomethane by removal of CO_2 in biogas using water absorption column with microbubble technique. To provide a device that can effectively create microbubble using venturi ejector. The removal of CO_2 was studied by prototype scale unit using simulated biogas by mixing of CO_2 and N_2 at 20-50% CO_2. a series of microbubble generation system, water absorption columns and CH_4 separation columns was constructed and tested. Regeneration system for releasing CO_2 by spray column with countercurrent airflow were designed to separate CO_2 from the CO_2 absorbed water. Finally, the optimum condition of biomethane production from biogas receiving from a wastewater treatment of SONGKLA CANNING PCL. was investigated. The results of this research are likely lead to future utilization in biomethane production at the industrial level.

1.2 Objective

1. To produce biomethane by CO_2 removal from biogas using water absorption with microbubble generation unit.

2. To design and investigate the optimum condition of CO_2 removal from simulated biogas and real biogas by laboratory and prototype unit testing.

3. To regenerate the CO_2-rich water by using a counter-current air stripping unit for recirculating operation of the water absorbent.

1.3 Scope of work

1. Simulated biogas at concentration of about 20-50% CO_2 producing from CO_2 and N_2 gases were used for optimum testing.

2. The experimental prototype of water absorption column with microbubble technique using venturi ejector were designed and used for removal of CO_2 from simulated biogas.

3. Six parameters were studied in an experimental prototype unit including gas flow rate, water flow rate, size of venturi ejector, concentration of CO_2, size of bubbles, and L/G ratio.

4. A series of tube absorber and gas separation column was applied in the system to reduce pressure drop from the absorption column and increase percentage recovery of treated gas.

5. The regeneration of CO_2 absorbed water for re-circulation the liquid absorbent into the absorption process were studied and tested by using a counter-current air stripping unit.

6. Upgrading the quality of biogas from anaerobic fermentation to produce biomethane by removing CO_2 and H_2S in order to enrich its CH_4 content up to 90%.

1.4 Expected Benefits

1. The new technique of water absorption column with microbubble generated from venturi ejector can effectively be proven to remove CO_2 from biogas.

2. Guidelines of the experimental prototype for removal of CO_2 in biogas, which has high efficiency and suitable for biomethane production.

3. Promoting the use of industrial waste to add value in the energy field, which is upgrades biogas to produce biomethane.

4. Biomethane production with low cost can possible be applied for household and industrial instead of LPG.

CHAPTER 2

LITERATURE REVIEW

2.1 Theory and principle

2.1.1 Biogas

Biogas is the type of biofuel that is naturally produced from the decomposition of organic waste, such as animal waste and food scraps, break down in an anaerobic environment they release a blend of gases, primarily CH_4 and CO_2. Since this decomposition happens in an anaerobic environment, the process of producing biogas is also known as anaerobic digestion.

Anaerobic digestion as shown in Figure 1. is a natural form waste to energy that uses the process of fermentation to breakdown organic matter. Animal waste, food scraps, wastewater, and swage are all example of organic matter that can produce biogas by anaerobic digestion. Due to the high content of biogas (50-70%) biogas is combustible, and therefore, produces a deep blue flame and can be used as an energy source.

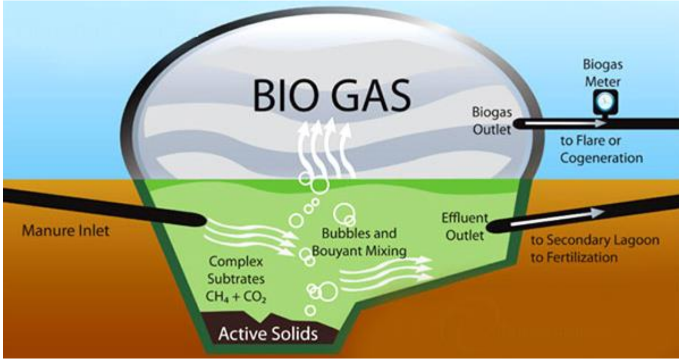

Figure 2.1 Anaerobic digestion

2.1.2 Biogas Composition

Biogas primarily consists of CH_4 and CO_2 with a small amount of N_2, H_2, H_2S, and water. The detailed composition of biogas is discussed in table1.

Table 2.1 Typical Biogas Composition

Compound	Formula	%
Methane	CH_4	50-70
Carbon dioxide	CO_2	30-50
Nitrogen	N_2	0-1
Hydrogen	H_2	0-5
Hydrogen sulfide	H_2S	0.1-0.3
water	H_2O	saturated

Energy Content: 500-700 Btu/SCF

In some cases, biogas contains siloxanes. They are formed from the anaerobic decomposition of materials commonly found in soaps and detergents.

1) Methane (CH_4)

CH_4 is a hydrocarbon that is a gas at room temperature (30°C). Its molecular formula is CH_4, so it has one carbon atom and four hydrogen atoms per molecule. It is often found as the main part of natural gas. CH_4 is a greenhouse gas 23 times more effective than CO_2.

2) Carbon dioxide (CO_2)

CO_2 is a clear gas composed of one atom of carbon (C) and two atoms of oxygen (O). CO_2 is one of many molecules where carbon is commonly found on the Earth. It does not burn, and in standard temperature and pressure conditions, it is stable, inert, and non-toxic. CO_2 occurs naturally in small amounts (about 0.04 percent) in the Earth's atmosphere.

3) Hydrogen sulfide (H_2S)

H_2S is a colorless gas having a strong odor of rotten eggs. Gas is very toxic by inhalation. H_2S occurs naturally in crude petroleum, natural gas, volcanic gases, and hot springs. It can also result from bacterial breakdown of organic matter.

Table 2.2 properties of CH_4, CO_2, and H_2S

	CH_4	**CO_2**	**H_2S**
Molecular weight, (kg/mol)	16.04	44.01	34.08
Density, at 1.013 bar, 15 °C	0.66	1.87	1.45
Critical Temperature, (°C)	-82.7	31	100
Pressure Temperature, (bar)	45.96	73.825	89.37
Compressibility Factor, (Z), at 1.013 bar, 15 °C	0.998	0.9942	0.9915
Sp. Gr., at 1.013 bar, 15 °C)	0.55	1.521	1.189
Specific Volume, at 1.013 bar, 21 °C	1.48	0.547	0.699
Heat capacity at constant pressure, (C_p), at 1.013 bar, 25 °C (KJ/mol-K)	0.035	0.037	0.034
Heat capacity at constant volume, (C_v), at 1.013 bar, 25 °C (KJ/mol-K)	0.027	0.028	-
Ratio, (C_p/C_v), at 1.013 bar, 25 °C	1.3054	1.2938	-
Thermal conductivity, at 1.013 bar, 0 °C (mW/m-K)	32.81	14.65	12.98
High heating value, at 1.013 bar, 15.6 °C (MJ/m^3)	37.63	-	12
Lower heating value, at 1.013 bar, 15 °C (MJ/m^3)	33.91	-	-
Solubility in water, at 1.013 bar, °C (vol/vol)	0.054	1.7163	4.67
Auto-ignition temperature, (°C)	595	-	270

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2.1.3 Application of biogas

Biogas has varied and uses for instance heating in household, cooking, and lighting. From the industrial aspect for example transportation fuel after being upgraded to biomethane combined heat, and power (CHP) generation, and upgraded to natural gas quality for other purposes. (Bharathiraja., 2018)

2.1.4 Biomethane

Biomethane is a renewable energy source produced by the natural breakdown of organic material green waste, household waste, agricultural waste, food industry waste, and even industrial waste. The process of breaking down this material in an oxygen-free environment produces biogas, which is then purified to become biomethane. This can be used as a vehicle fuel, distributed in the mains gas supply or used to generate green power.

Uses of biomethane can be reduced environmental pollution not only because it removes fossil fuel related pollution. As an alternative source of both electricity and heat, biomethane helps preserve forests and biodiversity by providing reduced levels of harmful greenhouse gas. Moreover, the use of biomethane does not increase the concentration of greenhouse gases in the atmosphere because CO_2 and other gases that create the greenhouse effect are released into the atmosphere during the decomposition process of organic matter. (Environmental benefits of biomethane., 2012)

For the utilization of biomethane in Thailand, there is no standard definition of biomethane. For the purpose of use, which focuses on the use of fuel for the internal combustion engine. Therefore, the standard should be referenced according to the Department of Energy Business, MINISTRY OF ENERGY, Subject: Defining characteristic and quality of Natural Gas for Vehicle (NGV), BE 2018, as shown in Table 2.3.

Table 2.3 Requirement and standard method according to the Department of Energy Business, MINISTRY OF ENERGY, BE 2018

Requirements	**Standard**	**Standard method**
1. Water dew point at pressure 20,000 kPa	≤ 4.4	ASTM 1142
2. Hydrocarbon dew point at pressure 4,500 kPa with less than 1% of liquid condensate 3. Methane number (MN Number) 4. Hydrogen, (%vol.) 5. Carbon dioxide (%vol.) 6. Oxygen (%vol.)	≤ 10.0 ≥ 65 ≤ 0.1 ≤ 18 ≤ 1.0	ASTM 1945 Calculation by Equation of state and GRI Method
7. Wobbe index*, (MJ/m^3)	≥ 39 and ≤ 44	ASTM 3350
8. Hydrogen sulfide, (mg/m^3) 9. Sulphur (mg/m^3)	≤ 23 ≤ 50	ASTM 5504

*Wobbe index (WI) is the indication of the heating value of the gas from the pipeline at the orifice where a burner is located, this could be a gas turbine or a boiler.

2.1.5 Biogas Upgrading

Biogas upgrading is a facility that is used to concentrate the CH_4 in biogas. The system removal CO_2, H_2S, humidity, and contaminants from biogas. The presence of H_2S and CO_2 mat effect the performance of biogas. Therefore, it must be removed before its use is crucial to improving the quality of biogas. The technique used for upgrading biogas to biomethane including water absorption, adsorption, PSA/VSA, cryogenic separation, biological methane enrichment, and membrane separation. The purified biogas is also called “biomethane”. The removal of humidity, CO_2, and H_2S as shown in table 2.4

1) Removal of H_2S

The H_2S content of biogas about 0.1-0.3%. This contaminant, beside the damage that H_2S can cause in piping and motor, bad smell, unhealthy and environmentally hazardous sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4). It is typically removed in an early state in biogas.

2) Removal of CO_2

After removal of H_2S, it is necessary to remove CO_2. The CO_2 is present in biogas with very high concentration. Its presence may result in reduced energy content, the lower heating value of the gas and the concentration of methane is not fixed causing incomplete combustion, unstable flame, and the performance of the system decreases.

3) Removal of humidity

Presence of humidity in biogas to be used as fuel may corrode parts of engine and fuel supply system. Also, this humidity may react with SO_2. This reaction produced H_2SO_4 which may corrode engine pipeline carrying exhaust gases and combustion system. The CO_2 reacts with humidity present in biogas to form a weak acid which will result to attack metals.

Table 2.4 Removal of humidity, CO_2 and H_2S from biogas

Component	Process	Method
Humidity	Adsorption	1. Silica gel 2. Molecular Sieves 3. Alumina
	Absorption	1. Ethylene Glycon at low temperature 2. selexol
	Refrigeration	1. Temperature about 2 ºC
CO_2 and H_2S	Adsorption	1. Organic solvent 2. Alkaline solution 3. Amines solution
	Absorption	1. Molecular Sieves 2. Activated Carbon 3. Alumina
	Membrane Separation	1. Hollow fiber Membrane

2.1.6 Removal of CO_2 and H_2S in biogas

1) CO_2 contamination problems in biogas

Biogas has methane (CH_4) mixed has a high heating value of about 35.64 MJ/m^3, but the large proportion of CO_2 mixed in biogas which will result in the lower heating value (21.6 MJ/m^3). In addition, the large proportion of CO_2 in biogas causes the concentration of methane (CH_4) is not fixed causing incomplete combustion, unstable flame, and the performance of system decreases. Therefore, it is necessary to upgrading biogas by reducing the proportion of CO_2 to produce biomethane with the component of methane about 95%. Various technologies are used to removal of CO_2 contaminants in biogas for producing biomethane as shown in Table 2.5.

Table 2.5 Advantages and disadvantages of technique to remove CO_2

Technique	**The purity of methane (% CH_4)**	**Advantages**	**Disadvantages**
Membrane	90-94%	1. High CH_4 purity 2. High efficiency of remove CO_2	1. Expensive investment 2. High energy demand 3. Complex setup
Water scrubbing	>97%	1. No chemicals 2. Simple in operation 3. Economical 4. High CH_4 purity	1. Requires a huge amount of fresh water 2. Expensive operation
MEA Chemical scrubber method	>98 %	1. High efficiency for remove H_2S 2. High efficiency more than Water scrubbing 3. Low CH_4 losses	1. Expensive investment 2. High energy demand 3. The heat required for regeneration
Pressure swing adsorption method - carbon molecular sieves - zeolites - alumina silicates	>95%	1. High efficiency for the adsorption process 2. Operate with low pressure 3. Easy maintenance	1. Expensive investment 2. CH_4 losses 3. Complex setup

2) H_2S contamination problems and H_2S removal in biogas

H_2S in biogas occurs naturally from the degradation of organic containing sulfur or sulfate with bacteria in anaerobic digestion. H_2S, also known as rotten egg, its have nuisance and disturbance to the community, industry, and areas that have a biological waste treatment process. H_2S has a high dissolved in water, can adhere to the soil, water sources, and sea. Many types of microorganism in the environment can oxidize H_2S to become sulfate and sulfur element.

H_2S is highly toxic to organism and plants. Contamination of H_2S at the level about 0-5 ppm in the air be able to olfactory. At the level above 10 ppm affect health, while the level more than 600 ppm causes lethal. H_2S in biogas is corrosive to most equipment such as pipelines, compressors, gas storage tanks, engines, etc. and acts as a strong poison for fuel cells and reformer catalysts. Furthermore, H_2S combustion leads to sulfur dioxide (SO_2) emission, which has harmful environmental effects (Allegue & Hinge., 2014). Therefore, it is necessary to the removal of H_2S early in the process of biogas upgrading. From the standard found that the level of H_2S contaminated in biogas should not exceed 4,000 ppm and commercial should less than 4 ppm as shown in Table 2.6

Table 2.6 Metrics for biogas quality based on the H_2S concentration (Martin, 2008)

Concentration of H_2S	**Usefulness of biogas**
4,000 ppm	Typical Biogas
600 ppm	High Quality Biogas
< 100 ppm	Safe for Natural Gas lines
< 4 ppm	Can be Sold Commercially

2.1.7 Absorption Process

1) Absorption

Gas absorption is a process in which atoms or molecules transfer from gas phase to liquid phase, a gas is contacted with a liquid for the preferentially dissolving component of gas and to provide a solution of them in the liquid as shown in Figure 2.2. There may be chemical and physical absorption.

1.1 Chemical absorption is a process when the absorbed component is bonded in the liquid phase as a chemical compound practically complete absorption is possible. Physical absorption is a process when gas dilution is not accompanied by a chemical reaction the component is absorbed until its partial pressure becomes higher than the equilibrium pressure of the solution. In the case of CO_2, the solubility of the gas depends on the solvent physical and chemical properties.

1.2 Physical absorption is a process when gaseous molecules of CO_2 are attached to liquid molecules with weak intermolecular forces, the physical is described as physical absorption. Therefore, the physical absorption process is usually operated at high pressure and low temperature to increase the CO_2 solubility in the absorbing liquid (Abdeen et al., 2016).

The method of gas absorption including of a packed column, plate tower, and simple spray column. However, the above method is mass transfer is not very efficient and blockages, the spray could lead to a large yield loss and some can not handle extremely high or low flow rate. The microbubbles 50-200 µm can increase the surface area and has the potential of enhancing gas-liquid mass transfer efficiency, thus it can be applied in the gas absorption process.

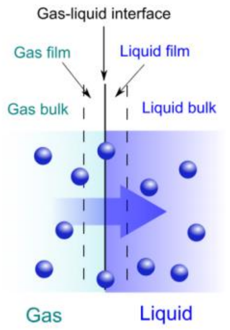


Figure 2.2 Gas-Liquid absorption.

2) Absorption process of CO_2 using water

Physical absorption used water to absorb CO_2. The driving force for the CO_2 in the solvent due to the solubility. Mostly, the solubility will increase with increasing pressure and decrease temperature. Generally, physical absorption will be taken into consideration when the CO_2 partial pressure is more than 3.5 bar and bulk removal of CO_2 is required (Ban., 2014). Factors affecting the physical process using water for removal of CO_2 as follows:

1. Pressure and temperature: the ability to absorbed CO_2 increase with high pressure and low temperature.
2. Contact time: the ability to absorbed CO_2 increase with increasing contact time due to longer solubility of CO_2 in water.
3. Surface area: the ability to absorbed CO_2 increase with more surface area.
4. pH of water: the ability to absorbed CO_2 increase with increasing pH.

CO_2 reacts with water a carbonic acid is formed as follows equation (1):

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO^-_3 \quad (1)$$

2.1.8 Microbubble generator

The microbubble that generated by venturi ejector due to the shear forces encountered in the diverging part. Normal macro bubbles rapidly rise and burst at the water surface, whereas microbubbles can exist for a long period underwater surface.

The microbubbles tend to gradually decrease in size and eventually disappear due to the dissolution of the interior gas into surround water. The extremely small diameter of microbubbles 50-200 µm can increase the total surface area of the cumulative bubbles and has the potential of enhancing gas-liquid mass transfer efficiency (Shangguan et al., 2018).

2.1.9 Venturi Ejector

A venturi ejector based on microbubble generation system makes use of conservation equations of mass and energy. The venturi ejector with its three unique sections including of the inlet, the suction throat and the outlet as shown in Figure 2.3. Water feed in through the inlet and as the section of the inlet to a minimum area at the throat, a low-pressure zone is created and gas is sucked in through the suction manifold. The gas phase and liquid phase flow of water along with the gas traverse the remaining section of the venturi injector where the microbubble generated due to the shear forces encountered in the diverging part (Li Pan., 2006).

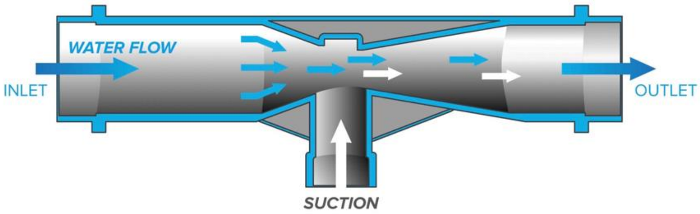


Figure 2.3 Venturi Ejector.

An evolution of the idea of using inline static mixer obtaining excellent mixing performances. After venturi ejector, the inline static mixer is installed where its internal blade vigorously breaks the CO_2 gas bubbles into microbubbles which increase the total surface area of the cumulative bubbles. This increase the CO_2 gas to liquid mass transfer surface area. Which in turn increase the efficiency of CO_2 mixing and increase the contact between the CO_2 gas and the water to maximize the amount of CO_2 dissolved in water. Finer the size of bubble more surface area which comes in contact with the water medium for CO_2 gas to liquid transfer. In Figure 2.4. It can be seen that finer the bubble more will be the number of bubbles in the same volume and more overall surface area.

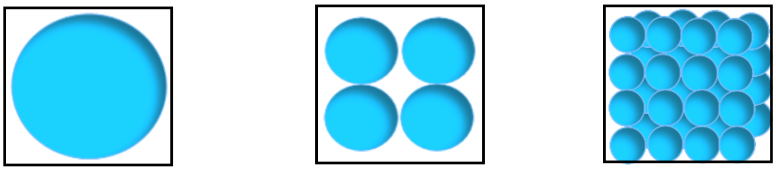


Figure 2.4 Bubbles in the same volume.

2.1.10 Inline Static Mixers

The inline static mixer is a distribute inside a pipe. This mixer is designed to create a pressure drop in two-phase flow through two perforated plates place facing one another and provide energy for dispersion as shown in Figure 2.5. Moreover, opposed jets are formed to create further shear, useful for breakup and homogenization of dispersed drops. Total energy per unit mass, E_m, as follows in equation (2):

$$E_m = Q\frac{\Delta P}{\rho V} \qquad (2)$$

Where Q is the flow rate, ΔP is the pressure drop, ρ is the liquid density, and V is the mixer volume.

The pressure drop (ΔP) can be either measured for a given design or estimated based on distributing open area and physical properties of the emulsion. In this type of mixer, energy dissipation can be on the order of 0.4 kW/kg. The maximum drop size of dispersion, d_{max}, is related to E_m as follows in equation (3):

$$d_{max} \alpha E_m^{-0.4} (\frac{\rho}{\sigma})^{-0.6} \qquad (3)$$

Where σ is the interfacial tension

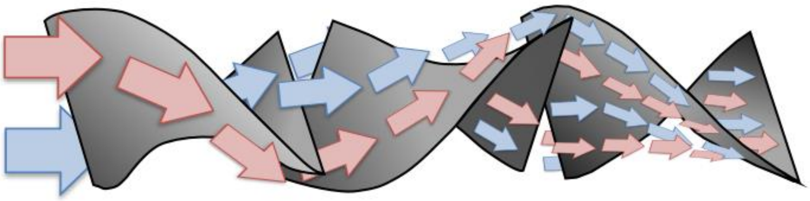


Figure 2.5 Inline static mixer flow diagram.

2.1.11 Measuring microbubble size

The microbubble was produced by venturi ejector. The size of microbubble was affected by gas flow rate. A bubbles size of the cumulative bubbles was measured by automated bubble size measurement to obtain the bubbles size distribution as well as the average diameter of the bubbles. The bubble size was determined by a MATLAB image segmentation program. From the image generated, the size of the microbubble data can be collected and analyzed by Microsoft Excel. Generally, the size of microbubble will increase with increasing the gas flow rate.

2.1.12 Absorption process using microbubble

Physical absorption is one of the well-established technologies used to remove CO_2 from biogas (Ban et al., 2014). The microbubble technique for the physical absorption process; whereby gas bubbles whose diameter is smaller than 50 µm spread throughout water. This microbubble offers numerous advantages in comparison to the conventional size bubble, such as in terms of very slow rising velocity. These special characteristics cause the gas bubbles to stay longer in the water result in high retention time means high solubility in the liquid phase. In addition, the characteristics of microbubble also result in the high gas-liquid contact area, which is increases mass transfer efficiency (Juwana et al., 2019).

2.1.13 Dissolution of CO_2 in water

1) CO_2 gas transfer to an aqueous solution

CO_2 molecules must first pass the air and water barrier to dissolved in water. When CO_2 crosses the water surface, the molecules gain shell water molecules and transfer from CO_2 gas or $CO_{2(g)}$ to CO_2 in an aqueous solution, or $CO_{2(aq)}$ according to equation (4):

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \qquad (4)$$

2) Reaction of CO_2 dissolving in water

Not all CO_2 molecules dissolved in water due to a fraction of them react with water to form carbonic acid (H_2CO_3) reacts as follows equation (5):

$$CO_{2(aq)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)} \tag{5}$$

3) Equilibrium between the dissolved CO_2 and H_2CO_3

Equilibrium is established between $CO_{2(aq)}$, $H_2O_{(l)}$, and $H_2CO_{3(l)}$ is shown in equation (6). Carbonic acid is weak and can dissociate to bicarbonate ($H_2CO_3^-$), hydrogen is produced from these reactions, which gives bicarbonate water a slightly acid pH as described by the reaction:

$$CO_{2(aq)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)} \leftrightarrow H^+ + HCO_3^- \tag{6}$$

4) Henry's law

Dissolution of CO_2 in water occurs spontaneously in nature. The amount of CO_2 that can be absorbed in water is given Henry's law is shown in equation (7), which state that the concentration of a CO_2 (c_{CO2}) dissolved in a liquid is proportionality, K_H is called Henry's constant and its value depends on the gas solvent and temperature.

$$c_{CO_2} = K_H * P_{CO_2} \tag{7}$$

For CO_2 the solubility increases with decreasing water temperature. Based on Henry's law, high pressure and low temperature will increase the amount of CO_2 absorbed by water. (Beiron., 2017)

2.1.14 Dissolution of CH_4 and N_2 in water

The solubility of CH_4 depends on several parameters, which are temperature pressure and salinity (Edwards., 2012). The interaction between molecules based on their polarities. CH_4 is hydrophobic in nature, given its non-polar structure. There are no lone pair electrons or any empty p-orbitals. So no recipient is fit for accepting a co-valency from the two lone pair electrons of the O_2 atoms in water. Hence, at room temperature and above it, CH_4 is insoluble in water. But in sub-cooled state, ie, below 0 °C, the pi-orbitals of C facilitate electron motion, and then CH_4's solubility increases. Figure. 2.6 show the solubility of CH_4 in water. This plot indicated that the solubility of CH_4 increases with decreaseing temperature.

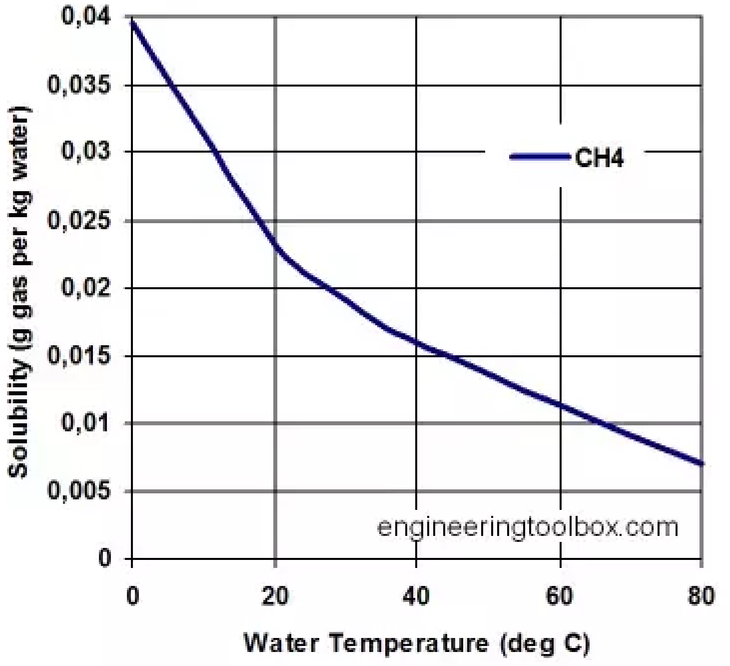


Figure 2.6 The solubility of CH_4 in water as a function of temperature.

Figure. 2.7 shows the solubility of N_2 in water. An intermolecular force of attraction applies to N_2, to H_2O molecules and to an N_2-H_2O interaction. Water has strong dipole forces because of hydrogen bonding. N_2 only has dispersion forces which are weak and more temporary. Therefore, at room temperature, N_2 is insoluble in water. From below plot, N_2 is soluble in water at 20 °C. And observed that the solubility of N_2 increases with decreasing temperature

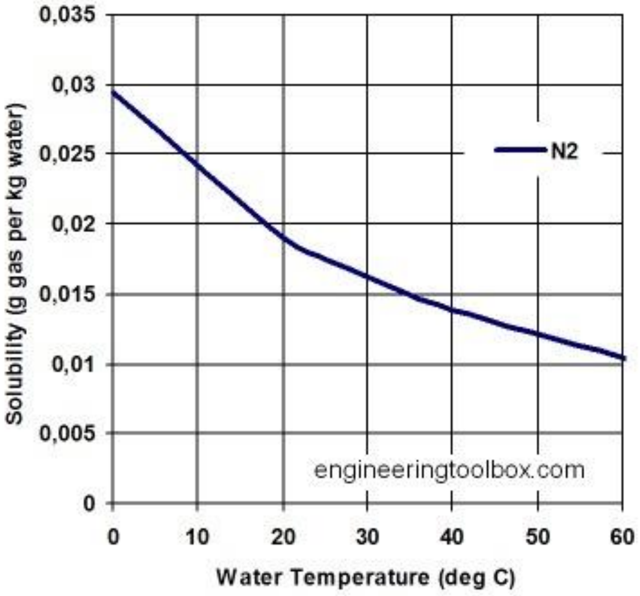


Figure 2.7 Solubility of N_2 in water as a function of temperature.

2.1.15 Desorption of CO_2 from water.

Process of removal of CO_2 from CO_2-rich water called “The regeneration process”. The regeneration process of water can be released CO_2 for the water gap to re-absorbed by counter-current air flow stream. This regenerates CO_2 saturated water can be releasing CO_2 from water and recirculated to the absorber for reuse. O_2 from air contact with CO_2-rich water has a resulting in deformation of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) to form CO_2 gas, which the CO_2 gas can separate from water. Figure 2.8. shows the solubility of CO_2 in water as a function of temperature.

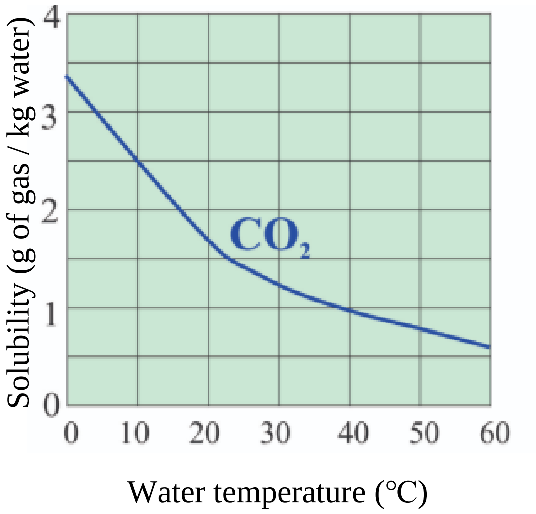


Figure 2.8 The solubility of CO_2 in water as a function of temperature.

There are many methods to release CO_2 from the water, such as heat, chemicals, solvent, and biological process, as follows:

1) Thermal regeneration: This method must control the temperature to appropriate for the substance that needs regeneration. Because it involves energy consumption. However, it is necessary to choose a suitable method for regeneration CO_2 saturated water. And should choose the appropriate reactor due to heat may cause corrosion and clog from the pyrolysis of remaining organic compound.

2) Chemical regeneration: This method is regeneration CO_2 saturated water by using chemicals. The disadvantage of this method is the price of a reagent which is expensive and the use of large quantities of chemicals may affect the operator and the environment.

3) Bioregeneration: The disadvantage of this method is to take a long time to the regeneration of CO_2 saturated water and be able to use only biodegradable substances.

2.2 Literature Reviews

2.2.1 Techniques of CO2 removal for upgrading biogas.

Ryckebosch et al., 2011 studied techniques for transformation of biogas to biomethane, various techniques were studied for removal CO_2 including chemical absorption, PSA/VSA, membrane technology, cyclonic separation, biological removal and absorption with water. This research showed that the absorption with water has high efficiency (>97% CH_4), low CH_4 losses (<2%), easy in operation and regeneration possible.

Tippayawong and Thanompongchart., 2010 studied method for biogas scrubbing. Chemical absorption of CO_2 and H_2S by aqueous solution in a packed column was experimentally investigated. The aqueous solution including sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) and mono-ethanolamine (MEA). Test result revealed that the aqueous solution used was effective in reacting with CO_2 in biogas (over 90% removal efficiency), creating CH_4 enrich fuel.

Yu et al., 2012, studied CO_2 capture by absorption and adsorption techniques. According to studies, it was found that chemical absorption is definitely more suitable than physical absorption to achieve CO_2 capture purpose. However, chemical absorption is an energy intensive process in which more than 60% of total energy consumed in stripper from thermal regeneration of CO_2-rich chemical absorption

Malie et al., 2007 studied the CO_2 absorption using monoethanolamine (MEA) as an absorbent in the continuous process. The digester was kept in a water bath to maintain a constant temperature throughout the experiments. N_2 was used to purge and generate an anaerobic condition in the process. 10-30 %wt. of MEA solution was used as an absorbent. The result showed that CO_2 removal efficiency increased from 66% at room temperature and 77% at 40 ℃.

Malie et al., 2017 studied CO_2 absorption in biogas using Sodium hydroxide (NaOH) as an absorbent at the concentration about 1M, 2M, and 3M as shown in Figure 2.9 They've found that the concentration increased, the absorption rate and CO_2 removal efficiency were increased. The highest CO_2 removal efficiency was recorded to be 66%.

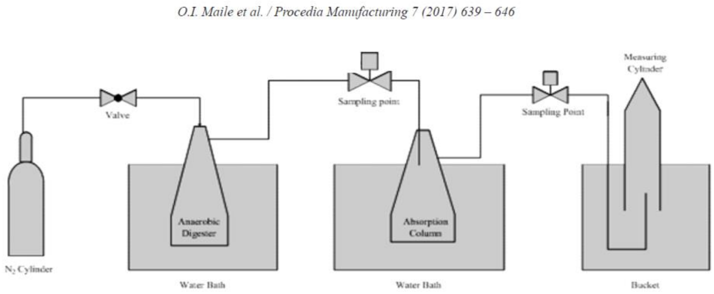


Figure 2.9 CO_2 absorption process using Sodium hydroxide (NaOH) as an absorbent (Malie et al., 2017).

Malie et al., 2017 studied biogas cleaning system using Fe-EDTA solution to absorb CO_2 and H_2S from the residual biomass treatment in bench-scale and pilot-scale as shown in Figure 2.10 The experimental investigation of L/G ratio, Fe-EDTA liquid flow, gas flow rate, and concentration of Fe-EDTA with CCRD method. Both of bench-scale and pilot-scale were found a similar trend. That is increased L/G ratio and Fe-EDTA concentration, the H_2S removal efficiency was increased. The H_2S removal efficiency was 99% after 35 minutes in bench-scale, using Fe-EDTA 0.2 mol/L and L/G ratio 1.27. On a pilot-scale, the H_2S removal efficiency was 98% with CO_2 removal 18%.

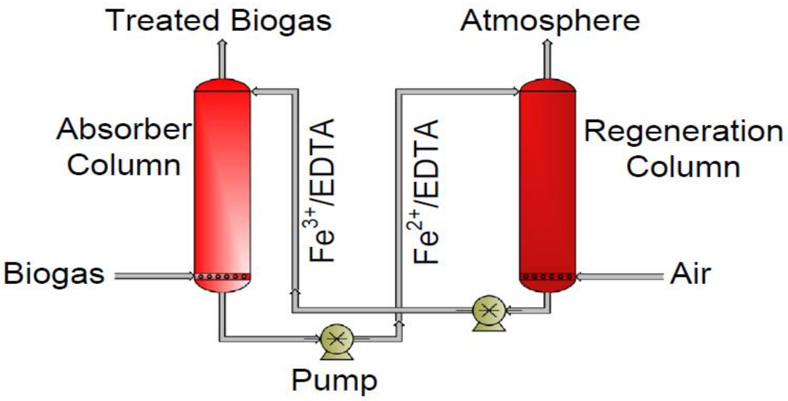


Figure 2.10 Biogas cleaning system (Malie et al., 2017).

Liu et al., 2015 studied multistage cross-flow membrane reactors with a continuous process as shown in Figure 2.11. Various parameters consisted of concentration $Ca(OH)_2$, flow rate, additives, gas flow rate membrane length and the connecting pipe length were investigated to select suitable parameters. The result showed that long membrane, high slurry gas flow rate, connecting pipe, the dosage of additive and low gas flow rate, causing the high CO_2 removal efficiency. While the concentration of $Ca(OH)_2$ has little effect on the process. After that, suitable parameters were introduced in the 2-stage membrane reactor that can create gases that have CO_2 less than 3% and generate nano Calcium carbonate ($CaCO_3$) with a size of 72.8 nm.

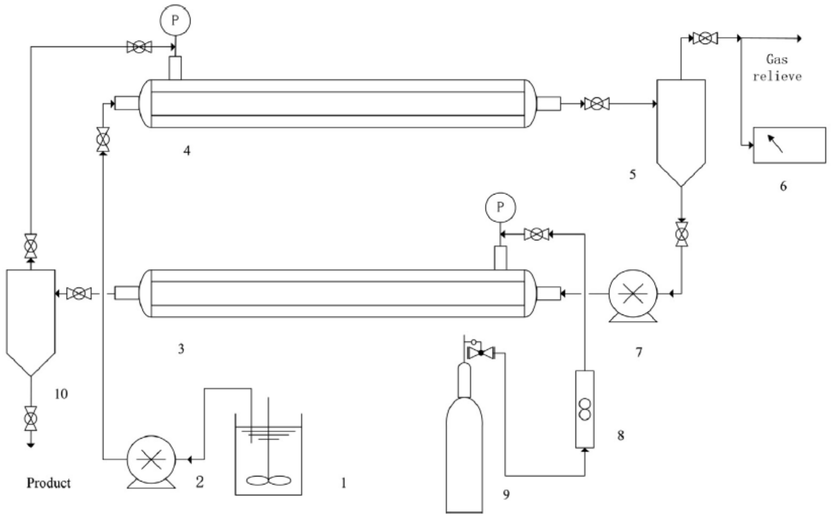


Figure 2.11 Multistage cross-flow membrane reactors with a continuous process 1: Solution tank 2 and **7**: Peristaltic pump 3: Second stage reactor 4: First stage reactor 5 and 10: Gas and liquid separation equipment 6: Gas analysis equipment 8: rotameter 9: Gas cylinder (Liu et al., 2015).

Khan et al., 2015 studied CO_2 absorption from fuel gas using 2-amino-2-methyl-1-propanol (AMP) and monoethanolamine (MEA) as an absorbent. To compare the effectiveness of both absorbent types. Regeneration process using thermal regeneration method with considering absorption rate, the amount of CO_2 entering, the amount of CO_2 remaining after the regeneration process, and the percentage of CO_2 absorption. They are found that the absorption rate of AMP and MEA is (2.11-4.03)*10^{-5} kmol/m^2s and (5.36-9.55)*10^{-5} kmol/m^2s, respectively. MEA can absorb up to 99.13% and AMPcan absorb up to 98.88%. The regeneration of AMP is in the range of 96.39-97.26%, better than MEA which is n the range of 79.91-81.51%.

Rongwong et al., 2012 studied CO_2 and H_2S adsorption from biogas with capillary membrane contactor. Synthetic biogas contains H_2S about 250-1000 ppm, CO_2 and CH_4 about 20-40%. This process using water and monoethanolamine (MEA) as an absorbent. The effect of liquid flow rate, gas flow rate, gas composition, adsorption efficiency, and specificity of H_2S were investigated with mass transfer resistance analysis of capillary membrane contactor system. The result showed that the MEA solution had more CO_2 and H_2S adsorption rate than water. The H_2S adsorption rate increased, the gas and liquid flow rate were increased, the concentration of H_2S was increased. While the CO_2 adsorption rate is slightly higher with the liquid flow rate and MEA concentration is higher. The increasing concentration of CO_2 causes the hydrogen flux to decrease. The result of the analysis of the mass transfer resistance and H_2S. In contrast, the mass transfer of CO_2 depends on the liquid resistance. The resistance of membrane controls the CO_2 but does not affect on H_2S adsorption. The effect of wet membrane on CO_2 and H_2S adsorption at 6 hours showed that CO_2 flux decreased about 7.6% and the flux of H_2S was slightly changed.

Kadam and Panwar, 2017 studied various parameters of biogas technology. That is widely used. To compare various parameters consisted of pre-cleaning needed, working pressure, methane loss, methane content, electricity consumption, heat requirement, and controllability compared to nominal load. The water scrubbing technique is the most popular, followed by PSA and chemical absorption as shown in table 2.7 and 2.8

Table 2.7 Comparison of various parameters in each technique of biogas purification

Parameter	PSA	Water scrubbing	Organic physical scrubbing	Chemical scrubbing
Pre-cleaning needed	Yes	No	No	Yes
Working pressure, (bar)	4-7	4-7	4-7	No pressure
Methane loss	<3%/6-10%	<1%/<2%	2-4%	<0.1%
Methane content in upgraded biogas	>96%	>97%	>96%	>99%
Electricity consumption, (kWh/Nm^3)	0.25	<0.25	0.24-0.33	<0.15
Heat requirement, (℃)	No	No	10-100%	50-100%
Controllability compared to nominal load	+/- 10-15%	50-100%	10-100%	50-100%
References	>20	>20	2	-

Table 2.8 Comparison of technical availability and maintenance cost

Upgrading technology	**Technical availability, (%)**	**Maintenance cost, (€/yr)**
PSA	94	56,000
Water scrubbing	96	15,000
Chemical (amine) scrubbing	91	59,000
Physical absorption	96	39,000
Membrane separation	98	25,000

in each technology of biogas purification

2.2.2 Physical absorption for removal CO_2 with water.

Xiao et al., 2014 studied CO_2 removal from biogas by water washing system. Various parameter including to CO_2 content, pressure and liquid to gas ratio were investigated. The volume fraction of CO_2 in the simulated gas in the range of 25% to 45 . The pressure in system of about 0.8-1.2 MPa and the gas flow rate of 400-700 L/h. The flow rate on the top water and cooling water in the heat exchanger were adjusted at 100-200 and 150 L/h, respectively. The outlet gas stream of the absorption tower was collected. Concentration of CO_2 was analyzed by a gas chromatograph every 0.5 h. The result showed that CO_2 removal ratio was increased from 34.6% to 94.2% as the liquid-to-gas ratio increase from 0.14 to 0.50. Relatively higher pressure improves CO_2 removal ratio. The lower temperature is beneficial for CO_2 removal.

Rasi et al., 2007 studied a pilot-scale counter-current absorption process for upgrading landfill gas to produce vehicle fuel using absorption and desorption unit, water was used as an absorbent. Upgrading efficiency was studied using pressure at 10, 15, 20, 25, and 30 bar, water flow rate at 5 and 10 L/min and gas flow rate at 50 and 100 L/min. The sampling was measured with Perkin-Elmer Auto system XL gas chromatograph by using a thermal conductivity detector (TCD). The result showed that methane content above 90% at pressure 20 bar with 10 L/min of water flow rate and carbon dioxide removal efficiency increase with increasing pressure at a constant absorbent flow rate.

Rasi et al., 2014 studied biogas upgrading using water as an absorbent with high pressure as shown in Figure 2.12. The system consisted of absorption, desorption and gas drying. The biogas was upgraded in two phases with two columns operating in sequence in pressure up to 180 bar, and initial pressure about 8 and 10 bar. The content of CH_4, CO_2, and N_2 in the product gas is in the range of 83-92.1%, 4.4-6.3%, and 2.5-7.4%, respectively. The H_2S removal efficiency over 99%.

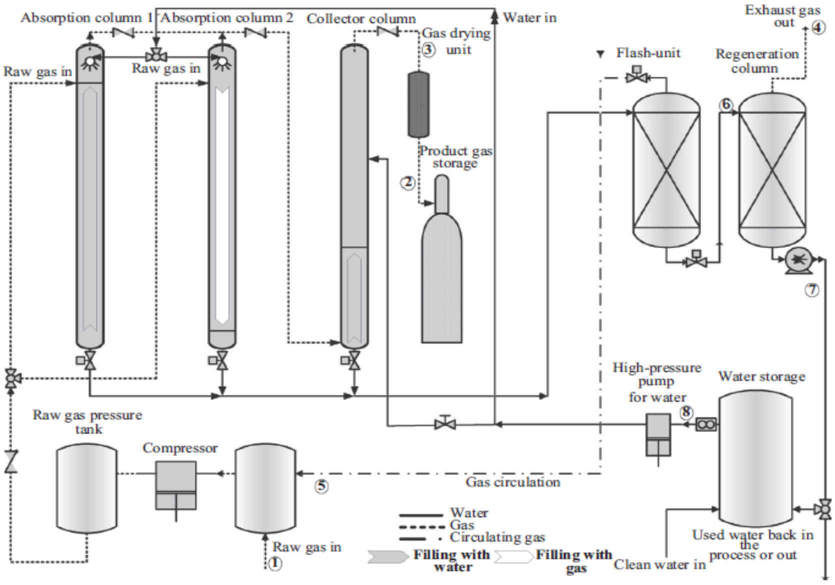


Figure 2.12 Process of biogas upgrading using water as an absorbent with high pressure 1: raw gas 2: Gas after drying unit 3: Gas drying 4: Exhaust gas out 5: Gas circulation 6: Water inlert 7: Water outlet 8: water from water storage tank (Rasi et al., 2014).

Shah and Nagarsheth., 2015 studied low-cost biogas purification system and they can convert raw biogas into bio CNG which can be used using vehicle fuel, using water scrubbing. The column was used at 6 feet 4 inch in a pipe made of UPVC having diameter 4 inches. Water was pumped using a pump of capacity 1100 L/h and head of 10 feet and was sprayed through a nozzle. The result showed that the percentage of methane and carbon dioxide in raw biogas which was 61.22% and 32.01%, respectively. After scrubbing the percentage of CH_4 increase to 89.54% and the percentage of CO_2 decrease to 5.02%.

Islamiyah et al., 2015 studied to designing a biogas purification of water scrubbers to reduce CO_2 and H_2S in the biogas. Purification column of biogas a diameter 6 dim and column height of 1.5 m. The mass ratio of water and cow manure

1:1 inside the biogas reactor. The result showed that the efficiency level of H_2S gas from removal was 32.8% and the level of CO_2 which has 21.2% efficiency. As for purification tool that has been designed is capable of reducing CO_2 and H_2S in the biogas in very short period of 15 min. This is due to the H_2S gas has a high solubility in water than CO_2. The solubility of H_2S in the liquid phase is higher than CO_2 at the same pressure and temperature.

Boateng and Kwofile., 2009 studied a method of biogas purification by using water scrubbing. The apparatus used in this study contained a 300 mm in diameter and 9800 mm in a height of scrubber. The pressure of biogas and water used for scrubbing were 1000 kPa and 1300 kPa respectively. The result showed that the designed biogas water scrubber is able to remove 93% v/v of CO_2 present in raw biogas.

2.2.3 Solubility of CO_2 in water

Someya et al., 2005 studied the solubility of CO_2 in pure water was investigated under high pressure conditions, from 7 to 12 MPa. Temperature varied between 2.5-20 °C. CO_2 clathrate formed at temperatures below approximately 10 °C. Saturated concentration of CO_2were determined from expanding dissolved gas. It’s was found that the solubility in the presence of the hydrate universally decreases with decreasing temperature and pressure.

Sevio and Englezos., 2001 studied the solubility of CO_2 in pure water in the presence of CO_2 gas hydrate have been measured at temperatures between 273-284 K and pressure between 20-60 bar. It was found that the solubility decreases with decreasing temperature in the hydrate formation region and the solubility is not a strong function of pressure over the hydrate formation region.

2.2.4 Microbubble generator

Yin et al., 2015 studied in a venturi type bubble generator to evaluate the development of the bubble size distribution in the flowing water stream through small feed holes, it breaks into bubbles in the diverging section of the venturi tube as shown in Figure 2.13 The gas flow rate ranges from 0.007 to 0.152 m^3/h. The liquid flow rate ranges from 7 to 19 m^3/h. Renolds number ranges from 107,000 to 291,000 and the velocity ratio of gas phase to liquid phase ranges from 0.053 to 0.32. The result showed that the bubble size has a great influence on the mass transfer rate. Base on the results of Kress's formulation on turbulence dissipation rate, the bubble size correlation with Renolds number and the surface tension coefficient was derived.

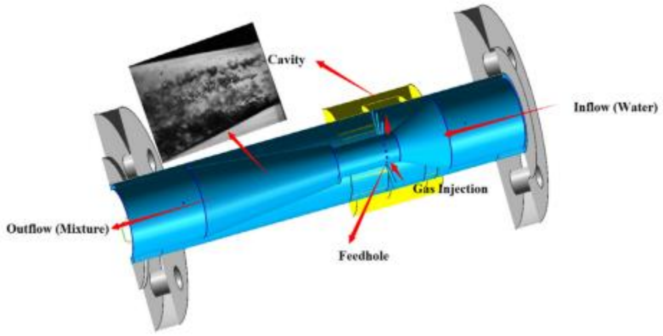


Figure 2.13 Bubble generator configuration with the flow paths information (Yin et al., 2015).

Sadatomi et al., 2005 studied a new microbubble generator with a spherical body in a flowing water tube as shown in Figure 2.14. In the generator, pressurized water is introduced into a pipe with a spherical body in the core. Placing the microbubble generator at the depth of 0.21 m in a water tank of 0.15 m^3. The different pipe diameter, D = 11, 12 and 13 mm, at fixed sphere diameter of 9.53 mm. In the experimental, the hydraulic power needed to introduce water, the bubble generation efficiency, and the variation of the dissolved oxygen in water after bubbling were obtained by changing the water supply rate systematically. The result showed that the optimum diameter ratio of spherical body to the pipe is 0.865 and confirmed that the generator could generate microbubble with a lesser energy consumption rate within 40 W and raise effectively the dissolved oxygen.

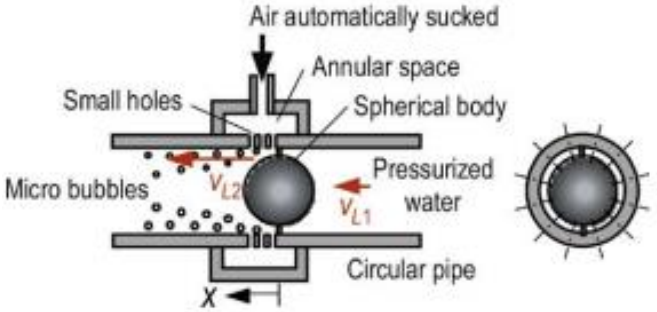


Figure 2.14 Illustration of Sadatomi's micro-bubble generator (Sadatomi et al., 2005).

Ohnari and Suppanasha, 2006 studied the use of vortical flow from the pump to created a rotating flow, causing the pressure drop in the central axis. The gas is sucked into the low-pressure area. The gas and liquid were mixed to become microbubbles due to the shear forces, occurring in a cylindrical as shown in Figure 2.15. The liquid flow rate can be increased to 12 LPH. The rotating speed of gas and liquid mixing can be used in the range of 300-600 RPS. The liquid-to-gas ratio is in the range of 1/7-1/15. The diameter of the bubbles is in the range of 10-50 µm.

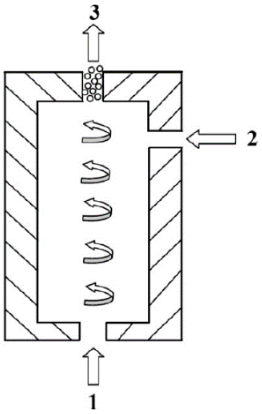


Figure 2.15 Microbubble generator 1: Liquid inlet, 2: Gas inlet, 3: microbubble (Ohnari and Suppanasha, 2006).

Fujikawa et al., 2003 generated microbubbles using venturi. The gas and liquid were sent into venturi at the same time to create microbubbles as shown in Figure 2.16. The fluid pressure is compressed into the entrance. When passing through the pipe, the acceleration of gas and liquid due to pressure drop resulting in a size of 100 µm of the bubbles.

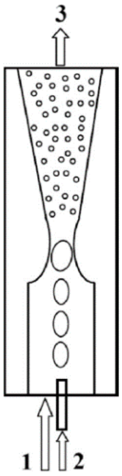


Figure 2.16 Venturi type

Venturi type 1: liquid inlet 2: gas inlet 3: microbubble (Fujikawa et al., 2003).

Yanuno et al., 2004 created microbubbles using microchannel technique as shown in Figure 2.17. The average size of bubbles that can be created in the range of 33.6-51.1 µm. The size of the microchannel is 15*15 m^2 with a diameter of 1 mm at the center. The four edges are 100 µm in the height and the length of 10 nm had been to create on the microchannel.

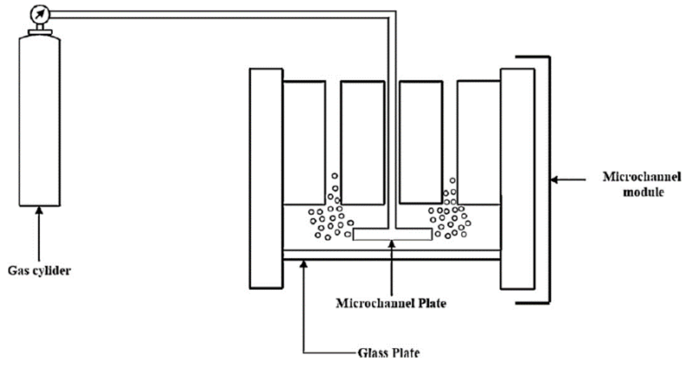


Figure 2.17 The microbubble generator using microchannel (Yanuno et al., 2004).

Hasagawa et al., 2008 developed low-power and compact nozzle with the slit inside the pipe as shown in Figure 2.18. The liquid flow rate is 13.5 L/min. The pump creates pressure inside the nozzle to be lower than outside, resulting in the gas to be sucked by itself and through the slit inside the pipe. The shear force is created by changing the liquid flow direction from the angle of the slit which generated the microbubbles. The size of microbubbles is in the range of 40-50 µm.

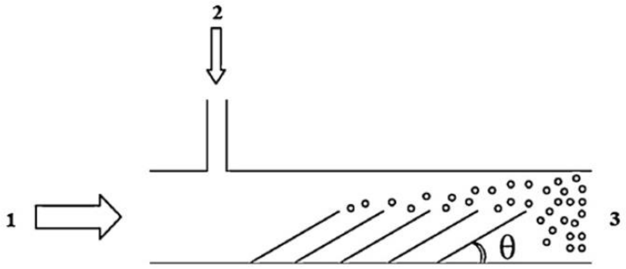


Figure 2.18 The small bubbles generator using shear force in a pipe and slit 1: Liquid inlet 2: Gas inlet 3: microbubble (Hasagawa et al., 2008).

2.2.5 Microbubble enhancing absorption

Juwana et al., 2019 studied the characteristics of oxygen (O_2) dissolution into the water in aeration using an orifice type microbubble generator (MBG). The average diameter of the bubble generated in this work is in the range of 300 µm and 1000 µm. The three parameters, air flow rate ranges from 0.1-1.0 L/min, water flow rate ranges from 30-80 L/min and the volumetric mass transfer coefficient of O_2 were investigated. The results confirmed that the size of microbubble depends on air and water flow rates. The gas flow rate increase the average bubble diameter was increased. Conversely, the water flow rate increase the average bubble diameter was increased. Moreover, the O_2 volumetric mass transfer coefficient increase with an increased water flow rate.

Xiao and Li., 2019 studied the simultaneous removal of NO and SO_2 using the microbubble gas-liquid dispersion system (MBGLS). The effects of the temperature of the absorption liquid, initial pH and the additives air, H_2O_2 and/or $Na_2S_2O_8$ were brought into the MBGLS were investigated. The result indicated that NO removal efficiency and SO_2 removal efficiency reached 78% and 94.4%, respectively. The additives significantly improved the removal performance of the MBGLS. Under the room temperature and pH=8, the addition of SO_2 and air was removed completely and the NO removal efficiency reached 99.5% with $Na_2S_2O_8$ to H_2O_2 molar ratio was 0.005/0.05.

Ying et al., 2013 studied the enhancing of mass transfer in microbubble driven airlift bioreactor for microalgal culture. The effect of microfluidic microbubbles on overall gas-liquid mass transfer (CO_2 dissolution and O_2 removal) was tested under five different flow rates. The effect of different liquid substrate on CO_2 mass transfer properties was also tested. The results indicated that the K_La can be enhanced by either increasing the dosing flowrate or decreasing the bubble size. However, increasing the flow rate to achieve a higher K_La would ultimately lower the CO_2 capture efficiency. In order to achieve both higher CO_2 mass transfer rate and CO_2 capture efficiency, decreasing bubble size by using microbubble.

CHAPTER 3

MATERIAL & METHODOLOGIES

In this research, it was intended to determine the optimum condition of biomethane production from biogas using water absorption with microbubble technique. In our previous work, simulated was tested biogas to confirm that the CO_2 is removed from the system and prove that the system upgraded biogas to biomethane by observing N_2 concentration in outlet gas stream. In the end, we used biogas to prove that the system upgraded biogas to biomethane by investigating CH_4 concentration in outlet gas stream. Regeneration of CO_2-rich water also studied for releasing CO_2 from CO_2-rich water and water can be reused continuously in the system. Results in this system can reduce energy consumption, which reduces operating costs. The detail of material, equipments, and methodologies of this research can be explained as follows:

3.1 Materials and equipment

The experimental unit was in the Department of Chemical Engineering, Prince of Songkla University. The experiments were done by using the CO_2 and N_2 gases with a purity that was introduced into and mixed well in a gas mixing unit to produce simulated biogas having 20-40% CO_2. The simulated biogas is fed into the CO_2 absorption process for a prototype unit and development of prototype for removal of CO_2 in biogas. Biogas from the wastewater treatment system of SONGKLA CANNING PCL. was applied in the system. The materials and equipment for CO_2 absorption process for the study of biomethane production can be divided into four parts as follows:

3.1.1 Tap water: Tap water was used in this research from the Department of Chemical Engineering, Prince of Songkla University, Hatyai Thailand.

3.1.2 Biogas feed to system

1. Simulated biogas

The materials and equipment are prepared and used as follows:

1.1 The pure CO_2 gas cylinders were purchased from Linde (Thailand) Public Company Limited.

1.2 The pure N_2 gas cylinders were purchased from Linde (Thailand) Public Company Limited.

1.3 Gas mixing unit: A cylinder tank with a diameter 0.18 m and height 1 m.

1.4 Gas flow meter: A gas flow meter (rotameter) is a device that measures the gas flow rate of simulated biogas and biogas in the range of 0-10 L/min, 1-5 L/min and 1-3 L/min. The device is installed according to the resolution of the use of the gas stream entered.

2. Biogas from anaerobic fermentation

Biogas was used in the CO_2 absorption process to produce biomethane production deriving from SONGKLA CANNING PCL., Songkla Thailand. The amount of wastewater entering the treatment system about 2500-3000 cubic per day that can produce biogas continuously. Biogas produced in the wastewater treatment system mainly composed of CH_4 about 69.94%, CO_2 about 27.25%, and H_2S more than 1000 ppm.

Figure 3.1 Anaerobic fermentation of wastewater treatment system.

3.1.3 Biogas sample storage

1. Wheel inner tube: 20 tube pneumatic tires with a volume of 30 – 40 L as shown in Figure 3.2 in order to collect the biogas from SONGKLA CANNING PCL. for the experimental purpose in the development of prototype unit. The wheels must be cleaned by purging with N_2 in order to prevent the contamination by other gases in the stored gases because the contaminations might result in erroneously experimental results. While storing the biogas, the tube pneumatic tires would pass the moisture removal system in order to dehumidify the biogas.

Figure 3.2 Biogas storage wheel.

2. Air compressor: A device as shown in Figure 3.3, was used for collecting the biogas from the wastewater treatment system of SONGKLA CANNING PCL. for the experimental purpose. The air compressor oil free kt-of-30 had a capacity of 30 L and the pressure of 7 bar. It was also used for increasing the pressure for transferring the biogases into the venturi ejector since the ejector had a high-pressure drop. Hence, the biogas must be sucked from the storage wheels into the air compressor before the biogas was transferred into the venturi ejector in order to overcome the pressure drop in the ejector.

Figure 3.3 Air compressor.

3.1.4 Equipments of the experimental setup

1. Venturi ejector: A black plastic venturi ejector as shown in Figure 3.4 was applied to create microbubbles of simulated biogas and biogas in liquid water. 0.25-inch and 0.5-inch venturi ejector were used in this research.

Figure 3.4 Microbubble generator.

2. Inline static mixer: A device that is an excellent mixing of the gas bubbles with the aqueous phase as shown in Figure 3.5.

Figure 3.5 Inline static mixer.

3. Pipe fitting and silicone tube: A device for connecting the gas stream entering and exit from the process, which is separated and combined in many points.

4. Rotameter: A device for measurement of gas flow rate and liquid flow rate. The rotameter for measuring the gas flow rate of simulated biogas and biogas in the range of 0-10 L/min, 1-5 L/min and 1-3 L/min. For measuring water flow rate the rotameter in the range of 5-50 L/min was used.

5. Water storage tank: A 100 L plastic water storage tank for filling the water before fed to the process and use as a collecting CO_2 saturated water for circulating water system.

6. Water pump: 0.37 kW/0.5 HP centrifugal pump is used in the process. The pump is used for the transfer of liquid into the process.

7. Absorption column: 25 L of an acrylic absorption column with a diameter of 0.18 m and height 1 m, diagram.

8. Tube absorber: The tube absorber that is improved in order to result in the absorption in the spiral tube that is 0.016 meters in dia. 10 m. of long and to mix and absorb the CO_2 bubbles in the water instead of being absorbed in the column.

9. Gas separation columns: A PVC pipe was used in the experiments were designed in order to obtain two columns with a diameter of 0.3 m. and a height of 1.8 m. for separate the high amount of CH_4 gas after taking CO_2 from the water

10. Spray nozzles: A full cone sprial nozzle at a spray angle of 60 and 120 would be installed inside the gas separation columns as shown in Figure 3.6 for spraying the water in order to release gases that are not absorbed in the water from the water inside the columns.

Figure 3.6 Spray nozzle.

11. pH meter (models PH100 and PH110): A device for measuring the pH of water in the CO_2 absorption process, which is used as a Pen type, is shown in Figure 3.7 pH indicates the saturation of CO_2 in the water or the amount of CO_2 dissolved in water.

Figure 3.7 pH meter.

12. Impinger: A device as shown in Figure 3.8 used for collecting gas samples by absorbing the gas in the liquid contained in the bottle. After that, take the liquid that has been titrated for analysis of the concentration of gas that need to be measured.

Figure 3.8 Impinger.

13. Silica gel: A blue silica gel was used to absorb moisture from biogas in order to obtain dry biogas.

14. Steel wool: 0.8 kg of steel wool is contained in the H_2S removal column to react with H_2S in biogas feed stream.

3.1.5 Equipments for gas sampling and analysis

1. Gas chromatography, GC: A device used in analytical chemistry for separating and analyzing gas compounds without decomposition. In this research, use a gas chromatography 14A, Shimadzu, Japan with a TCD detector and Porapak Q packed column.

2. Gastec pump: A pump (model LP-1200) comprises a handheld Gastec sampling pump and Gastec detector tubes as shown in Figure 3.9. A device is used with a sorbent tube and tubing for connecting the components. After that, pull the handle all the way out until locks at one stroke. Wait 45 seconds and confirm the completion of the sampling. Then, read the concentration level at the interface where the stained reagent meets the unstained reagent.

Figure 3.9 Gastec pump.

3. Detector tube: In this research, two types of detector tubes were used. For analysis, the concentration of CO_2 and H_2S as shown in Figure 3.10. The colour in the detector tube changes as the gas is drawn in. Simply wait the required sampling time and read the measurement at the end of the colour changed layer. However, the sorbent tube should be chosen with the appropriate concentration for use.

(A) (B)

Figure 3.10 Detector tubes for analysis the concentration of CO_2 (A) and H_2S (B).

4. Sampling pump: A pump for collecting gas samples into a sampling bag for analysis of the concentration of gases. The pump must be able to control the gas flow rate consistently and high accuracy, as shown in Figure 3.11.

Figure 3.11 Sampling pump.

5. Sampling bag: 1 L of the sampling bag as shown in Figure 3.12 was used to collect gas samples. Make sure that, it should not contaminate by any means. Filling the gas into a sampling bag up to 90% of the total capacity to avoid the leakages and bag deformation. For reuse, flush the sampling bag thoroughly with inert gas or purified air 2-3 times.

Figure 3.12 Sampling bag for collect gas sampling.

3.2 Research methodologies

In this research, the production of biomethane to upgrade the quality of biogas by removing CO_2 and H_2S in order to enrich CH_4 content up to the natural gas, which is 90%. The removal of CO_2 in biogas using water absorption column and microbubbles technique. The removal of H_2S in biogas using a spray column with steel wool. The CO_2 saturated water can be recirculation continuously in the system by the regeneration process. In order to save resources and have low operating costs. The details of the research methodology and data analysis can be described as follows:

3.2.1 Biogas preparation system

There are two types of biogas were used in the system. First, simulated biogas was used to find the optimum conditions. Then, the biogas from the wastewater treatment system was used in the system to produce biomethane.

1. Simulated biogas generation system: In the prototype unit, the simulated biogas generated by mixing of CO_2 and N_2 from gas cylinders. The N_2 gas is used as the main component of simulated biogas because N_2 has similarly low water solubility as CH_4 in biogas. The simulated biogas generation system as shown in Figure 3.13.

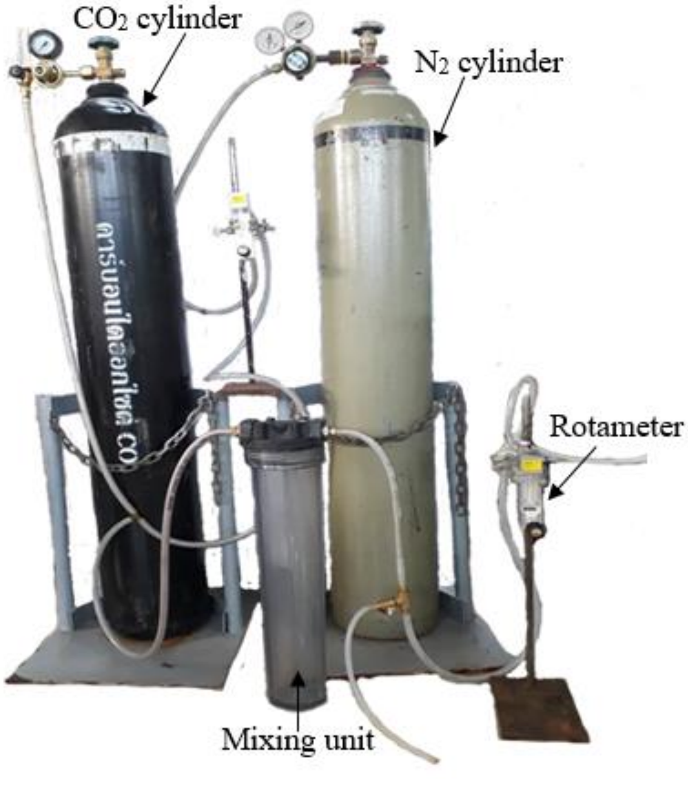


Figure 3.13 Simulated biogas generation system.

1.1 Prepare CO_2 and N_2 gas 6 m^3 cylinders tank and pressure 250 bar which is installed according to safety guidelines. There are two sets of a valve, which are used to adjust the gas flow rate from cylinders.

1.2 The proportions of CO_2 and N_2 are adjusted using a manual valve. And use rotameter for reading flow rate in the range of 1-5 L/min.

1.3 The both gas through the rotameter into the mixing tank for well mixed and stable concentration before sent into the system.

1.4 The concentration of CO_2 was analyzed by gas chromatography.

2. Biogas from anaerobic fermentation

Proceeding for collect biogas from wastewater treatment of SONGKLA CANNING PCL as follows:

2.1 The components of biogas consisted of CH_4, CO_2 and H_2S were measured. The concentration of CH_4 and CO_2 were analyzed by gas chromatography. The H_2S concentration in gas stream was performed using a detector tube method. Biogas produced in the wastewater treatment system from SONGKLA CANNING PCL. mainly composed of CH_4 about 69.94%, CO_2 about 27.25%, and H_2S more than 1000 ppm.

2.2 An inner tube pneumatic tires and compressor were used to collect biogas. The removal of H_2S unit was installed to control the concentration of H_2S (<1000 ppm) (Martin.,2008) before fed into the system. The removal of H_2S using the spray column with 0.8 kg of steel wool, which is to prevent the corrosion in the compressor.

3.2.2 Microbubble generator system

In this research, a venturi ejector was used to generate a microbubble. In addition, the device was used to increase the surface area between the gas phase and the liquid phase. Resulting in an increase in the CO_2 removal efficiency in the system. The details of the microbubble generator system can be described as follows:

1. The venturi ejector has a cylindrical made of black plastic. There are three unique sections including the inlet, the suction throat and the outlet as shown in Figure 3.4

2. Install the venturi ejector in the system as shown in Figure 3.14 Water feed through the inlet and as the section of the inlet to a minimum area of at the throat, a low-pressure zone is created and gas is sucked in through the suction at the same time.

3. The water along with the simulated biogas in the venturi ejector, which is to create a microbubble due to the shear forces encountered in the low-pressure zone.

Figure 3.14 Microbubble generator system.

3.2.3 Absorption Column

Absorption column was a tool that makes CO_2 be absorbed in water as an absorbent. In this study, the microbubble structure was applied to creating gas bubbles with large gas surface areas. CO_2 has better solubility than those of N_2 and CH_4 for about 70 times. Accordingly, N_2 and CH_4 in the gases still were in the main gas flows and not dissolved with CO_2. Therefore, CO_2 was taken and removed from the gases. For this test, the mixing of simulated biogas bubbles and liquid water by using microbubble generator was fed to the bottom of column. The CO_2 was absorbed into water flow and upward to the top and flow out of the column. The N_2 that is not absorbed was separated from the water. The absorption column was installed as shown in Figure 3.16.

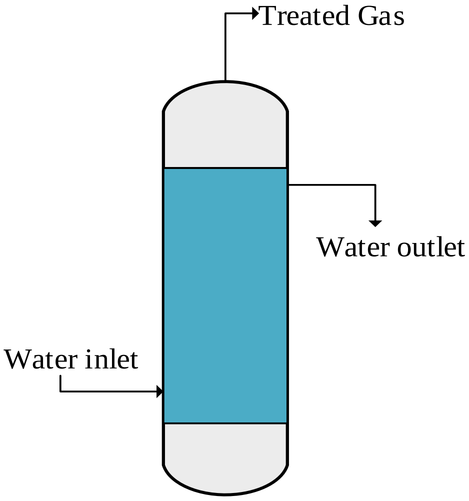


Figure 3.15 Schematic diagram of absorption column.

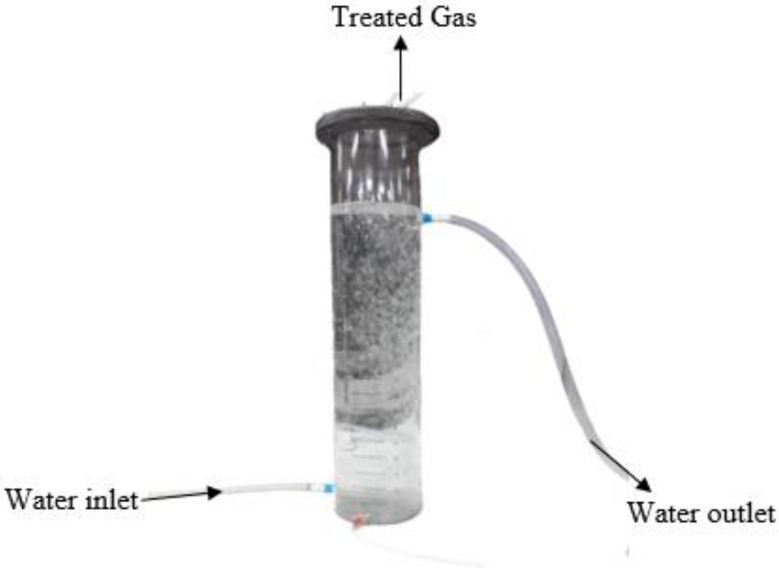


Figure 3.16 Absorption column.

3.2.4 Tube Absorber

It was found that the veritcle cylindrical column in the absorption column unit is not appropriate for the device because of the excessively high pressure drop of water passing through bottom of column. Consequently, the high energies were required for inputting the water into the system. It was also difficult for separating the treated gas with very low gas product recovery. Thus, the development of prototype were done by using tube absorber that is 0.016 meters in dia., 10 m of long. Mixing and absorbing the CO_2 bubbles in water by the tube absorber were done instead of being absorbed in the verticle column as shown in Figure 3.17. In order to increase percent recovery of the treated gas stream, 2 gas separation columns were installed after the tube absorber. Additionally, a pump was used to feed the mixing of gas bubbles and water to the gas separation column which consumed energies.

Figure 3.17 Tube absorber for separated CO_2 from biogas.

3.2.5 Gas separation column

Gas separation columns were used to separate the treated gas bubbles from the liquid absorbents as shown in Figure 3.18. The separated gases by using simulated biogas would be N_2 with over 90% concentration. In case of using biogas as a feed, the separated gases would be biomethane with the concentration of CH_4 gas that is over 90% and other gases is 10%. The gases separated from the liquids were released from the top of the column. The water would be leaved from the lower part of the column for restoring the water condition.

Figure 3.18 Treated gas separation column.

Gas separation columns used in the experiments were designed in order to obtain two columns with a diameter of 0.3 m and a height of 1.8 m to separate the high amount of treated gas after taking CO_2 with water. The spray nozzles would be installed inside the columns as shown in Figure 3.6 for spraying the water in order to release N_2 and CH_4 gases that are not absorbed in the water inside the columns.

3.2.6 Desorption test

For the desorption test, air bubble was used to contact with CO_2-rich water. The tests were performed in laboratory scale by investigating the effect of various temperatures 30, 40, 50, and 60 °C as shown in Figure 3.19. Then, the releasing of CO_2 from water was arranged by introducing CO_2 gas bubbles into 200 ml water in the impinger until CO_2-rich water (pH of water does not change). Air was fed into the impinger for releasing CO_2 from water. The outlet CO_2 concentration were measured. These result were applied to the experimental design in prototype unit. The pH of water outlet was investigated.

(A) (B)

Figure 3.19 Desorption test in a laboratory-scale**;** Introducing CO_2 gas bubble into water (A) and releasing of CO_2 from water with various temperature (B)

3.2.7 Absorbent regeneration Unit

Water absorbent containing CO_2 would be transferred to the regeneration system for releasing CO_2. The rich absorbent was sprayed from the top of column to make counter current flow with air stream for saturating the CO_2 gas from water. Then, the water can be reused continuously. The water would pass the full cone spiral nozzles in order to distribute tiny drops, and CO_2 could be separated from the water with O_2 from the air in order to reactions. The diagram of the regeneration system was designed as shown in Figure 3.20, and the picture of the installation of the regeneration system is shown in Figure 3.21.

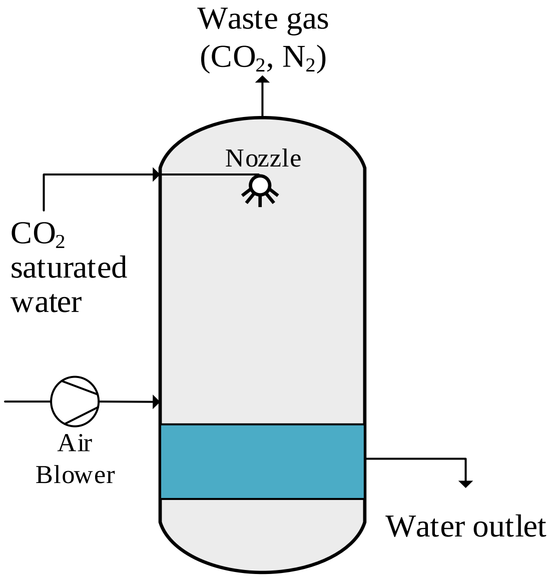


Figure 3.20 Schematic diagram of the regeneration system.

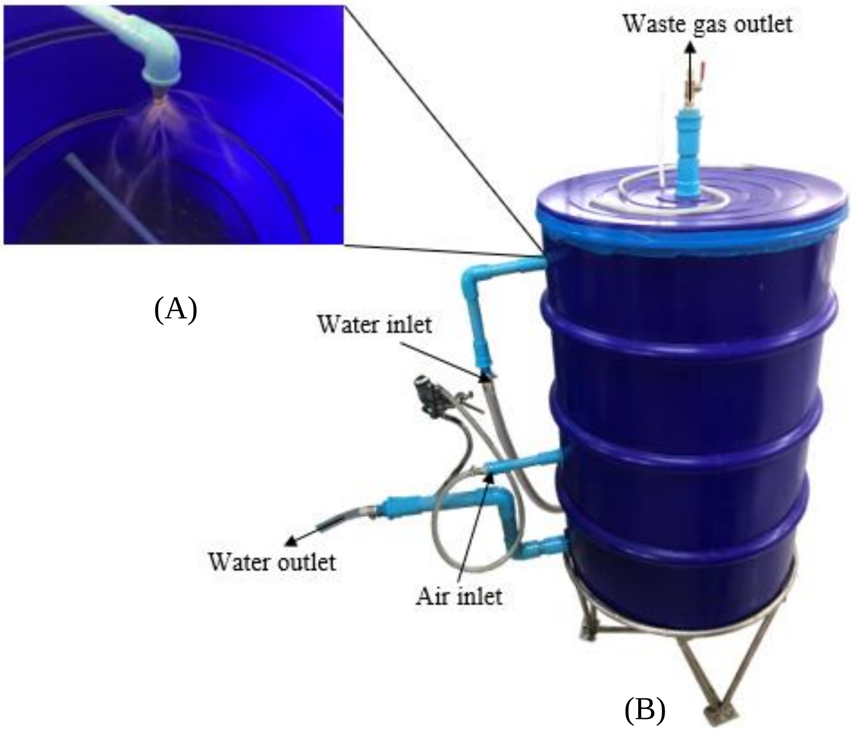


Figure 3.21 Spray nozzle (A) and Regeneration system (B).

3.2.8 H_2S treatment unit.

Before sending the biogas to biomethane production system, a column with steel wool was installed for removal of H_2S in the biogas. The column contained steel wool can capture and interact with H_2S in the biogas. The weight of the steel wool was 0.8 kg. The steel wool was inside the column with a diameter of 0.076 m and a height of 1 m. The biogas was transferred to the bottom of the column. The water also was introduced to the top of the column and flow through the steel wool with the flow rate of 10 L/min in order to absorb H_2S from the biogas. At the same time, the reaction of the H_2S with the steel surfaces was effectively done for H_2S removal. The treated biogas would flow out of the top of the column for studying the removal of CO_2. The diagram of the H_2S treatment unit was drawn and shown in Figure 3.22, and the column used in the H_2S treatment unit is shown in Figure 3.23.

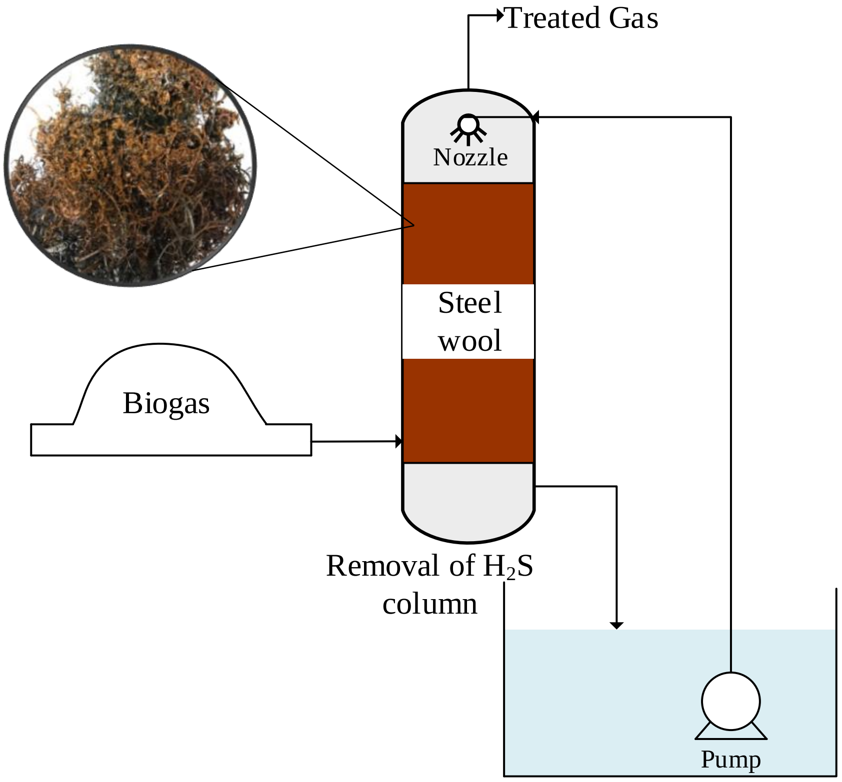


Figure 3.22 Schematic diagram of the H_2S treatment unit.

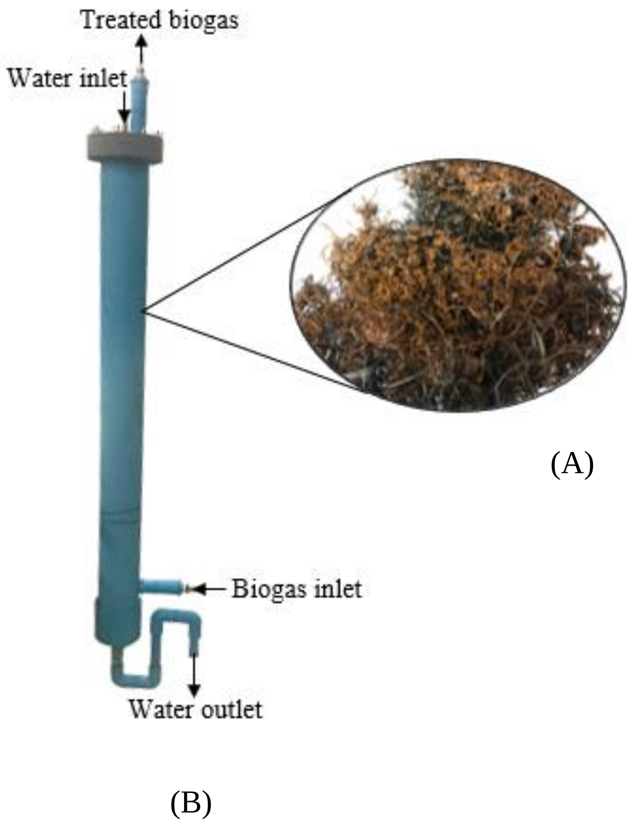
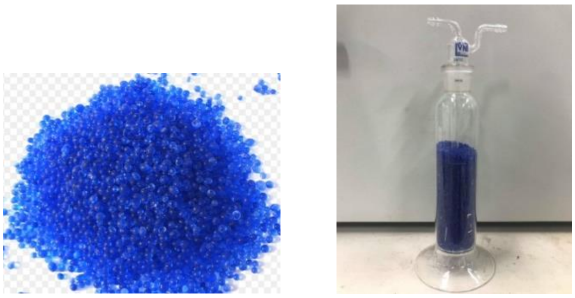


Figure 3.23 Steel wool (A) and the column of the H_2S treatment unit (B).

3.2.9 Moisture removal unit.

To obtain the dry biogas for this experiment, moisture removal unit was installed for removal of the moisture containing in biogas sampled deriving from the wastewater treatment system of SONGKLA CANNING PCL. The moisture removal unit uses the silica gel in the impingers in order to evenly distribute the biogas through the silica gel.



(A) (B)

Figure 3.24 Silica gel (A) and moisture removal system (B).

3.2.10 Experimental setup of a prototype unit

1) Absorption column

The research on CO_2 absorption process has been carried out in a prototype unit as shown in Figure 3.25. A vertical cylindrical acrylic column was used to increase retention time and increase surface area for absorption of CO_2 gas and water. The system using simulated biogas to study the CO_2 removal efficiency of the system. The concentration of CO_2 in simulated biogas which is close to the CO_2 present in biogas. In order to carry out the design and development of the prototype installation for the experiments to remove CO_2 from simulated biogas. To be able to find the optimum conditions to reduce the CO_2 concentration. From the design of CO_2 removal from biogas in the prototype unit, bring to assembly and installation as shown in Figure 3.26. The steps of experiments of the process are as follows:

1. The CO_2 simulated biogas generation system: CO_2 and N_2 gases with purity from cylinders through flow meter at the desired flow rate to produce simulated biogas. The CO_2 and N_2 gases are mixed in the mixing tank.

2. There is the sampling point after the mixing gas leaves the mixing tank. It passes through the rotameter No.1 to measure the flow of simulated biogas with the ratio to the specified concentration before entering to the CO_2 absorption process.

3. The simulated biogas is fed into the venturi ejector in the inlet area and mixed with water that is pumped by a pump from freshwater at the same time.

4. The flow of water along with the gas traverse in the venturi ejector where the microbubble generated due to the shear forces.

5. After the venturi ejector, the inline static mixer is installed where it obtaining excellent mixing performances.

6. Then, sent to the absorption column to increase contact time which increases the CO_2 removal efficiency in the system. The CO_2 gas that is separated after CO_2 absorption using water as an absorbent was analyzed by gas chromatography.

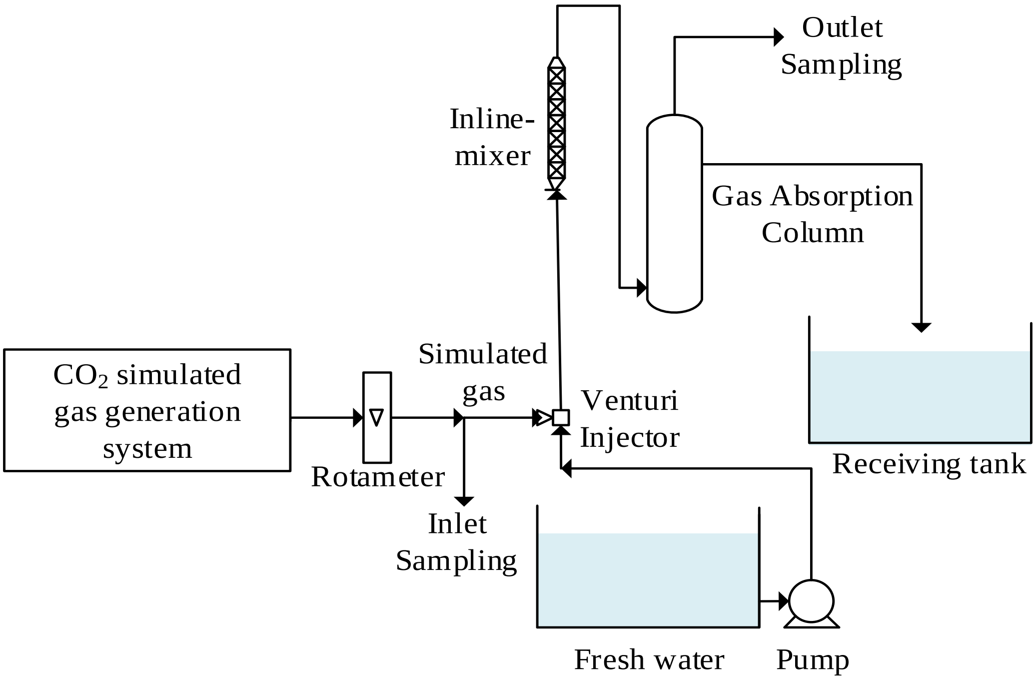


Figure 3.25 Schematic diagram of CO_2 removal from biogas with a prototype unit.

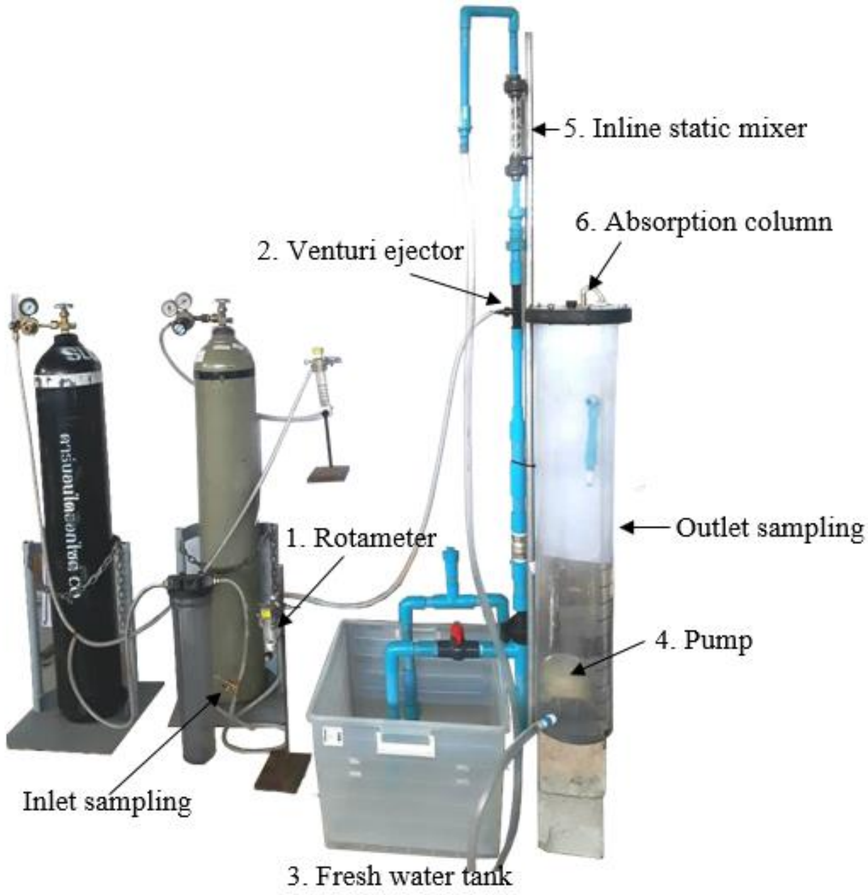


Figure 3.26 CO_2 removal from biogas with a prototype unit.

2) Tube absorber with gas separator column

In a prototype unit, bring to the development of the system by designing tube absorber with gas separator column for decreasing pressure drop occurring in the absorption column and increasing percent recovery of treated gas. The setup for CO_2 removal prototype unit was tested by using simulated biogas and biogas from anaerobic fermentation. The details of the designing and installation as follows:

1. The design of prototype for CO_2 absorption using water tube absorber and microbubble technique as shown in Figure 3.28 The biogas produced in the wastewater treatment system from SONGKLA CANNING PCL. was used in the system.

2. Due to the damage that H_2S can cause in the system. Therefore, it should be removed from biogas before fed into the system. The spray column with steel

wool was used to remove H_2S. Resulting in the concentration of H_2S in biogas feed stream lower than 100 ppm.

3. The concentration of H_2S was analyzed by detector tube method using sorbent tube with a Gastec pump.

4. There are three points for collect gas sampling including inlet sampling, outlet sampling, and waste gas sampling. The gas concentration can be measured by gas chromatography.

3) Regenerator unit

The regeneration process was installed to release CO_2 for the water gap to re-absorbed by spray column. The CO_2-rich water spray through the nozzle and use countercurrent airflow to separate CO_2 from the water.

The steps of CO_2 absorption experiments as follows:

1. The experimental run by introducing biogas from wastewater treatment of SONGKLA CANNING PCL. was fed to the H_2S removal system. After the removal of H_2S, cleaning biogas was collected in inner tube pneumatic tires.

2. The cleaning biogas was fed into venturi ejector to produce microbubble. The CO_2 gas bubbles are absorbed in water was sent to tube absorber to increase percent recovery of treated gas and reduce pressure drop in the column.

3. After that sent into the CH_4 separation column to separated CH_4 from a feed stream. The concentration of CH_4 in treated gas was analyzed by gas chromatography.

4. The CO_2-rich water was sent to the regeneration system to release CO_2 from the water. The water was measured by pH meter and used to re-absorbed in the system.

5. The L/G ratio in the system was calculated from the feed gas flow rate. The water used in the system is from two sources which are the water that passes through the regeneration system (L_1) and make up water about 5% (L_2).

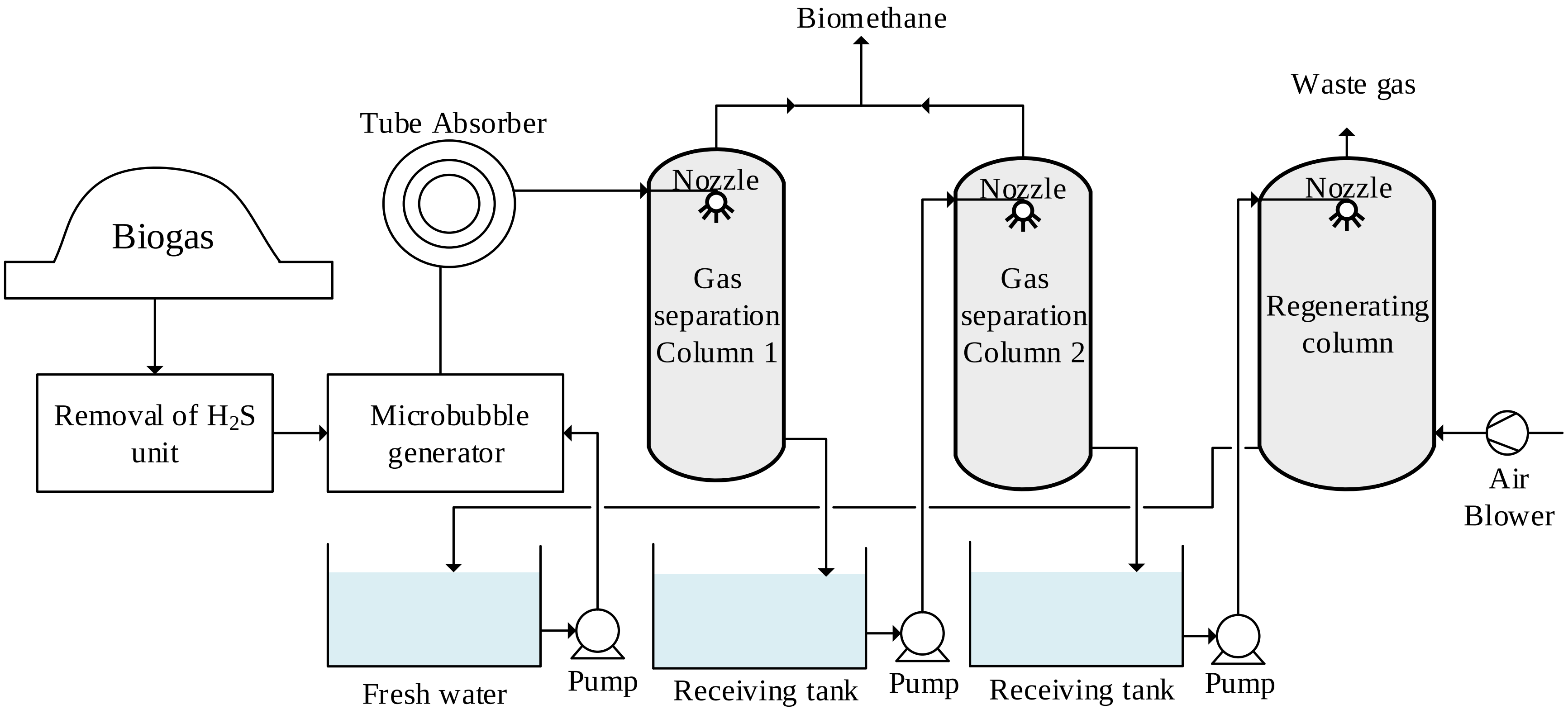


Figure 3.27 Schematic diagram of the production of biomethane using CO_2 removal from biogas.

(1) Microbubble generator unit

(2) Tube absorber

(3) Gas separation unit

(4) Regeneration unit

Figure 3.28 Production of biomethane using CO_2 removal from biogas.

3.2.11 Experimental design for optimum condition.

1) Absorption column

The optimum condition for removal of CO_2 using water absorption column with microbubble technique was investigated using simulated biogas. The five parameters were controlled and measured as following:

a) Size of venturi at 0.25 and 0.50 inches.
b) Gas flow rate about 2, 4, 6, 8, 10 l/min.
c) Water flow rate at 9, 12, 15 and 17 l/min.
d) Concentration of CO_2 in simulated biogas at 20-70 %CO_2.
e) L/G ratio (1.5-7.5)

Response of the experiments can be measured to find for optimum condition.

a) Size of bubbles.
b) Inlet and outlet gas CO_2 concentration.
c) Efficiency of the system.

2) Tube Absorber

To study the optimum condition of tube absorber to reduce pressure drop in the system and increase percent recovery by investigating CH_4 and N_2 concentration in treated gas stream. The main parameter that affects tube absorber is a gas flow rate of about 2, 4, 6, 8, and 10 L/min.

Response of the experiments were investigated to find for optimum condition.

a) Retention time
b) Entering and treated gas of CH_4 and N_2 concentration
c) CO_2 removal efficiency
d) Percent recovery of treated gas

3) Desorption column

The optimum condition of the desorption column was studied. The experiments were done by investigating air flow rate of about 5-30 L/min.

Response of the experiments were investigated to find for optimum condition.

a) pH of water

b) CO_2 concentration in waste gas stream

c) CO_2 removal efficiency

3.2.12 Gas analysis and calculation

The concentration of CH_4 and CO_2 in the entering and treated gas stream were analyzed by gas chromatography. The H_2S concentration in the gas stream was performed using a detector tube method. The CO_2 removal efficiency was calculated by the equation (1)

$$\eta_{CO_2} = \frac{[CO_{2,inlet}]-[CO_{2,outlet}]}{[CO_{2,inlet}]} \times 100 \qquad (1)$$

Here η_{CO_2} is CO_2 removal efficiency, $[CO_{2,\ inlet}]$ is the inlet volumetric flow rate of CO_2 (L/min) and $[CO_{2,\ outlet}]$ is outlet volumetric flow rate of CO_2 (L/min).

In this research, gas chromatography with a TCD detector and Porapak Q packed column were used for analysis concentration of CH_4, CO_2, and N_2 from entering and exiting in gas stream. The details of the analysis can be divided into three parts as follows:

Figure 3.29 Gas Chromatography, GC.

1. Conditions of analysis of gas concentrations

The concentration of gases was analyzed by gas chromatography 14A, Shimadzu, Japan. The conditions are as follows:

Detector: Thermal Conductivity Detector	Column:PorapakQ, Shimadzu
Carrier gas: Helium gas (He)	Injector temperature: 60ºC
Column temperature: 60ºC	Detector temperature: 60ºC
Current: 60 mA	

2. Calibration Curve

The calibration curve was prepared with the quantitative analyses using the standard gases from the scientific equipment center of Prince of Songkla University with the concentration ratio of CH_4, CO_2, and N_2 of 60%, 35%, and 5%, respectively as well as the chromatography 14A, Shimadzu. By conducting the analyses with the mentioned conditions, the chromatograms were obtained and showed the three main peaks. The first peak was at 0.79 minutes with the concentration of N_2 of 5%. The second peak was at 1.073 minutes with the concentration of CH_4 of 60%. The third peak was at 1.840 minutes with the concentration of CO_2 of 35% as shown in Figure 3.31.

The peak area is shown in Table 3.1. The calibration curve was plotted by using the results.

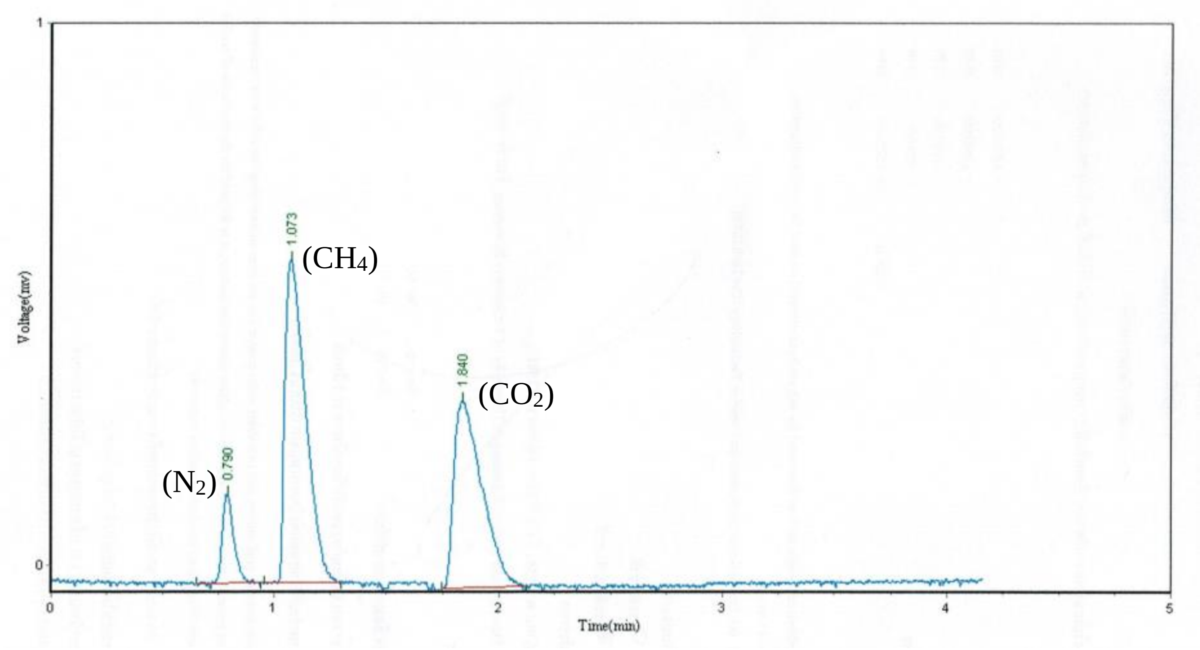


Figure 3.30 Chromatogram of standard gas.

Table 3.1 Peak area

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		0.790	164.000	625.90	8.2926
2		1.073	595.659	3819.15	50.6005
3		1.840	348.511	3102.60	41.1068
Total			1108.170	7547.60	100.000

3. Component Concentration Analysis with Sampled Gases

To calculate the concentrations in the sampled gases, the processes were similar to those of analyzing the calibration curve. By the analyses, the calibration curve must be done for the purpose of accuracy in order to reduce the fluctuations of the factors or conditions. Then, the obtained peak area was compared to the calibration peak area in order to calculate the concentrations of the components in the sample gases.

3.2.13 Microbubble size determination

In this research, the size of microbubble was measured by the automated bubble size measurement as shown in Figure 3.31. A bubbles size of the cumulative bubbles was determined by a MATLAB image segmentation program. From the image generated, the size of the microbubble data can be collected and analyzed by Microsoft Excel.

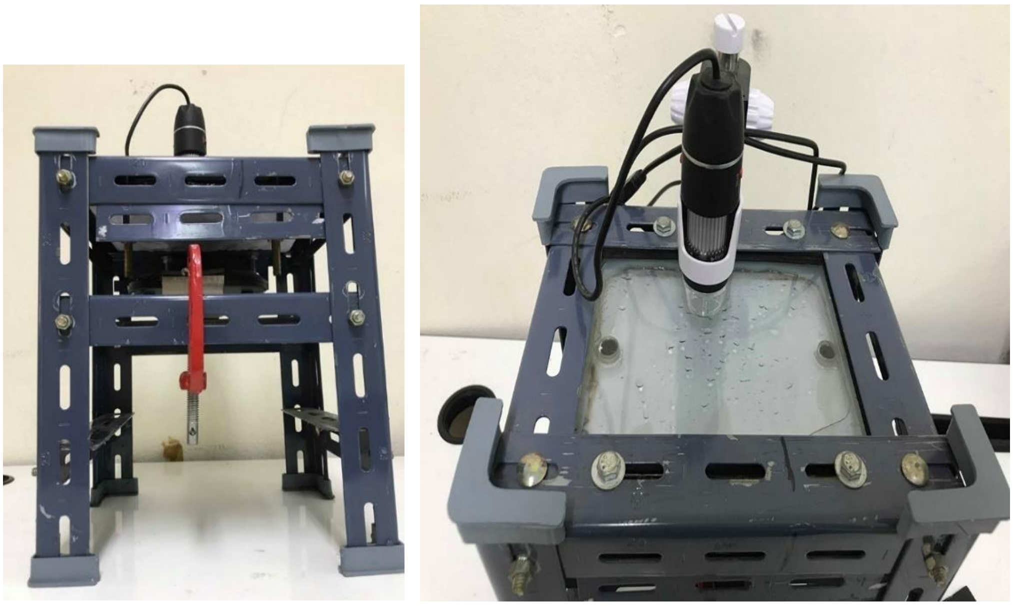


Figure 3.31 Automated bubble size measurement.

CHAPTER 4

RESULTS & DISCUSSION

In this research, biomethane production using water absorption with microbubble technique was studied. The CO_2 removals from biogas were designed using simulated biogas and real biogas from anaerobic fermentation with prototype unit. The experimental unit consisted of a series of simulated biogas by mixing of CO_2 and N_2 at 20-50% CO_2, the microbubble generation system, the water absorption unit, the treated gas separation columns, and the regeneration system. The prototype unit was developed and installed to monitor optimum conditions. The details of the result and discussion for all experiments are presented as following.

4.1 Standard curve

The standard curve was arranged and analyzed using the standard gases consisted of the three main gases, which is CH_4, CO_2, and N_2. The concentration of gases was analyzed by gas chromatography, at the condition as follows:

Detector: Thermal Conductivity Detector Column:Porapak Q, Shimadzu
Carrier gas: Helium gas (He) Injector temperature: 60ºC
Column temperature: 60ºC Detector temperature: 60ºC
Current: 60 mA

The chromatogram of standard gas as shown in Figure 3.30 appears in three main peaks. The first peak at 0.79 minutes is N_2 about 5%. The second peak at 1.073 minutes is CH_4 about 60%, and the third peak at 1.840 minutes CO_2 about 35%. The standard curve of concentration of CO_2 from standard gas as shown in Figure 4.1.

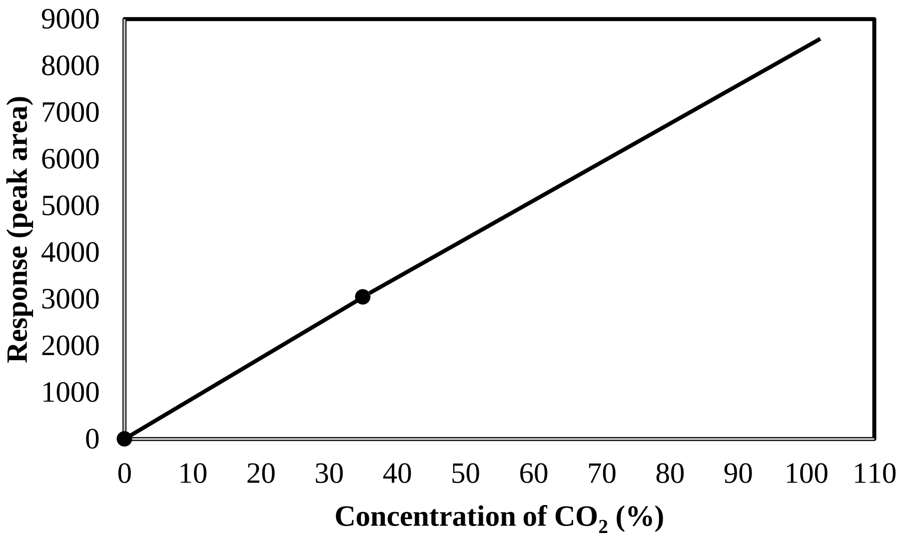


Figure 4.1 Standard curve for analysis of the concentration of CO_2.

4.2 Simulated biogas preparation

4.2.1 System Installation

In this research, the prototype unit was conducted and trialed by using simulated biogas system before using the real biogas. The details simulated biogas preparation are as follows:

1. The simulated biogas generated by mixing CO_2 and N_2 gases from gas cylinders. The concentration of CO_2 in simulated biogas about 20-40% CO_2 which is close to present in real biogas.

2. Feed both gases into the mixing tank to achieve a consistent gas concentration. The desired flow rates were adjusted by a manual valve and measured by rotameter in the range of 1-5 L/min.

3. The gas mixing tank is a tank that receives CO_2 and N_2 gases for well mixing at the desired concentration before sending the simulated biogas to the CO_2 removal process.

Simulated biogas was prepared at the CO_2 concentration in the range of 20-40%, and sent into the CO_2 removal prototype process as shown in Figure 3.28. The concentration of CO_2 was analyzed by gas chromatography.

4.1.2 CO_2 concentration in simulated biogas

The preparations of simulated biogas were conducted by adjusting the ratio of CO_2 and N_2 flow rate from cylinders and sending to the mixing tank. The concentration of CO_2 was analyzed by gas chromatography and calculated comparing to the standard curve as shown the result in table 4.1

Table 4.1 CO_2 concentration in simulated biogas prepared by adjusting the CO_2:N_2 volumetric flow rate ratio (CO_2: N_2)

The CO_2: N_2 volumetric flow rate ratio (L/min)	**CO_2 Concentration (%)**
5:0 (pure CO_2)	100
4:1	78.94
3:2	64.52
2:3	40.06
1:4	21.11
0:5 pure N_2	0

The result indicated that ratio of CO_2:N_2 consistent with % CO_2 concentration in sumulated biogas. The CO_2:N_2 volumetric flow rate at ratio of about 2:3 can achieve a concentration of CO_2 40%, which is close to the CO_2 concentration in biogas. Therefore, the setting CO_2:N_2 ratio of 2:3 was chosen for all experiments. Various ratios of gas stream getting various % CO_2 concentration were analyzed for the peak area. A curve plotting between peak area and concentration of CO_2 in simulated biogas were compared with standard curve as shown in Figure 4.2.

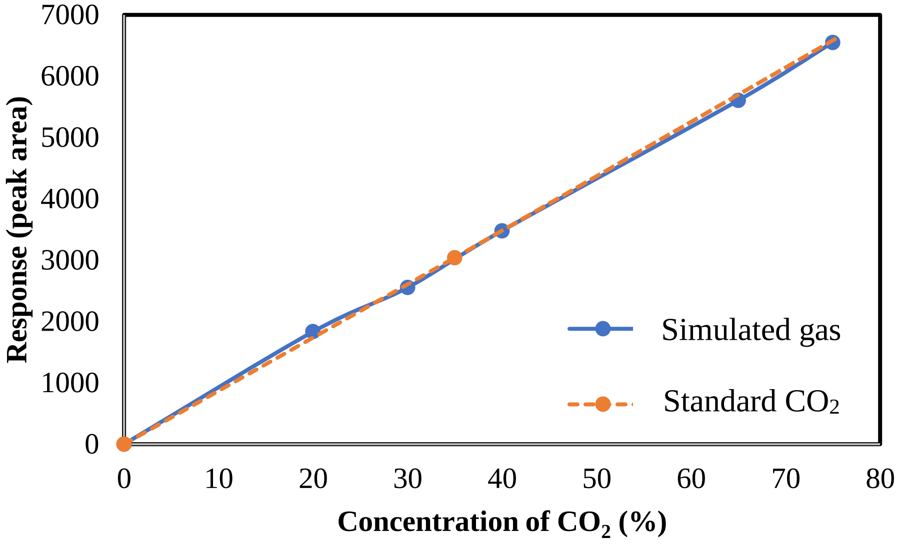


Figure 4.2 Comparison of peak area from various CO_2 concentration of simulated biogas and standard gas.

In the above Figure, the curve from preparations of simulated biogas fitted well with the standard curve. It can be said that the peak area obtained from the prepared mixing gas consistent with the peak area from standard gas. Hence, the mixing gas obtained from the ratio of CO_2:N_2 volumetric flow rate can be applied to prepare the simulated biogas at required CO_2 concentration.

4.2 Size of microbubble

Microbubble was generated by feeding the simulated biogas and liquid water into a venturi ejector. The high pressure of gas feed passing through the venturi throat forms numerous fine gas bubble that provides turbulent mixing between the gas and liquid phases. Pressure change in the diverging nozzle induces bubble breakup. To investigate size of the fine bubble generated by 0.50-inch venturi ejector, a MATLAB image segmentation program was used by determining the cumulative bubbles. The size of bubbles was tested using 15 L/min of water flow rate and varying the gas flow rate from 2 to 8 L/min. Figure 4.3 showed the gas bubbles image with various gas flow rates. The result showed that the gas flow rate affected the size of bubbles. The size of bubbles is small when the gas flow rate is low. When considering the microbubble generation by venturi ejector, it is understood that the optimal gas flow rate is important to generate a size of bubbles.

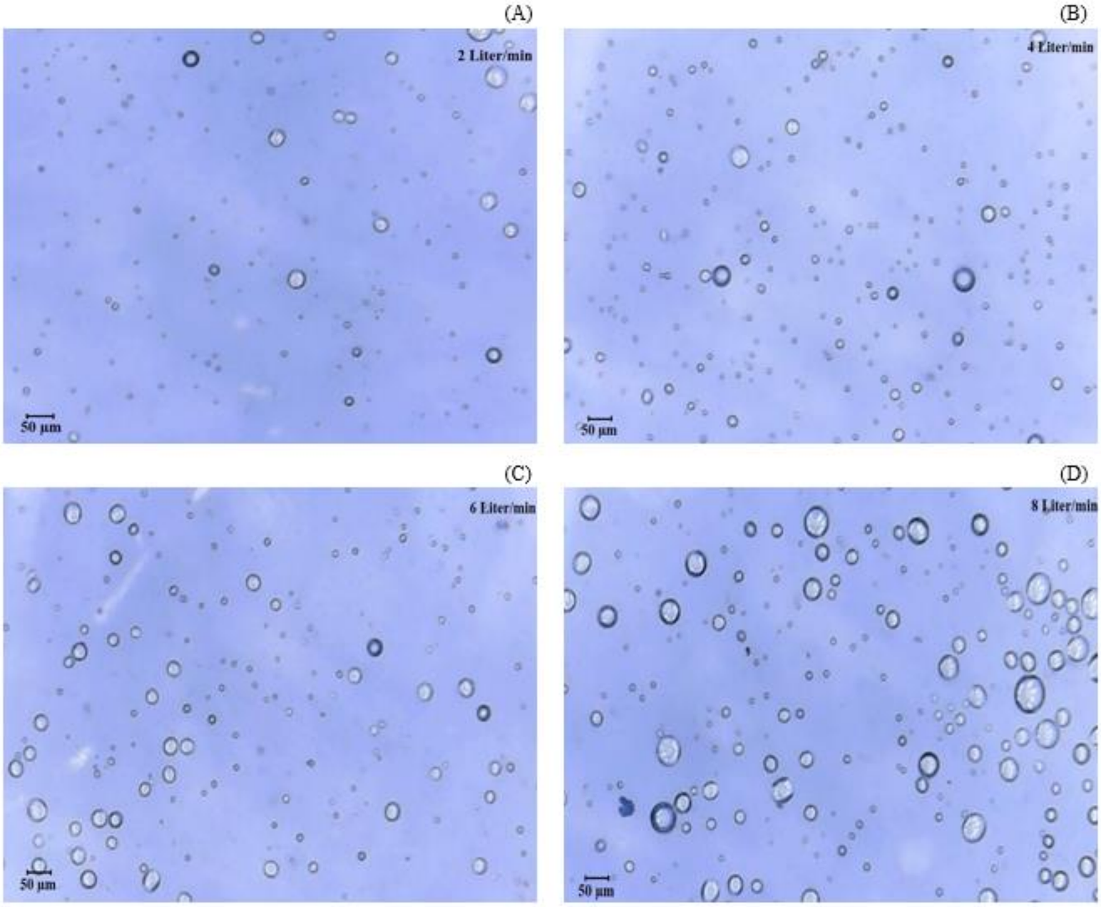


Figure 4.3 Images and gas bubbles size at gas flow rate of 2 L/min (A), 4 L/min (B), 6 L/min (C), and 8 L/min (D) using 0.50-inch venturi ejector.

Figure 4.4 showed the gas bubbles size at various gas flow rates. It was observed that the size of microbubble increased with increasing gas flow rate. Lower gas-injection rates were used to provide the lower gas bubble size. The lowest bubbles size of 20.83 µm was achieved at 2 L/min of gas flow rate. It also observed that all gas flow rate can form microbubbles in the size range of 20-30 µm. It was observed that at the gas flow rate of less than 4 L/min, the size of bubbles was similar. To reduce the energy consumption the optimum flow condition for generation of tiny microbubbles effectively was 4 L/min of gas flow rate.

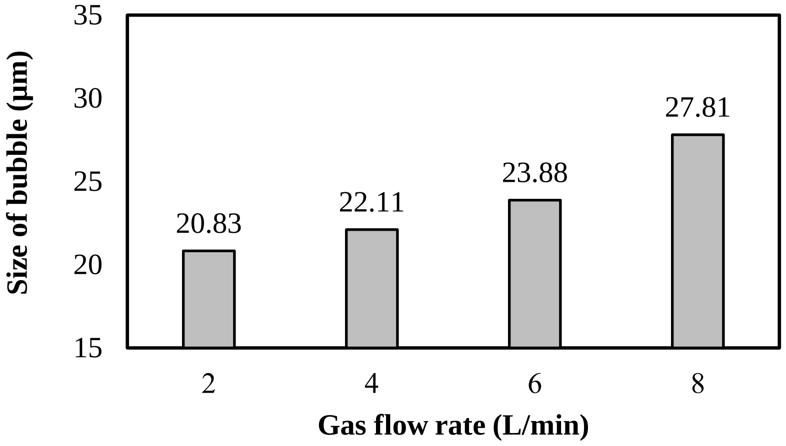


Figure 4.4 Size of gas bubbles on the various simulated biogas flow rate using 0.50-inch venturi ejector as microbubble generator.

4.3 Absorption column prototype unit

4.3.1 Installation of prototype unit

The initial research on the CO_2 absorption process has been carried out in a prototype unit as shown in Figure 3.26. The system using simulated biogas to study the CO_2 removal efficiency of the system at ambient pressure and room temperature. The concentration of CO_2 in simulated biogas which is close to the CO_2 present in biogas. Each experimental run by introducing simulated biogas through flow meters at desired flow rates at a concentration of 40% CO_2, which was fed to the venturi ejector. The water was pumped to the venturi ejector at the same time. The gas bubbles with water transferred to the inline static mixer to increase mixing performance. After that, water with gas bubbles was sent into the bottom of absorption column, the CO_2 saturated water was collected in the receiving tank. The system allowing at least 10 minutes for the system to reach a steady-state before taking samples. At steady-state, the concentration of CO_2 in feed gas stream and treated gas were analyzed by gas chromatography. The result of CO_2 removal efficiency with a prototype unit can be explained as follows:

4.3.2 Effect of gas flow rate

The effect of simulated biogas flow rate at 2-10 L/min was observed on CO_2 removal using water absorption column with microbubble generation technique as presented in Figure. 4.5. The water flow rate of 15 L/min, CO_2 content in the simulated biogas of 40% and the 0.25-inch venturi ejector were fixed. The result indicated that the highest CO_2 removal of about 56% was achieved with the flow condition for the generation of tiny microbubbles was the lowest simulated biogas flow rate of 2 L/min. The final treated gas concentration of 56.47 % CO_2 and flow rate 2 L/min. The results suggested that in addition to the enhancement of mass transfer, microbubbles, which had higher inner pressure, could improve the absorption of CO_2 in water.

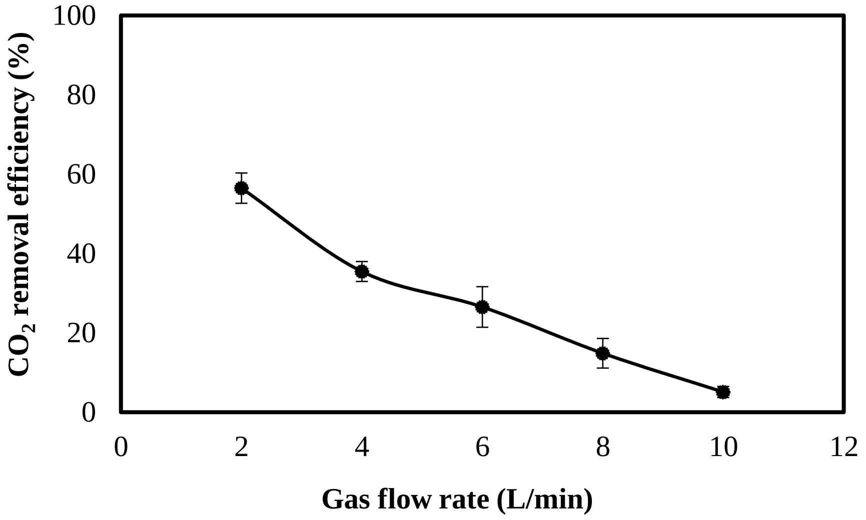


Figure 4.5 Effect of various gas flow rate on CO_2 removal using the 0.25-inch of venturi ejector for microbubble generation.

For the CO_2 absorption with water, the used of lowest gas flow rate which is a waste of energy consumption. Therefore, 4 L/min of gas flow rate was applied for all following experiments. From the below plot, it was observed that the CO_2 removal efficiency decreased as the gas flow rate increased. This is probably due to size of microbubble and retention time of the gas in absorbent liquid that limited the CO_2 absorption in the water.

4.3.3 Effect of water flow rate on CO_2 removal

The effect of water flow rate on CO_2 absorption was studied using prototype unit of water absorption column and microbubble generator. Simulated biogas at the initial CO_2 concentration of 40% CO_2 was used with 0.25-inch of venturi ejection for microbubble generation unit as plotted in Figure 4.6. The testing could be controlled by adjusting the water flow rate of 9, 12, 15, and 17 L/min with a gas flow rate kept constant of 4 L/min. The entering and exiting of gas stream were investigated and calculated for CO_2 removal efficiency.

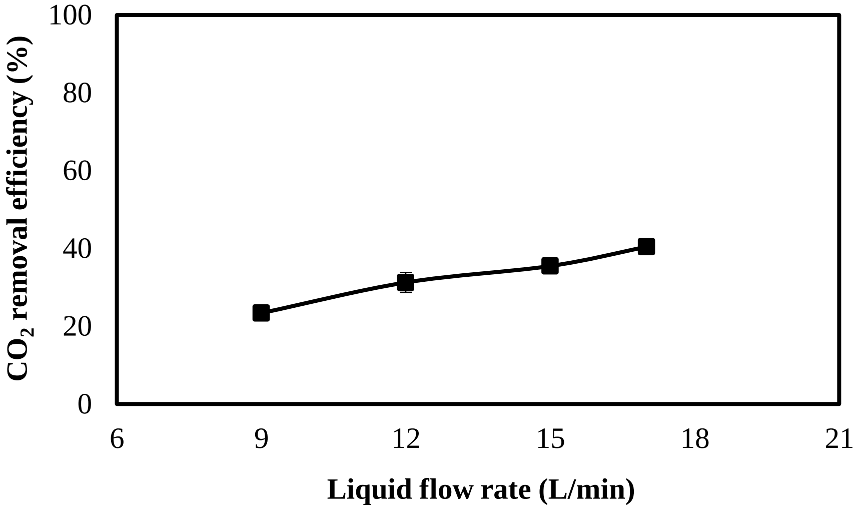


Figure 4.6 Effect of water flow rate on CO_2 removal with the 0.25-inch of venturi ejector.

It was observed that the CO_2 removal efficiency was increased from 23.38% to 40.41% as the water flow rate varied from 9 to 17 L/min at 0.25-inch of venturi ejector. Final treated gas concentration of the size of venturi ejector 0.25-inch and was 40.41 %CO_2. This result match with (Tan et al., 2012) who attributed the increase of water flow rate provides a large bulk of liquid phase is available for absorbing more CO_2 gas. However, the use of venturi ejector requires a water flow rate that is appropriate for the size of venturi ejector to increase CO_2 absorption in water.

4.3.4 Effect of venturi ejector size by varying gas flow rate

To study effect of venturi ejector size on the CO_2 removal the 0.25-inch and 0.5-inch venturi were used. The studied using a constant water flow rate of 15 L/min and varying the gas flow rate from 2 to 10 L/min. The entering and exiting of gas stream were investigated as shown the result of CO_2 removal efficiency in Figure 4.7.

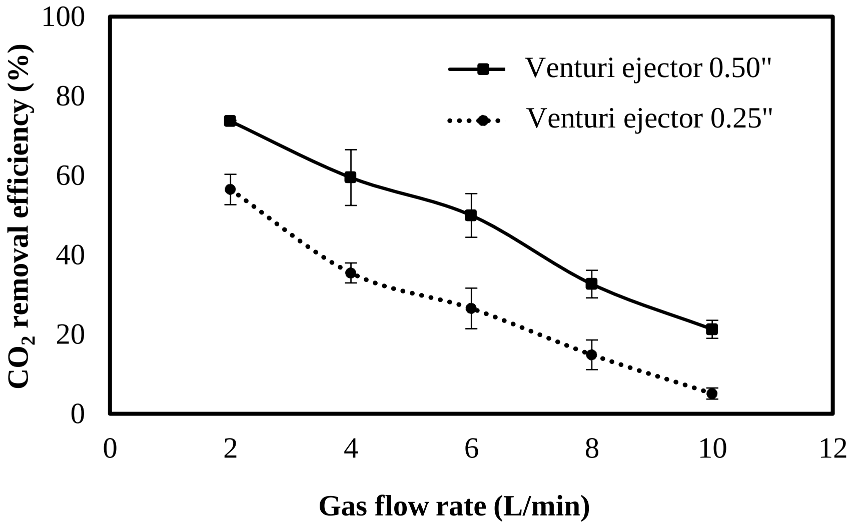


Figure 4.7 Size of venturi ejector on CO_2 removal with various simulated biogas flow rates by absorption column prototype unit.

The result indicated that the venturi size of 0. 50-inch provided better CO_2 removal efficiency. This is probably because the 0. 25-inch venturi had a larger pressure drop affecting the distribution of the gas bubbles in the water. Results from the study also showed that the 0.50-inch provides the highest CO_2 removal efficiency of about 73% achieved with the gas flow rate of 2 L/min. Final treated gas concentration of 56.47 % CO_2 of 0.25-inch venturi and 85.79 % CO_2 of 0.50-inch venturi.

4.3.5 Effect of venturi ejector size by varying water flow rate

The effect of water flow rate on CO_2 removal efficiency by using 0.25-inch and 0.50-inch venturi ejector for microbubble generation can be plotted in Figure 4.8. The experiments were performed by fixing the gas flow rate at 4 L/min and varying the water flow rate from 9 to 17 L/min. Both 0.25-inch and 0.5-inch were found a similar trend of CO_2 removal efficiency. The water flow rate increased, the percentage of CO_2 removal was increased. According to CO_2 is a component that sparingly soluble, large water circulation is required and the design is governed by liquid phase mass transfer coefficient. It was observed that the using of 0.5-inch venturi much for microbubble generator gave CO_2 removal efficiency higher than the using of 0.25-inch venturi. Therefore, the 0. 50-inch venturi was chosen as an optimum microbubble generator tool for all experiments that follow.

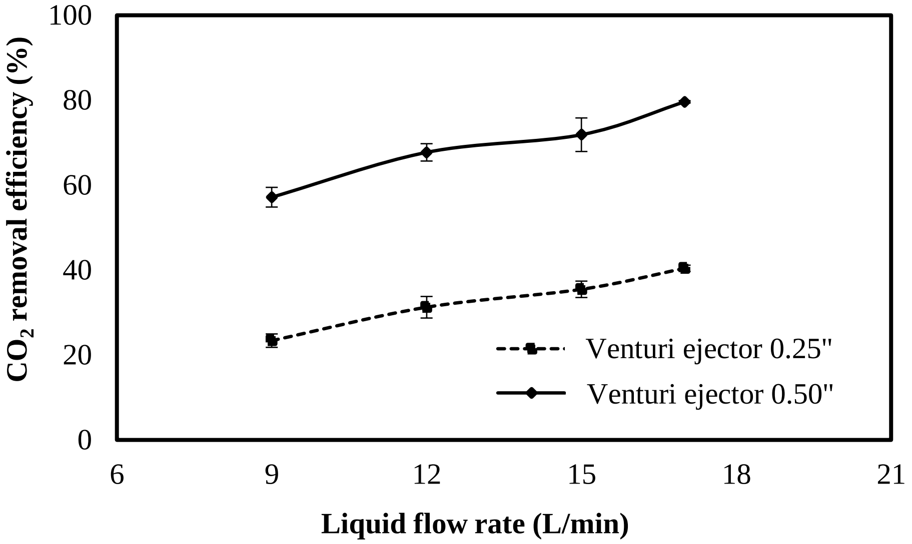


Figure 4.8 Effect of venturi ejector size on CO_2 removal with various water flow rates by absorption column prototype unit.

4.3.6 Effect of inline static mixer on the CO_2 removal

The inline static mixer was applied to CO_2 absorption system of prototype unit. The device was applied for the purpose of excellent mixing between gas bubbles and water. The venturi ejector for forming microbubble with inline static mixer was investigated. The effect of gas flow rate on CO_2 removal was studied using various gas flow rates of 2-10 L/min with a constant water flow rate of 15 L/min. The initial CO_2 concentration of 40% CO_2 and 0.50-inch venturi. The system allowing at least 10 minutes for the system to reach a steady-state before taking samples. The entering and exiting of gas stream were investigated. Figure 4.9 shows the CO_2 removal efficiency as a function of the performance of inline static mixer.

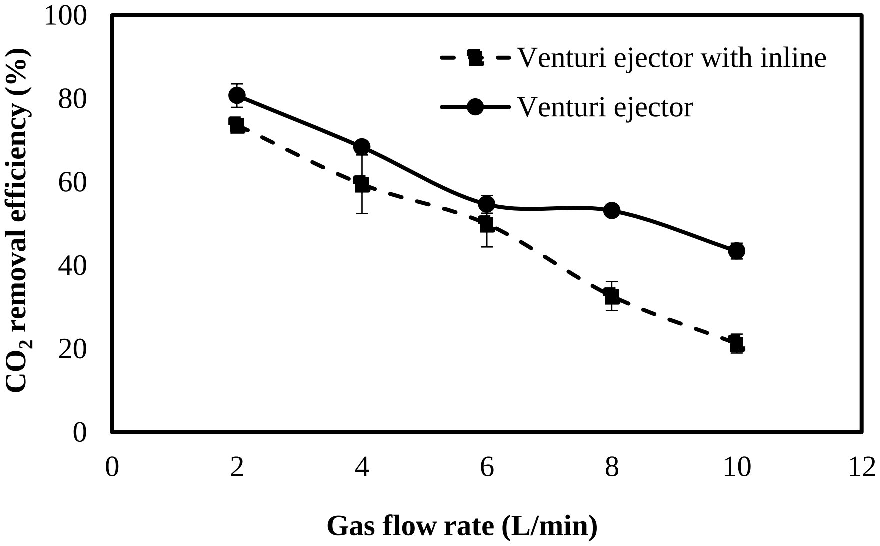


Figure 4.9 Effect of inline static mixer in the prototype unit on CO_2 removal efficiency at various gas flow rate.

The result showed that the use of inline static mixer provides little lower CO_2 removal efficiency. This may be because the inline static mixer can break and combine the bubble after the tiny gas bubbles with water flow out from the venturi ejector. Resulting in shorter contact time and lower surface area leads to decrease contacting area between gas bubbles and water. Therefore, the venturi ejector with non-inline static mixer was chosen for all experiments that follow. The result also presented that the increasing gas flow rate effected to decreasing in CO_2 removal efficiency running by the prototype unit.

4.3.7 Effect of CO_2 concentration on CO_2 removal efficiency

The effect of CO_2 concentration on CO_2 removal efficiency was studied using 4 L/min of gas flow rate, 15 L/min of water flow rate, and 0.50-inch venture ejector. Various concentration of CO_2 from 20% to 70% was investigated. The results are shown in Figure 4.10. The increase of CO_2 concentrations from 20% to 70% obviously decreased CO_2 removal efficiency. The CO_2 absorption at range of 20-40%

CO_2 provided the removal efficiency of about 70% and getting the final CO_2 concentration of 74.94 %CO_2 in the specification of biomethane. But for the CO_2 concentration higher than 40% the CO_2 removal efficiency was decreased. This result matches with Tan et al., 2012 and Ndriritu et al., 2013 who attributed, at the initial, the higher amount of water molecules per unit volume are available for absorbing more CO_2 and then the diffusion of CO_2 within the water molecules being constant even as the concentration of CO_2 increased. The results proved that the water absorption with microbubble technique can be effectively applied for removal of CO_2 from real biogas.

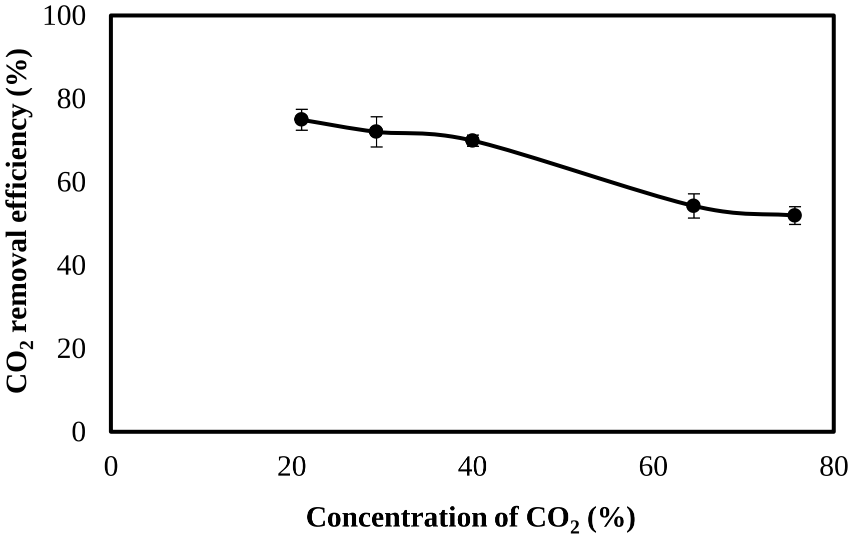


Figure 4.10 Effect of CO_2 concentration in simulated biogas on CO_2 removal efficiency.

4.4 CO_2 removal with the developed prototype unit

4.4.1 Development of prototype unit

The previous prototype unit was the experiments of the CO_2 absorption process using water absorption column with microbubble technique. Development of the system bring into the designing and creating new setup for CO_2 removal from biogas unit as shown in Figure 3.28. First, the simulated biogas was used in the system to find for the optimum condition and prove that the system can effectively remove CO_2. The developing system consisted of four main units which are microbubble generator, tube absorber, gas separator, and regeneration unit. At the end, biogas from anaerobic fermentation was applied in the system to study the biogas upgrading for producing biomethane. The concentration of gases in feed gas stream and treated gas stream were analyzed by gas chromatography. The developed prototype unit was effectively performed and described the result for the CO_2 removal efficiency.

4.4.2 Effect of L/G ratio on CO_2 removal

The L/G ratio of biomethane production on CO_2 absorption using water tube absorber with microbubble technique were studied. The experiments were conducted by varying L/G ratio in the range of 1.87-7.50 by varying simulated gas flow rate 2, 4, 6, and 8 l/min. The water flow rate kept constant at 15 L/min for all experiments. The ambient pressure and room temperature were used in the tests. Figure 4.11 shows the effect of L/G ratio on CO_2 removal efficiency. The results indicated that the highest CO_2 removal efficiency was obtained of about 95% at L/G 7.50. That is the CO_2 concentration in outlet gas stream lower than 5%. Hence, this system can be upgrading biogas to biomethane.

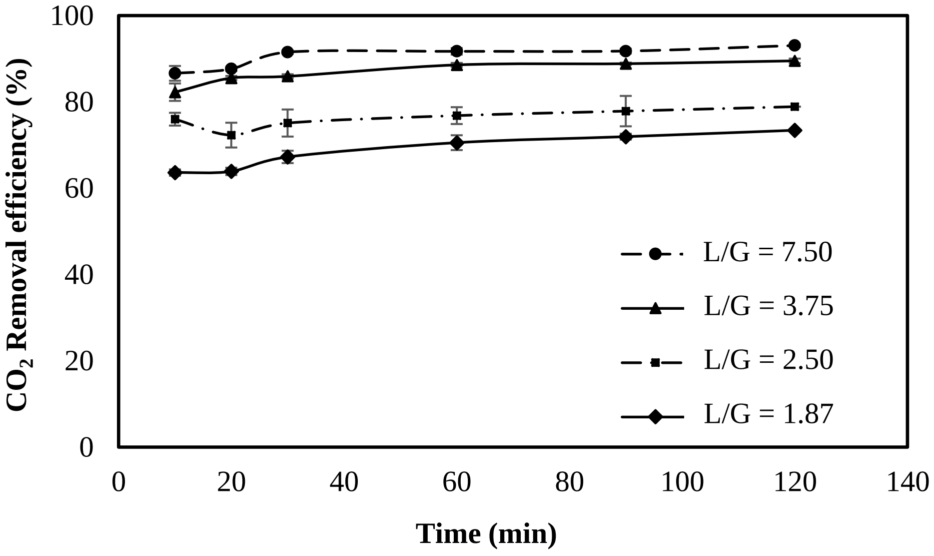


Figure 4.11 Effect of L/G ratio on CO_2 removal efficiency at the constant water flow rate at 15 L/min.

From the above plot, as can be seen that the increase of L/G ratio obviously increased CO_2 removal efficiency. followed by a slight increase with time until absorption equilibrium was achieved after 30 min. It should be noted that the CO_2 removal efficiency is mainly affected by the first 30 min on CO_2 absorption. The increase in CO_2 removal efficiency at the initial stage was probably due to the large bulk of liquid phase available on the absorbent. Increasing of L/G ratio, which is increases the amount of CO_2 in the gas phase while the bulk of liquid phase is constant. Results in the limited of CO_2 absorbed in water (Ndiritu et al., 2013). The results also showed that the increases of L/G ratio from 3.75 to 7.50 provide a slight increase in CO_2 removal efficiency. Therefore, the L/G ratio of 3.75 was chosen for all experiments that follow.

These results were consistent with Kasikamphaiboon et al., 2013 and Xiao et al., 2014 who presented that a lower L/G ratio results in a relatively faster CO_2 absorption and CO_2 removal efficiency slightly increase with increases the L/G ratio.

4.4.2 Effect of initial CO_2 concentration on CO_2 removal

To confirm this system can be upgrading biogas to biomethane by removing CO_2 from biogas. The initial CO_2 concentrations in simulated biogas in the range of 30-50%, which is close to the concentration of CO_2 in biogas was used in the tests. The effect of initial CO_2 on CO_2 removal was investigated by fixing 4 L/min of gas flow rate and 15 L/min of water flow rate as shown in Figure 4.12 The result revealed that increased initial CO_2 concentration in the simulated biogas stream, the CO_2 removal efficiency was decreased. CO_2 removal efficiency higher than 85%. This result confirmed the system can be upgrading biogas to biomethane.

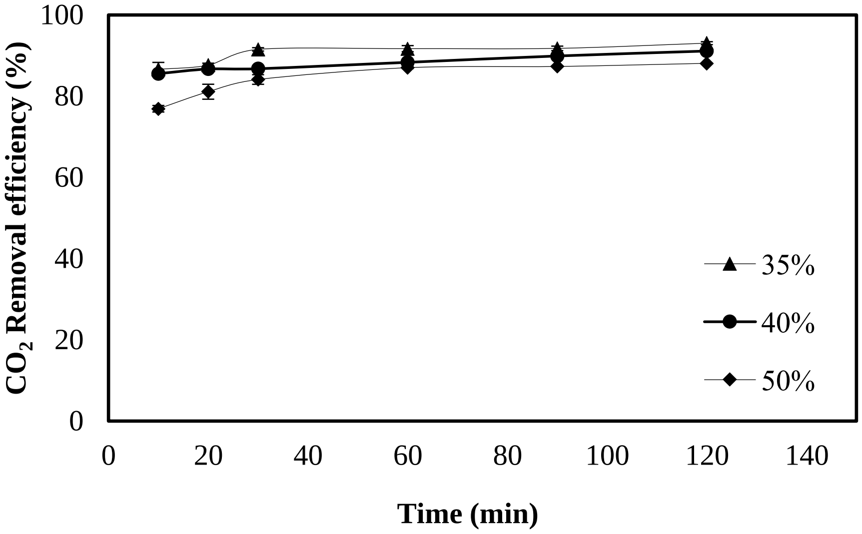


Figure 4.12 Effect of initial CO_2 concentration in simulated biogas stream on CO_2 removal by absorption combining with microbubble technique.

4.5 CO_2 desorption from saturated water tests

4.5.1 Effect of heating and stirring on CO_2 desorption

The experiments run were set using bigger 500 ml with gas distributor. To get CO_2-rich waters, the pure CO_2 was added through the gas distributor at 4 L/min in 500 ml tap water for 15 minutes. The initial tap water and CO_2-rich waters have pH value at pH 7.5 and 5.1, respectively. CO_2-rich water were heated with and without stirrer hotplate for 20 minutes at various constant temperatures of 30, 40, 50 and 60°C. The results of changing in pH of water after testing were measured and recorded as plotted in Figure 4.13.

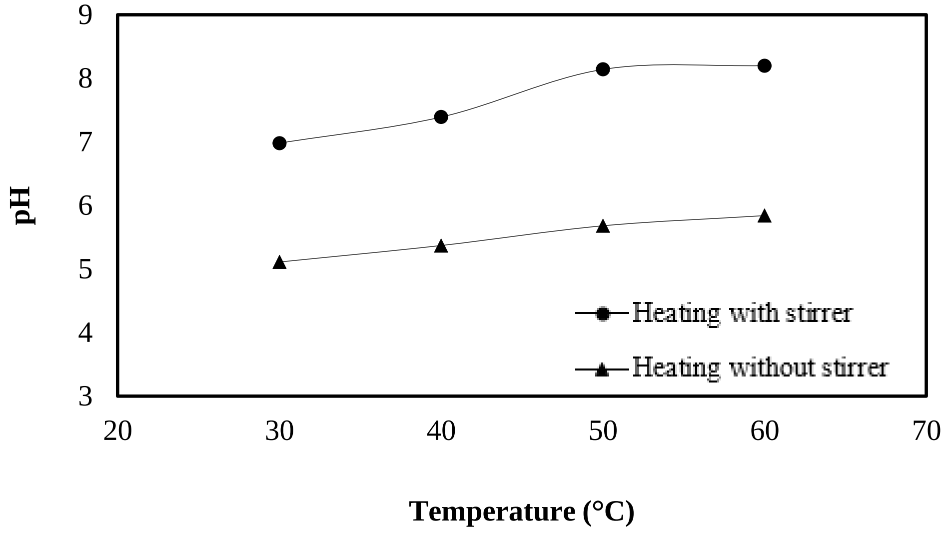


Figure 4.13 Effect of pH on the regeneration unit at various temperatures.

During the CO_2 desorption test, pH of water in the bigger was gradually reduced from initial pH of 7.5 It was observed that at room temperature of 30^{o}C the heated without stirrer obtained pH value of 5.0, while heated with a stirrer, pH value of 7.0 was obtained. These results also observed that an increase in the temperature to 50°C and 60°C with stirrer, can increase the pH value to around pH 8.0. The heated with stirrer offers better CO_2 desorption with a higher pH value.

It can be described that during bubbling the pure CO_2 gas in water, the CO_2 reacts with water to form carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) as presented in Equation (4.1). As a dissolving of H_2CO_3 in water, making it slightly acidic. After heating and stirring, H_2CO_3 and HCO_3^- were changed back to CO_2 gas and removed from water, results in high pH value. Obviously stirring the CO_2 saturated water had more effected on the desorption of CO_2. It may be because of O_2 from atmosphere can contact with water during stirrer and H_2CO_3 transform to CO_2 as described in Equation (4.2) and (4.3).

$$CO_{2(g)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)} \qquad (4.1)$$

$$2H_2CO_{3(aq)} + O_{2(g)} \leftrightarrow 3CO_{3(g)} + 2H_2O_{(l)} \qquad (4.2)$$

$$2CO_{3(g)} \leftrightarrow 2CO_{2(g)} + O_{2(g)} \qquad (4.3)$$

4.5.2 Result of CO_2 desorption from water

To study for the desorption of CO_2 from water absorbent, the tests of releasing CO_2 from water in a laboratory were investigated. These tests were used as guidance for designing the regeneration unit applying in the CO_2 absorption system. The experiments were set in impinger as shown in Figure 3.19 Pure CO_2 gas and air were used with rotameter for measuring the gas flow rate. pH of water was monitored by pH meter.

The tests began by introducing the CO_2 gas 4 L/min bubbles into 200 ml tap water in the impinger until getting CO_2-rich water with pH of water does not change. This point the pH was found at 5.5. After that 4 L/min air was fed into the impinger for desorbing CO_2 from the CO_2-rich water for 10 minutes. CO_2 concentrations in gas releasing from the water were measured at time 0, 5, and 10 min. Three trials were conducted in an experiment. The results can be shown in Table 4.2. The high CO_2 concentration in gas outlet was achieved only in the initial period. This mean that CO_2 can be released from the water. The pH of water after feeding with air flow was 6.8. These results confirmed that CO_2 can be desorbed from CO_2-rich water by the air bubbling. Then the regeneration of CO_2 absorbed water can be done using airflow contacting with CO_2-rich water. It causes the water can be recirculated to re-absorb CO_2 into the process.

Table 4.2 CO_2 concentration in outlet gas stream on desorption unit in laboratory scale.

Experiments No.	Time (min)	Concentration of CO_2 (%CO_2)
1	0	30.88
	5	-
	10	-
2	0	30.61
	5	-
	10	-
3	0	29.46
	5	-
	10	-

4.6 Regeneration unit for CO_2 removal

4.6.1 Designing and testing

The regeneration unit was designed to release CO_2 from rich absorbent for water recirculation to re-absorb continuously in the system. Previously, the tests were performed in laboratory scale by investigating the effect of various temperatures 30, 40, 50, and 60 °C. The optimum condition in laboratory-scale brings to the design of the regeneration unit in the development of prototype system as shown in Figure 3.21. The counter current air flow was used for releasing the CO_2 gases from CO_2 saturated water. The experiments were done by varying air flow rate. The pH of water inlet and outlet was investigated. The results of CO_2 removal efficiency with the regeneration unit in development of a prototype unit were monitored and reported.

4.6.2 pH of water during regeneration

The experiments of CO_2 gas absorption and CO_2-rich water regeneration were continuously carried out by re-circulated water in the system. In the absorption unit, 4 L/min of simulated biogas flow rate and 15 L/min of water flow rate were used. The initial CO_2 concentration of 40% CO_2 in the simulated biogas stream was used in the tests. Fresh water with pH 7.4 was initially fed to the absorption system. At 10 minute operation time, the pH of water was changed from 6.0 to 7.4 by dissolving of CO_2 gas into the water in absorption unit. This react result in H_2CO formation in the water, causing the pH of water leaving the absorption unit lower than tap water. Water deriving from the absorption unit was continuously introduced to the regeneration unit and re-circulated back to absorb CO_2 in the absorption unit. 30 L/min of air flow rate was counter current flowed with CO_2-rich water spraying in the regeneration unit. The changes in pH of water by CO_2 desorbtion in the regeneration unit were investigated in this study. Figure 4.14 shows the comparison between pH of water inlet and outlet of the regeneration unit with time.

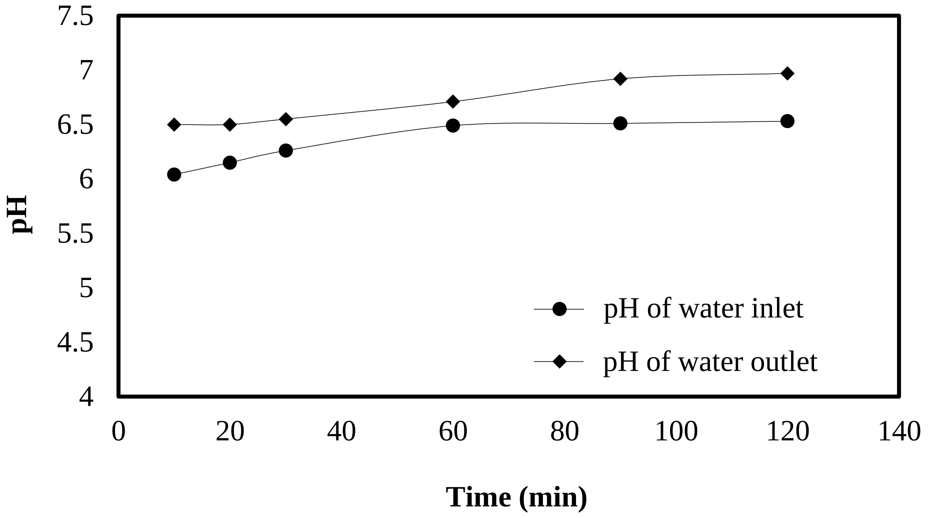


Figure 4.14 Comparison between pH of water inlet and outlet of regeneration unit.

It was observed that pH of the regenerated water of about 6.9 was achieved after passes through the regeneration unit at operation time of 120 minutes. The pH of CO_2 saturated water before feeding through the regeneration unit was changed from pH 6.0 at time 10 minute to pH 6.5 at time 120 minutes.

4.6.3 Effect on CO_2 removal by regeneration unit

The comparison results of CO_2 removal efficiency by absorption unit were presented by re-circulating absorbent water with and without regeneration as shown in Figure 4.15. The experimental tests by the prototype unit were operated for 120 minutes. The plot showed that the CO_2 removal efficiency with regeneration of the absorbent water had a little increased from 84.61% to 94.01% along the running time. In contrast, the CO_2 removal efficiency without regeneration of the absorbent water had decreased from 79.42% to 56.21%. These found because of the spent water absorbent without regeneration made the water saturated with CO_2. The limiting in CO_2 absorption occurred by the continuously re-circulated the saturated water which decreasing the CO_2 removal efficiency.

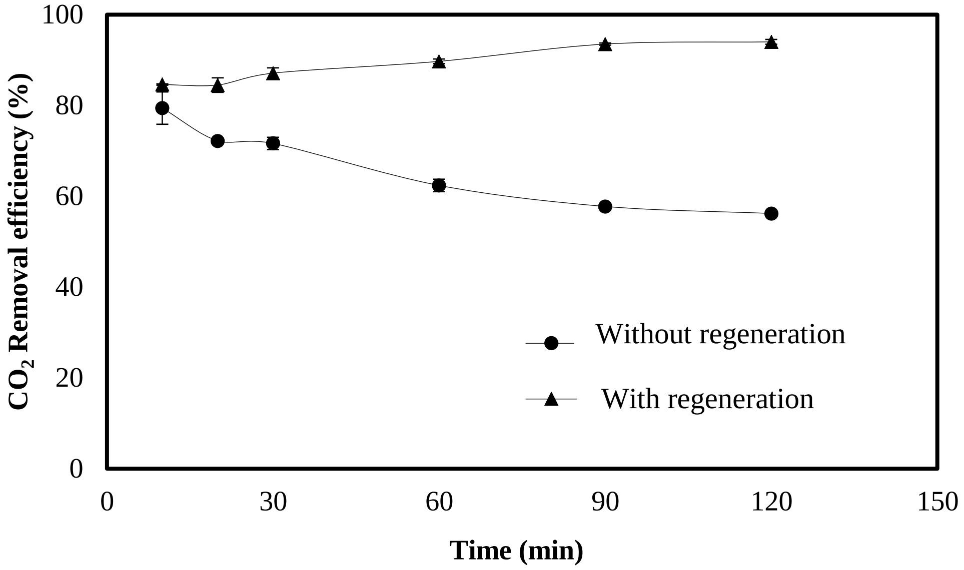


Figure 4.15 Regeneration of CO_2-rich water effect on CO_2 removal efficiency in water absorption unit.

4.6.4 Effect of air flow rate to regeneration unit

The experiments of CO_2 absorption from simulated biogas and regeneration of the water absorbent were studied for the effect of air flow rate. The effect of air flow rate 5-30 L/min on CO_2 removal efficiency were shown in Figure 4.16. The testing system carried out using a gas flow rate of 4 L/min, water flow rate of 15 L/min, and 40% CO_2 concentration in simulated biogas stream. Testing time of 120 minutes was continuously performed with regeneration and re-circulating the absorbent water back to absorb CO_2 in the absorption system. The CO_2 removal efficiency was monitored and calculated every 30 minutes.

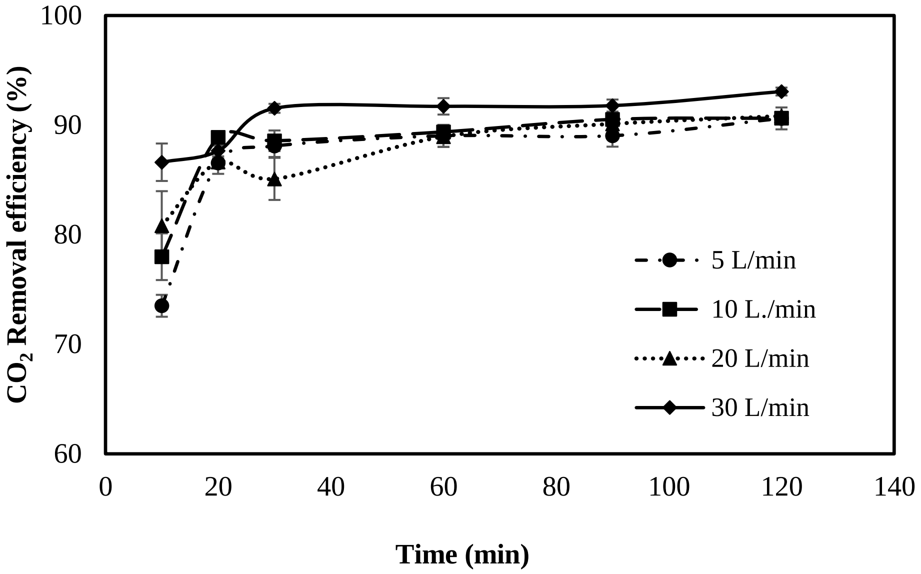


Figure 4.16 Effect of air flow rate feeding to regeneration unit on CO_2 removal efficiency of the absorption prototype system.

The results indicated that the increase in air flow rate from 5 to 30 L/min obliviously increased CO_2 removal efficiency. Initial run of 10 minutes, more different was found by the effect of air flow rate on CO_2 removal efficiency. Over 90% of CO_2 removal efficiency was obtained by using 30 L/min of air flow rate. It should be noted that the high air flow rate provides better desorbing of CO_2 gases from absorbent water. The counter current of air flow and CO_2-rich water has a result in a deformation of H_2CO_3 and HCO_3^- to form CO_2 gas. Indeed, an increase in air flow rate caused a large amount of O_2 to contact with carbonic acid (H_2CO_3) from CO_2 saturated water. Hence, the carbonic acid (H_2CO_3) transform to CO_2 gas caused CO_2 can be released from water as described in Equation (4.2)-(4.3) causing the water can be re-circulated back into the process.

4.7 Study of biomethane production

4.7.1 Biogas compositions

Biogas was derived from the chosen anaerobic wastewater treatment system of SONGKLA CANNING PCL. The biogas consisted of 2 main gas compounds (CH_4 and CO_2) and other kinds of gas as shown in Table 4.3. The composition by volume of biogas was measured by gas chromatography. The gas contains 69.94% of CH_4, 27.25% of CO_2, H_2S more than 800 ppm and 2% of others. Due to the damage of the system that can cause by H_2S, it is typically removed in the early state (Ryckebosch et al., 2011). From the standard, the level of H_2S contaminated in biogas should not exceed 4,000 ppm and safe for natural gas lines should less than 100 ppm (Martin, 2008). In these experiments, the concentration of H_2S was controlled by installation the steel wool column and spraying with water.

Table 4.3 Composition of biogas deriving from SONGKLA CANNING PCL.

Compounds	Concentration
Methane (CH_4); volume %	69.94
Carbon dioxide (CO_2); volume %	27.25
Hydrogen sulfide (H_2S); ppm	> 800
Oxygen (O_2); volume %	< 0.5
Nitrogen (N_2); volume %	2.02

4.7.2 H_2S removal from biogas

Spray column with steel wool was used to remove H_2S from biogas before feeding to the biomethane production system. The tested of H_2S removal from biogas by counter current flow between the biogas and water on the steel wool media. Constant water feed flow rate of 10 L/min and the biogas flow rate of 2 L/min were introduced the column. The H_2S concentrations in the feed and treated gas stream were measured using a detector tube method as illustrated in Figure 4.17. It was observed that the concentration of H_2S in gas feed stream had higher than 800 ppm. The outlet H_2S concentration of 25 ppm was obtained. After 5 minutes, the concentration of H_2S lower than 25 ppm throughout the experiment and the system reach a steady state.

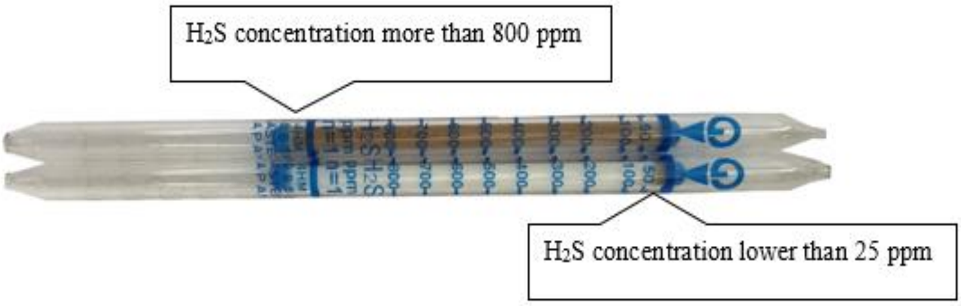


Figure 4.17 H_2S detector for the feed and treated gas streams.

4.7.3 Biomethane production by CO_2 removal

The optimum condition of the CO_2 absorption unit consisting of microbubble generator with tube absorber, gas separator, and regenerator unit was applied to test for biomethane production. Figure 4.18 shows the results of experiment to produce biomethane as carried out using 3.75 of L/G ratio in development prototype unit. Biogas using as a feed gas stream of the system was treated by H_2S removal system. The results observed that the biomethane with CH_4 concentration of 90-96 volume % was achieved from the system. This indicates that almost all CO_2 in the treated biogas stream was removed. Result also showed that over 85% of CO_2 removal efficiency was obtained when biogas from anaerobic fermentation was applied.

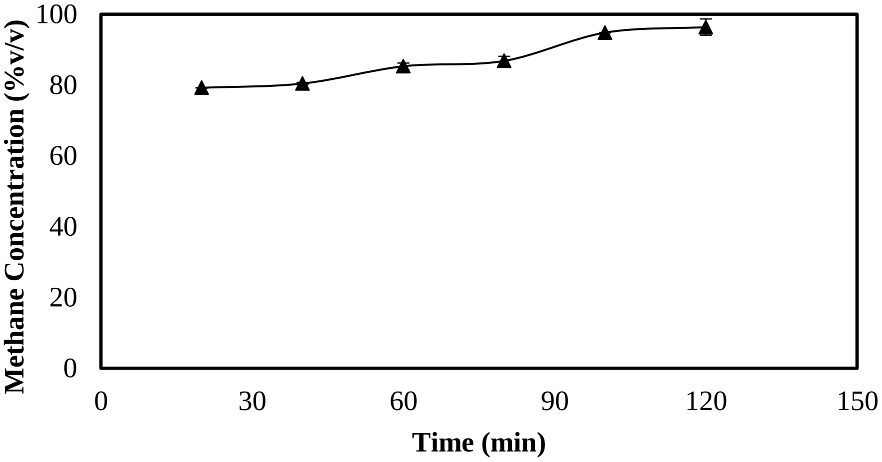


Figure 4.18 Outlet CH4 concentration in biomethane by CO2 removal from biogas using absorption unit with microbubble and regeneration unit.

The plots of CH_4 concentration in biomethane using CO_2 absorption unit is shown in Figure 4.18. It can be seen that the CH_4 contents that separated from the gas separate column were slightly increased with time. After 100 minutes operation, the concentration of CH_4 reached constantly at 96.36% which matches the specification for biomethane. An application of biomethane deriving from treating and getting specification as vehicle fuel or NGV was proposed by Kasikamphaiboon et al., 2013.

4.8 Analytical of methane loss

All of the biomethane production systems from biogas are always losing the CH_4 contents in the system. For this work, there is a loss of CH_4 contents, which is caused by some CH_4 gas dissolving into the water. Therefore, to reduce the loss of CH_4, a gas separation unit is installed. So that the CH_4 gas is most separated from the water, results in the least loss of CH_4. Table 4.4 shows the CH_4 loss from the CO_2 absorption system from biogas.

Table 4.4 CH_4 loss from the CO_2 absorption system from biogas

Gas	**Concentration (% v/v)**			**Methane Loss (% v/v)**
	Biogas	**Biomethane**	**Waste gas**	
CO_2	27.25	1	99	0.013%
CH_4	69.94	96.36	3.46	

Based on CH_4 and CO_2 balance as shown in Figure 4.19 The CH_4 loss was calculated as equation (4.4) (Kvist, T. and Aryal, N. 2019).

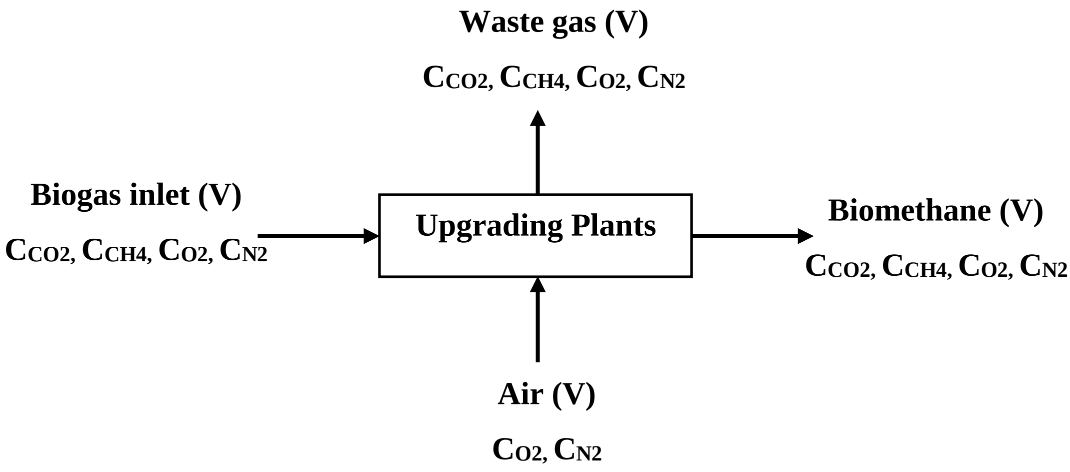


Figure 4.19 Gas sampling points in CO_2 absorption system from biogas.

$$\textbf{Methane Loss}=\frac{C_{CH_4,\ biogas}-\dfrac{C_{CO_2,\ biogas}\cdot C_{CH_4,\ biomethane}}{C_{CO_2,\ biomethane}}}{C_{CH_4,\ waste}-\dfrac{C_{CO_2,\ waste}\cdot C_{CH_4,\ biomethane}}{C_{CO_2,\ biomethane}}}\cdot\frac{C_{CH_4,\ waste}}{C_{CH_4,\ biogas}} \qquad (4.4)$$

Where C denotes the gas concentration in percentage.

The optimum conditions from the experiment were used to produce biomethane. As a result, the CH_4 loss from biomethane production by the CO_2 absorption system from biogas was achieved at 0.013% CH_4.

Kvist, T. and Aryal, N. (2019) found that the CH4 loss from the tested water scrubbers, which was 1.97% CH_4. Petersson, A. and Wellinger, A. (2009) observed the CH_4 loss on water scrubbing was achieved at 1-2% CH_4. It can be seen that the water scrubber system of above authors has a higher CH_4 loss than this work. Therefore, in this study, biomethane production using the water absorption column with microbubble technique was tested by atmospheric pressure and room temperature to reduce energy consumption and can lead to lower emission of CH_4.

4.9 Analytical economics

4.9.1 Electricity charge

Estimation of total electricity charge in the biomethane production using water absorption column with microbubble technique. The electricity charge was evaluated by the electric power of all electrical machines used to support the operation of biomethane production. The biogas flow rate in gas feed stream was used at 4 L/min accounted for 5760 L/day equal to 5.8 m^3/day. Calculation of biomethane production leads time as shown in Table 4.5 The rate of electricity consumption that used to produce biomethane consists of a one 0.029 kW of air blower, two 0.08 kW of pumps, and one 0.37 kW of pump as shown in Table 4.6

Table 4.5 Calculation of biomethane production leads time.

Biogas flow rate (L/min)	Water flow rate (L/min)	L/G ratio	Operating time (hours)	Amount of biogas used to remove (m^3/day)	Capacities of biomethane production (m^3/day)
4	15	3.75	24	5.8	5

Table 4.6 Calculation of electricity consumption rates in biomethane production using water absorption column with microbubble technique**.**

Machines	Electric Power (kW)	Operating time (hours)	Amount	Used Energy (kWh)
Blower	0.029	24	1	0.70
Pump	0.08	24	2	3.84
Pump	0.37	24	1	8.88
Rate of energy used	13.42 kWh/day			

From Table 4.6, calculation of electricity consumption rates in biomethane production using energy of 13.42 kWh/day. Operating 30 days per month accounted for 402.6 kWh/mount. Electricity Tariff for type 2.1 Small General Service(Normal Tariff/Progressive Rate). The details of calculation of electricity charge are follows:

Section 1 Base Tariff

Energy Charge	1,554.21	Baht
Service Charge	46.41	Baht
Total Base Tariff	**1,600.37**	**Baht**

Section 2 (F_t) Charge

Used Energy x F_t Rate	-46.60	Baht

Section 3 Tax 7%

(Base Tariff + F_t) x 7/100	108.76	Baht
Total Electricity Charge	**1,662.43**	**Baht**

4.9.2 Water Tariffs

The amount of water was used to produce biomethane by water absorption column with a microbubble technique. Calculation of water tariffs based on 15 L/min of water flow rate. The amount of water used in the biomethane production of 0.2 m^3/day. The operation that makes up 5% of the water every day accounted for 0.01 m^3/day equal to 0.30 m^3/ month. The calculation of water tariffs that used to produce biomethane is shown in Table 4.7.

Table 4.7 Calculation of water tariffs that used to produce biomethane

price/unit (Baht)	**Volume (m^3)**	**Total (Baht)**
16.00	0.30	4.80
Sub total *		150.00
Meter Service charge		30.00
VAT (7%)		12.60
Total		**192.60**

* Minimum 150 Baht/Month (9 m^3): PWA water tariff calculater system

4.9.3 Operating costs for biomethane production using water absorption column with microbubble technique

The design of biomethane production using water absorption column with microbubble technique. The operating costs of this system can be calculated to support a biogas flow rate of 4 L/min accounted for 5760 L/day equal to 5.8 m^3/day. Table 4.8 shown details of operating costs for biomethane production.

Table 4.8 Operating costs for biomethane production using water absorption column with microbubble technique

Amount of biogas used to remove (m^3/day)	**Capacities of biomethane production (m^3/day)**	**Operating time (hours)**	**Water Tariffs (Baht/day)**	**Electricity charge (Baht/day)**	**Cost of biomethane production (Baht)**
5.8	5	24	6.42	55.41	61.83
1	0.86	24			10.63

From analytical of operating cost for biomethane production using water absorption column with microbubble technique. It was observed that this system has a low operating cost, which was 10.63 baht/m^3. Therefore, the system is worth the investment.

CHAPTER 5

CONCLUSION

From the innovation of biomethane production by water absorption with microbubble technique. The system consists of the series of microbubble generation unit, water absorption column, H_2S removal unit, tube absorber with gas separation unit, and regeneration unit to release CO_2 from CO_2-rich water results in the water can be re-absorbed continuously in the system. The suitable conditions for experimental results can be described as follows:

5.1 Conclusion of CO_2 removal from biogas with a prototype unit

5.1.1 Experimental setup for CO_2 removal from a simulated biogas

The design and installation of a prototype unit for CO_2 removal from biogas consist of the three main units which are simulated biogas, microbubble generator, and absorption column. Venturi ejector was used to creating microbubble, the gas bubbles with water transfer into the absorption column to increase retention time between gas phase and liquid phase. The results indicated that the design and installation for CO_2 removal from biogas can be used effectively.

5.1.2 Suitable conditions of CO_2 removal from a simulated biogas

From the experimental results, the CO_2 removal from simulated biogas at the initial concentration of 20-40% CO_2 and using a 0.50-inch venturi ejector. The suitable condition that provides 75% of CO_2 removal efficiency at 4 L/min of gas flow rate and 15 L/min of water flow rate. This condition can be used as a guideline to develop the design and installation of the development of a prototype unit for CO_2 removal from biogas.

5.2 Conclusion of CO_2 removal from biogas with the development of a prototype unit

From the suitable conditions of experimental results of CO_2 removal from biogas with a prototype unit bring to develop the design and installation of development of a prototype unit for CO_2 removal from simulated biogas and biogas. The details can be described as follows:

5.2.1 Experimental setup for CO_2 removal from simulated biogas and biogas

There are four main units for CO_2 removal from simulated biogas and biogas. Each unit is described as below:

1. The CO_2 absorption unit: 0.50-inch venturi ejector was used to generating microbubble. The absorption column was used to reduce pressure drop and save energy consumption.
2. Tube absorber: tube absorber 0.016 meters in dia. 10 m of long was applied in order to increase retention time which increases CO_2 removal efficiency.
3. Gas separation column: 2 spray columns of 1.8 meters in height and 0.3 meters in order to separate the CH_4 gas from the water as much as possible.
4. Regeneration unit: a spray column of 1.0 meters in height and 0.6 meters in diameter with countercurrent airflow was used to separate CO_2 from CO_2-rich water.
5. H_2S removal unit: spray column with steel wool to remove H_2S from biogas. Results in the concentration of H_2S lower than 25 ppm in the cleaning biogas before fed into the CO_2 absorption system.

5.2.2 Suitable conditions of CO_2 removal from simulated biogas and biogas

1. Biogas from the wastewater treatment system of SONGKLA CANNING PCL. was fed into the H_2S removal unit with 2 L/min of biogas flow rate and 10 L/min of water flow rate. The H_2S concentration is reduced from over 800 ppm at the inlet to 25 ppm at the outlet.

2. Size of microbubble produced from venturi ejector increases as the gas flow rate increases. The small size of gas bubble results in higher the solubility of CO_2 in water. Thus, CO_2 removal efficiency has increased. Moreover, the uses of gas flow rate at 2-8 L/min with 15 L/min of water flow rate can generate the size of microbubble in the range of 20-30 µm.

3. An increase in L/G ratio results in increased CO_2 removal efficiency. The increasing of CO_2 removal efficiency increases at the initial, followed by a slight increase after 30 minutes. This is probably due to the limited of CO_2 dissolved in water. L/G ratio of up to 7.5 causes a slight increase in CO_2 removal efficiency. Thus, using L/G ratio higher than 3.75 may not be necessary.

4. The concentration of CO_2 in simulated biogas of about 35-50% is applied, the CO_2 removal efficiency over 80% is obtained which is efficient production of biomethane from biogas.

5. The result of the regeneration unit shows that after desorption pH of water is close to the tap water (pH about 6.9), results in water can be used to re-absorb continuously in the system. CO_2 removal efficiency up to 90% is obtained when using the airflow rate of 30 L/min.

6. The suitable condition for biomethane production that provides over 96% of CH_4 concentration or less than 4% of CO_2 concentration by gas flow rate 4 L/min, 3.75 of L/G ratio. CH_4 loss of 0.013% is achieved. The outlet CH_4 concentration over 90% which matches the purity of CH_4 specification for biomethane. An application that uses biogas as vehicle fuel or NGV (Kasikamphaiboon et al., 2013).

5.3 Operating cost

The operating cost of biomethane production by water absorption column with microbubble technique is 10.63 baht/m^3, which is worth investment. This research presents the design and installation of CO_2 removal from biogas with a prototype unit to produce biomethane for industrial applications.

5.4 Recommendation for future study

1. Biomethane production from this research can be used as vehicle fuel or NGV and LPG for a household. However, before using biomethane production, it should be compressing raw CH_4 gas with high-pressure compressors into storage tank.

2. Extensive study should be done to gather more information about the pH of CO_2-rich water on aquatic chemistry.

3. For an industrial application, this system should have an automatic control system for convenience and precision.

REFERENCES

Abdeen F. R.H., Mel M., Jami M. S., Ihsan S. I. and Ismail A.F. 2016. A review of chemical absorption of carbon dioxide for biogas upgrading. Chinese Journal of Chemical Engineering 24, 693–702.

Barlow PJ. 1994. An introduction to ozone generation.

Bethell, W. J. and Auckland (NZ). 2010. BIOGAS UPGRADING. PATENT No.: US 2010/0107872 A1

Caveny et al., 2000. Method for measuring and quantifying amounts of carbon from certain greenhouse gases sequestered in and by grassy and herbaceous plants above and below the soil surface. U.S. PATENT No.: 6,115,672.

Dexter, Z. D., Joseph, C. G., Zahrim, A. Y. (2016). A review on palm oil mill biogas plant wastewater treatment using coagulation-ozonation. International Conference on Chemical Engineering and Bioprocess Engineering. IOP Conf. Series: Earth and Environmental Science 36 012029.

Facta, M., Salam, Z., Buntat, Z., Yuniarto, A. (2010). Silent Discharge Ozonizer for Colour Removal of Treated Palm Oil Mill Effluent Using A Simple High Frequency Resonant Power Converter. IEEE International Conference on Power and Energy (PECon2010) , Nov 29 - Dec 1, Kuala Lumpur, Malaysia.

Fujikawa S., Zhang R., Hayama S. 2003. The control of micro-air-bubble generation by a rotational porous plate, International Journal of Multiphase Flow. Guoyi Peng, Volume 29 (2003) 1221-1236.

Islamiyah M., Soehartanto T., Hantoro R. and Abdurrahman A. 2014. Water Scurrbbing for Removal CO_2 and H_2S in Biogas from Manure. *Indonesia EBTKE-ConEx,* 126-131.

Kadam R., Panwar N.L. 2017. Recent advancement in biogas enrichment and its applications. Renewable and Sustainable Energy Reviews Volume 73 (2017) 892-903.

Kasikamphaiboon, P., Chungsiriporn, J., Bunyakan, C., & Wiyaratn, W. (2013). Simulateneous removal of CO_2 and H_2S using MEA solution in a packed column absorber for biogas upgrading. Songklanakarin Journal of Science and Technology, 35(6), 683-691.

Khan, I. U., Othman, M. H. D., Hashima, H., Matsuura, T., Ismail, A.F., DashtArzhandi, M. R. and Azelee. I. W., Biogas as a renewable energy fuel–Areview of biogas upgrading, utilisation and storage. Journal of Energy Conversion and Management 150, 277-294.

Kreetachat, T., Damrongsri, M., Punsuwon , V., Vaithanomsat, P., Chiemchaisri, C., Chomsurin, C. (2007) . Effects of ozonation process on lignin-derived compounds in pulp and paper mill effluents. Journal of Hazardous Materials, 142, 250–257.

Kvist, T. and Aryal, N. 2019. Methane loss from commercially operating biogas upgrading plants. Journal of Waste Management 87, 295–300.

Liu X. 2015. Continuous process of biogas purification and co-production of nano calcium carbonate in multistage membrane reactors.

Lung-Chyuan Chen. (2000) . Effects of Factors and Interacted Factors on The Optimal Decolorization Process of Methyl Orange by Ozone. Water Research, 34, 974-982.

Maia D. C., Niklevicz R. R., Arioli R., Frare L. M., Arroyo P. A., Gimenes M. L., Pereira N. C. 2017. Removal of H_2S and CO_2 from biogas in bench scale and the pilot scale using a regenerable Fe-EDTA solution Renewable Energy. Volume 109 (2017) 188-194.

Maile O. I., Muzenda E., Tesfagiorgis H. 2017. Chemical Absorption of Carbon Dioxide in Biogas Purification. Procedia Manufacturing Volume 7 (2017) 639-646.

Maile O. I., Tesfagiorgis H., Muzenda E. 2017. The potency of monoethanolamine in biogas purification and upgrading. South African Journal of Chemical Engineering Volume 24 (2017) 122-127.

Martin, J. H., 2008. A new method to evaluate hydrogen sulfide removal from biogas. Thesis for Master of Science, Biological and Agriculture Engineering, North Carolina State University.

Miltner, M., Makaruk, A. and Harasek. M. 2017. Review on available biogas upgrading technologies and innovations towards advanced solutions. Journal of Cleaner Production 161; 1329-1337.

Ohnari A. H., Shuppanasha N. J. 2006. All about Microbubbles. Japan.

Petersson, A. and Wellinger, A. (2009). Biogas upgrading technologies – developments and innovations. Task 37 - Energy from biogas and landfill gas. IEA Bioenergy.

Rasi S, Veijanen, A. and Rintala J. 2007. Trace compounds of biogas from different biogas production plants. Journal of Energy 32(8): 1375–80.

Rasi S., Läntelä J., Rintala J. 2014. Upgrading landfill gas using a high pressure water absorption process. Fuel. Volume 115 (2014) 539-543.

Rasi, S., Läntelä, J., Veijanen, A. and Rintala, J. 2008. Landfill gas upgrading with countercurrent water wash. Journal of Waste Management 28(9); 1528-1534.

Rautenbach et al., 2003. Method of utilizing a methane – containing biogas. U.S. PATENT No.: US 6,601,543 B2.

Rice R.G., Miller G.W., Robson C.M. & Hill A.G. (1980) .Ozone Utilization in Europe. In. AIChe Symposium Series, Ozone Institute, Toronto, 117-134

Ryckebosch E., Drouillon M. and Vervaeren H. 2011. Techniques for transformation of biogas to biomethane, Biomass and Bioenergy, 35, 1633-1645.

Sadatomi A. K. M. 2008. Fluids mixer and fluids mixing method.

Sadatomi M. 2003. Microbubble producing apparatus. Japanese Patent. JP.2003-30549.

Sahota, S., Shah, G., Ghosh, P., Kapoor, R., Sengupta, S., Singh, P., Vijay, V., Sahay, A., Vijay, V. K. and Thakur, I. S. 2018. Review of trends in biogas upgradation technologies and future perspectives. Bioresource Technology Reports, Volume 1, March 2018, P.79-88.

Serizawa, A., 2003. A study on drag reduction with microbubble injection nozzle for application to ships. Report of the Activities from Joint Research Projects, Research Institute of Appied Mechanice. Kyushu University (in Japanese)

Xiao, Y., Yuan, H., Pang, Y.,Chen, S., Zhu, B., Zou, D., Ma, J., Yu, L., & Li, X. (2014). CO_2 Removal from Biogas by Water Washing System. Chineses journal of Chemical Engineering, 22, 950-953.

Yasuno M., Sugiura S., Iwamoto S., Nakajima M., Shono A. and Satoh M. 2004. Monodispersed microbubble formation using microchannel technique. AIChE Journal (2004) Vol. 50, No. 12.

Zahrim, A.Y., Dexter, Z.D., Joseph, C.G., Hilal, N. (2017) . Effective coagulation-flocculation treatment of highly polluted palmoil mill biogas plant wastewater using dual coagulants:Decolourisation, kinetics and phytotoxicity studies. Journal of Water Process Engineering, 16, 258–269.

APPENDIX A

EXPERIMENTS DATA

Table A1 Peak area of CO_2 concentration in gas standard and simulated biogas (%CO_2)

	CO_2 concentration (%)	**Peak area**
Simulated biogas	0	0
	20	1834.35
	30	2554.23
	40	3480.28
	65	5605.68
	75	6552.02
Gas standard	35	3041

Table A2 Effect of various gas flow rate on CO_2 removal with the 0.25-inch of venturi at water flow rate 15 L/min

Gas flow rate (L/min)	**CO_2 removal efficiency (%CO_2)**			
	Run No. 1	**Run No. 2**	**Run No. 3**	**mean±SD**
2	53.77	54.79	60.85	56.47±3.82
4	34.87	33.35	38.25	35.47±2.51
6	27.97	30.54	20.68	26.53±5.11
8	12.85	12.46	19.11	14.85±3.73
10	5.69	6.12	3.51	5.09±1.40

Table A3 Effect of water flow rate on CO_2 removal with the 0.25-inch of venturi ejector at 4 L/min of gas flow rate

Water flow rate (L/min)	**CO_2 removal efficiency (%CO_2)**			
	Run No. 1	**Run No. 2**	**Run No. 3**	**mean±SD**
9	21.94	25.07	23.13	23.38±1.58
12	29.13	30.56	34.06	31.25±2.54
15	33.85	34.96	37.60	35.47±1.93
17	39.56	40.85	40.82	40.41±0.74

Table A4 Size of venturi ejector on CO_2 removal with the various gas flow rate

Size of microbubble	**Gas flow rate (L/min)**	**CO_2 removal efficiency (%CO_2)**			
		Run No. 1	**Run No. 2**	**Run No. 3**	**mean±SD**
0.25”	2	53.77	54.79	60.85	56.47±3.82
	4	34.87	33.35	38.25	35.47±2.51
	6	27.97	30.54	20.68	26.53±5.11
	8	12.85	12.46	19.11	14.85±3.73
	10	5.69	6.12	3.51	5.09±1.40
0.5”	2	85.55	85.79	86.02	85.79±0.23
	4	52.73	58.44	66.70	59.47±7.02
	6	51.61	54.15	43.60	49.94±5.50
	8	34.55	34.73	28.62	32.66±3.47
	10	21.43	23.43	18.90	21.27±2.27

Table A5 Size of venturi ejector on CO_2 removal with the various water flow rate

Size of microbubble	**Water flow rate (L/min)**	**CO_2 removal efficiency (%CO_2)**			
		Run No. 1	**Run No. 2**	**Run No. 3**	**mean±SD**
0.25”	9	21.94	25.07	23.13	23.38±1.58
	12	29.13	30.56	34.06	31.25±2.54
	15	33.85	34.96	37.60	35.47±1.93
	17	39.56	40.85	40.82	40.41±0.74
0.5”	9	57.05	59.59	54.96	57.16±2.32
	12	65.67	69.75	67.72	67.72±2.04
	15	68.95	70.33	76.36	71.88±3.95
	17	79.89	79.34	79.62	79.61±0.27

Table A6 Effect of gas flow rate on CO_2 removal efficiency as a function of the performance of inline static mixer

	Gas flow rate (L/min)	**CO_2 removal efficiency (%CO_2)**			
		Run No. 1	**Run No. 2**	**Run No. 3**	**mean±SD**
inline static mixer	2	85.55	85.79	86.02	85.79±0.23
	4	52.73	58.44	66.70	59.47±7.02
	6	51.61	54.15	43.60	49.94±5.50
	8	34.55	34.73	28.62	32.66±3.47
	10	21.43	23.43	18.90	21.27±2.27
Non inline static mixer	2	77.90	83.53	80.79	80.73±2.81
	4	68.94	67.78	68.57	68.38±0.38
	6	56.77	52.50	54.65	54.66±2.13
	8	53.41	53.25	53.13	53.14±0.14
	10	45.35	41.57	43.42	43.44±1.89

Table A7 Effect of water flow rate on CO_2 removal as a function of venturi ejector without an inline static mixer

Water flow rate (L/min)	**CO_2 removal efficiency (%CO_2)**			
	Run No. 1	**Run No. 2**	**Run No. 3**	**mean±SD**
9	59.83	61.14	60.46	60.48±0.65
12	60.51	61.87	61.22	61.20±0.68
15	65.68	67.45	72.01	68.38±3.27
17	74.27	76.73	75.53	75.51±1.24

Table A8 Effect of CO_2 concentration on CO_2 removal efficiency by 4 L/min of gas flow rate and 15 L/min of water flow rate

The initial CO_2 concentration (%CO_2)	**CO_2 removal efficiency (%CO_2)**			
	Run No. 1	**Run No. 2**	**Run No. 3**	**mean±SD**
20	77.01	72.15	75.63	74.94±2.51
30	68.48	75.75	71.86	72.04±3.63
40	68.37	70.86	70.53	69.92±1.35
60	55.42	56.39	50.94	54.25±2.91
70	53.60	52.68	49.54	51.94±2.13

Table A9 Effect of L/G ratio on CO_2 removal efficiency with the constant water flow rate at 15 L/min

L/G ratio	**Time (min)**	**CO_2 removal efficiency (%CO_2)**			
		Run No. 1	**Run No. 2**	**Run No. 3**	**mean±SD**
7.5	10	88.32	84.40	87.11	86.61±1.71
	20	87.14	88.13	87.65	87.64±0.49
	30	90.88	90.78	92.93	91.53±0.41
	60	90.39	91.65	92.55	91.71±1.08
	90	90.71	91.48	93.15	91.78±1.25
	120	92.62	92.35	94.21	93.06±1.01
3.75	10	84.27	80.23	82.25	82.25±2.02
	20	86.01	85.08	85.53	85.54±0.47
	30	85.44	86.40	85.92	85.92±0.48
	60	89.03	88.11	88.57	88.57±0.46
	90	88.59	89.11	88.85	88.85±0.26
	120	88.99	90.03	89.51	89.51±0.52
2.5	10	74.52	77.47	75.98	75.99±1.48
	20	69.43	75.17	72.30	72.30±2.87
	30	71.95	78.23	75.12	75.10±3.14
	60	74.86	78.77	76.83	76.82±1.95
	90	74.34	81.38	77.87	77.86±3.52
	120	78.88	78.90	78.89	78.89±0.01
1.875	10	62.89	64.35	63.62	63.62±0.73
	20	63.04	64.74	63.89	63.89±0.85
	30	68.68	65.81	67.27	67.25±1.43
	60	72.13	68.68	70.84	70.55±1.74
	90	71.25	72.62	71.95	71.94±0.68
	120	73.68	73.18	73.43	73.43±0.25

Table A10 Effect of initial CO_2 in simulated biogas stream on CO_2 removal

The initial CO_2 concentration (% CO_2)	Time (min)	CO_2 removal efficiency (% CO_2)			
		Run No.1	Run No. 2	Run No. 3	mean±SD
35%	10	88.32	84.40	87.11	86.61±1.71
	20	87.14	88.13	87.65	87.64±0.49
	30	90.88	90.78	92.93	91.53±0.41
	60	90.39	91.65	92.55	91.71±1.08
	90	90.71	91.48	93.15	91.78±1.25
	120	92.62	92.35	94.21	93.06±1.01
40%	10	84.84	86.28	85.57	85.56±0.72
	20	86.68	86.71	86.71	86.70±0.02
	30	86.35	86.36	86.31	86.34±0.02
	60	87.93	88.10	88.99	88.34±0.57
	90	89.69	90.11	89.90	89.90±0.21
	120	91.19	91.05	91.12	91.12±0.07
50%	10	76.12	77.71	76.90	76.91±0.80
	20	79.09	83.11	81.10	81.10±2.84
	30	85.29	82.93	84.11	84.11±1.18
	60	86.81	87.23	87.02	87.02±0.21
	90	87.26	87.38	87.32	87.32±0.06
	120	88.09	88.08	88.10	88.09±0.01

Table A11 Effect of pH on CO_2 removal efficiency

Time (min)	pH		
	pH in	pH out	pH of fresh water
10	6.04	6.50	7.4
20	6.15	6.50	
30	6.26	6.55	
60	6.49	6.71	
90	6.51	6.92	
120	6.53	6.97	

Table A12 Effect of the desorption of CO_2 saturated water on CO_2 removal at the L/G ratio 3.75

	Time (min)	**CO_2 removal efficiency (%CO_2)**			
		Run No. 1	**Run No. 2**	**Run No. 3**	**mean±SD**
Non-regeneration	10	75.85	82.98	79.43	79.42±3.56
	20	71.83	72.57	72.20	72.20±0.37
	30	72.99	70.28	71.66	71.64±1.35
	60	63.76	61.02	62.40	62.39±1.37
	90	58.34	57.19	57.76	57.76±0.58
	120	55.65	56.77	56.21	56.21±0.56
Regeneration	10	84.46	84.75	84.62	84.61±0.15
	20	82.89	86.09	84.49	84.49±1.60
	30	88.28	85.96	87.12	87.12±1.16
	60	89.21	90.23	89.71	89.72±0.51
	90	93.28	93.76	93.52	93.52±0.24
	120	93.89	94.00	94.14	94.01±0.13

Table A13 Effect of air flow rate on CO_2 removal efficiency

Gas flow rate (L/min)	Time (min)	CO_2 removal efficiency (%CO_2)			
		Run No.1	Run No.2	Run No. 3	mean±SD
5	10	71.10	75.91	73.52	73.51±2.41
	20	85.64	87.46	86.56	86.55±0.91
	30	88.85	87.33	87.97	88.09±0.76
	60	88.63	89.42	89.01	89.02±0.40
	90	87.98	90.08	89.03	89.03±1.05
	120	90.23	90.95	90.61	90.61±0.34
10	10	75.86	80.12	77.99	77.99±2.13
	20	88.68	89.09	88.89	88.89±0.20
	30	89.51	87.63	88.57	88.57±0.94
	60	89.32	89.42	89.93	89.38±0.05
	90	90.70	90.34	90.52	90.52±0.18
	120	90.86	90.41	90.63	90.63±0.22
20	10	77.65	83.96	80.82	80.81±3.16
	20	86.95	86.30	86.62	86.63±0.32
	30	83.17	87.01	85.09	85.09±1.92
	60	87.99	89.89	88.97	88.95±0.95
	90	89.92	90.30	90.11	90.11±0.19
	120	91.04	90.62	90.83	90.83±0.21
30	10	88.32	84.40	87.11	86.61±1.71
	20	87.14	88.13	87.65	87.64±0.49
	30	90.88	90.78	92.93	91.53±0.41
	60	90.39	91.65	92.55	91.71±1.08
	90	90.71	91.48	93.15	91.78±1.25
	120	92.62	92.35	94.21	93.06±1.01

Table A14 Entering and exiting of CH_4 concentration on CO_2 removal from biogas

CH_4 concentration in biogas inlet (%CH_4)	Time (min)	CH_4 concentration in biogas outlet (%CH_4)
69.94	10	79.22
	20	80.81
	30	85.30
	60	86.82
	90	93.40
	120	96.36

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