CHAPTER 2

Theory

This chapter presented methods of biogas production and introduced biomethane standard in the first part. The second and the third parts explained techniques of biogas upgrading by carbon dioxide absorption/regeneration with monoethanolamine solution. The last part was biomethane adsorption on porous medium.

2.1 Biogas Production and Biomethane Standard

2.1.1 Organics Matter Digestion Process

The organics matter digestion process by microorganism is divided into 2 processes which are an aerobic digestion and an anaerobic digestion.

1) An aerobic digestion

In aerobic digestion process, the organic matter is digested by aerobic bacteria group. It can produce carbon dioxide and a large amount of sludge. The carbon proportion in the raw material is converted to be the products as shown in Figure 2.1. In this process, high efficiency operation and short time treatment are obtained. However, the investment, the operating and the maintenance costs are quite high because the air is fed into the system and the excess sludge elimination is necessary.

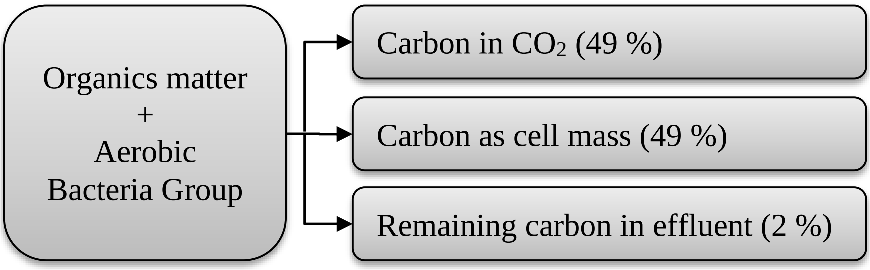


Figure 2.1 The organics matter digestion with aerobic bacteria group.

2) An anaerobic digestion

Around 80-90 % by weight of organics matter is digested by anaerobic bacteria group. Anaerobic digestion produces methane, carbon dioxide, a number of trace gases, some heat, and an end product of stabilized sludge. There are four stages in anaerobic digestion - hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Bacterial groups are responsible for acetate, hydrogen and carbon dioxide production in the first three stages. In the last stage, methanogenic archaea produces methane from acetate, or alternatively from hydrogen and carbon dioxide [Yu *et al.* 2014]. The carbon proportion in raw material is converted to be the product as shown in Figure 2.2. The biogas consists of methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), hydrogen (H_2) and hydrogen sulfide (H_2S) of which the concentrations of the first two components are 55-65 % and 35-45 % by volume, respectively. The methane is flammable so it could be used as fuel for generating heat or running engine.

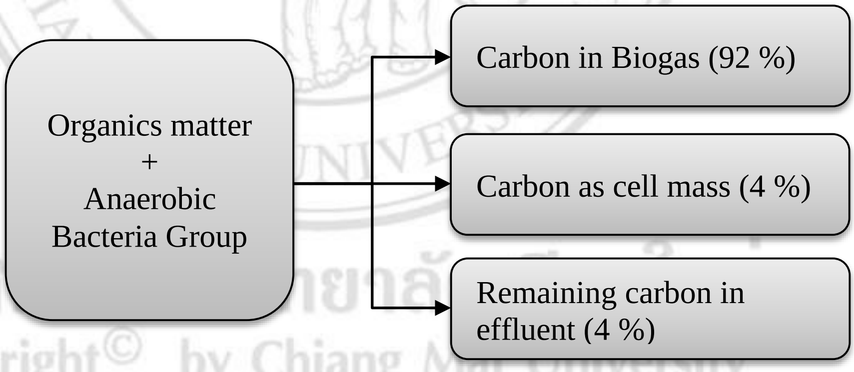


Figure 2.2 The organics matter digestion with anaerobic bacteria group.

The biogas utilizations give a lot of advantages over the conventional energy which are:

1) Alternative energy in term of LPG replacement for cooking and heating; diesel replacement for running engine for power generation.

2) Environmental aspect such as reduction of odor, toxic gases including disease or germs in the organic wastes. The main topic is to reduce methane emission for the organic waste to the environment. Moreover, the waste could be transformed into useful energy.

3) Agriculture advantage since the water from biogas production could be used for plant watering and the sludge from the biogas reservoir could be taken as fertilizer for improving soil quality.

It could be noted that the carbon dioxide component in the biogas is quite high. It could damage the engine or the system parts such as the corrosion in pipe line. In addition, it causes low heating value in the biogas. Therefore, reduction of carbon dioxide in biogas is necessary. The upgraded one could increase engine efficiency for power generation.

2.1.2 Biomethane [ERDI 2010]

The upgraded biogas with CO_2 and H_2S separation is called “Biomethane” or Renewable Natural Gas (RNG). When the biomethane is compressed into a tank for use as fuel for vehicle, this one was named Compressed Biomethane Gas (CBG). The quality of the biomethane was found to be close to compressed natural gas (CNG) or natural gas for vehicle (NGV). The standards of natural gas, such as the Society of Automotive Engineering J1616 (SAE J1616), California Air Resources Board (CARB), New Zealand Standard (NZS) and California Public Utilities Commission (CPUC) are given in Table 2.1

In Thailand, there is no biomethane quality standard, however, the biomethane for internal combustion engines or vehicles will be followed the Natural Gas Standard for vehicles as that launched out by the Department of Energy [Ministry of Energy 2014].

Table 2.1 Standard of Natural Gas [Laoonual *et al*. 2007].

Component	**SAE J1616 (1994)**	**CARB (1992)**	**NZS 5442 (1999)**	**CPUC Rule 30 (2002)**	**CARB (Draft)**
CH_4	-	> 88%	-	-	-
C_2H_6	-	< 6%	-	-	-
C_3+	-	<3%	-	-	-
C_4+	-	-	-	-	5%
C_6+	-	< 0.2%	-	-	-
N_2	-	-	-	-	-
CO_2	< 3%	< 0.1 %	-	< 3%	-
Inert Gas	-	1.5-4.5	-	< 4%	-
Sulfur	8-30 ppm	< 16 ppm	50 mg/m^3	< 0.75 grain/100 scf	< 1 grain/100 scf
Methane No.	-	-	-	-	> 80
Heating Value	-	-	-		-
Specific Gravity	-	-	< 0.8	-	-
Wobby Index	48.5-52.9	-	48-52	+/- 10%	-

Note: Unit is % by weight (Except as otherwise)

2.2 Biogas Upgrading

Separation of CO_2 separation in biogas could be classified into 6 processes as: physical absorption process, chemical absorption process, pressure swing absorption, membrane technology, cryogenic process, and biological process.

2.2.1 Physical Absorption Process

The water scrubbing of CO_2 by absorption process is purely physical. The biogas is pressurized and fed to the bottom of a packed column where water is fed at the top and the absorption process operates counter-currently. The water which exits the column with absorbed CO_2 could be regenerated and recirculated back to the absorption column [Vijay 2007]. This technique is not recommended when the composition of the hydrogen sulfide in the biogas is high, since the water turnout can be polluted with plain sulfur which causes corrosion in the equipment [Faroog *et al.* 2012]. In addition, polyethylene glycol is used in the process instead of water which was called selexol scrubbing process [Zafar 2015].

2.2.2 Chemical absorption process

The CO_2 separation by chemical absorption/desorption processes by alkanolamine solutions have been widely used in industry. The alkanolamines could be selected from monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA), and methyldiethanolamine (MDEA) [Bonenfant 2003]. In addition, aqua ammonia is also commonly used [Yeh *et al.* 2005].

2.2.3 Pressure Swing Adsorption (PSA)

Pressure swing adsorption (PSA) is a one method for the CO_2 separation from methane by adsorption/desorption on porous medium at different pressure. This system consists of 4 vessels filled with adsorption material. The gas leaving at the top of the adsorber vessel contains more than 97% of methane [Vijay 2007].

2.2.4 Membrane Separation

Membrane separation is based on the selective permeability property of membranes. Two basic systems exist: (1) gas-gas separation with a gas phase on both sides of the membrane, and (2) gas-liquid separation with a liquid absorbing the diffused molecules. Due to imperfect separation, multiple stages may be required. Because of this, an increase in methane loss is obtained. This can be partly prevented by recirculation [Ryckebosch *et al.* 2011].

2.2.5 Cryogenic Separation

The CH_4, CO_2 and other impurities are liquefied at different temperature/pressure conditions and biomethane could be produced and compressed into a storage tank. The raw biogas is dried to prevent moisture freezing then it is compressed till 8,000 kPa and after that it is cooled in the following cooling steps. The dried and compressed biogas is eventually cooled till -45 ^oC. The condensed CO_2 is removed and treated in a next step to recover the remained CH_4. The biogas is cooled further to -55 ^oC and afterward expanded to 800-1,000 kPa in an expansion tank, reaching a temperature of about -110 ^oC. In these conditions, there is a gas-solid phase with the solid phase being CO_2 and the gaseous phase containing more than 97% CH_4. The CH_4 gas stream is collected and heated before leaving the installation [Ryckebosch *et al.* 2011].

2.2.6 In situ Methane Enrichment

In production process, the feedstock qualities have been controlled such as the feed nutrition for the animals and the bacteria types for biomass digestion, etc., thus the methane concentration in the biogas yield could be increased [ERDI 2010].

The pro-and-con of each process on CO_2 separation could be shown as Table 2.2.

Table 2.2 Advantage and Disadvantage of CO_2 separation process [ERDI 2010].

Item	**PSA**	**Water Scrubbing**	**MEA**	**Membrane**
Characteristic Separation	Adsorption	Physical Process	Chemical Process	Membrane Using
Cleaning	Necessary	Unnecessary	Necessary	Necessary
Pressure(bar)	4-7	4-7	Atmosphere	16-40
Methane loss	3-10%	1-2%	<0.1%	-
Methane Concentration	>96%	>97%	>99%	90-94%
Energy Consumption (kWh/Nm^3)	0.25	<0.25	<0.15	-
System Temperature(^{o}C)	normal	normal	100	normal
Regeneration	Yes	Yes	Yes	-
Energy consumption in Regeneration Process	Moderate	Moderate	High	-

2.3 Biogas Upgrading by Absorption with Ethanolamine Solution and Regeneration of Used Solution

2.3.1 Amine Absorption Process

Monoethanolamine is produced by reacting ethylene oxide with aqueous ammonia and diethanolamine and triethanolamine are also coming out in the process. The ratio of the products can be controlled by changing the stoichiometry of the reactants [Weissermel *et al.* 2003].

Monoethanolamine (MEA), Diethanolamine (DEA), and Methyl Diglycolamine (DGA) are the chemicals which are commonly used in CO_2 absorption process. The chemical reaction equations of CO_2 sorption and desorption with these amines are shown as follows [Filburn *et al.* 2005]:

CO_2 sorption

$$RNH_2 + H_2O + CO_2 \longrightarrow RNH_3 + HCO_3^- \qquad (2.1)$$

CO_2 desorption

$$RNH_3 + HCO_3^- + \text{Heat } (100^oC) \longrightarrow RNH_2 + H_2O + CO_2 \qquad (2.2)$$

2.3.2 Absorption Characteristic [Lin and Shyu 1999, Wankat 2007 and Tippayawong and Thanompongchart 2010]

CO_2 can dissolve in alkaline or amine solution. The reaction depends mainly on pH, liquid solution and CO_2 concentration. The fraction of CO_2 in the biogas absorbed in a solution at time (*t*) is explained and shown in Figure 2.3.

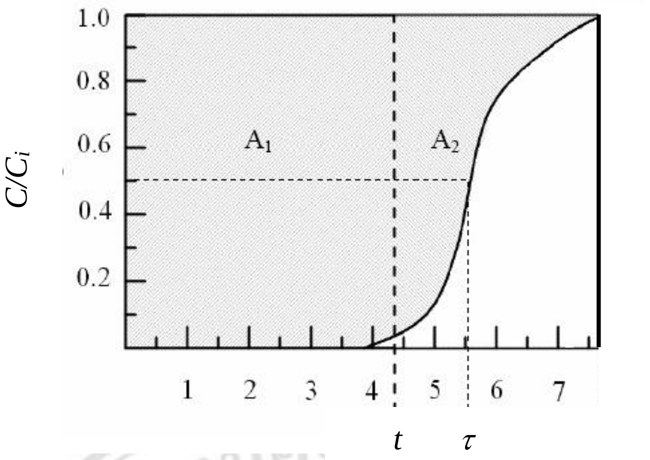


Figure 2.3 Concentration curve of CO_2 absorption process [Wankat 2007].

The ratio of absorbed CO_2 with the CO_2 concentration at the inlet of the absorption column could be denoted as

$$A_{ab} = 1 - \frac{C}{C_i} \tag{2.3}$$

where C_i is inlet CO_2 concentration at the initial time (% by volume), C is outlet CO_2 concentration at time t (% by volume).

The removal rate of CO_2 by absorption could be expressed as

$$\frac{dA}{dt} = +kA(1-A)\ . \tag{2.4}$$

After integration, we get

$$\ln\left(\frac{A(1-A_o)}{A_o(1-A)}\right) = k(\tau - t)\ . \tag{2.5}$$

The equation could be rearranged as

$$t = \frac{1}{k}\ln\left(\frac{C}{C_i - C}\right) + \tau \tag{2.6}$$

where k is the absorption constant (min^{-1}), τ is the characteristic absorption time when 50% of absorbed CO_2 is achieved (min).

From the above equation, it could be seen that the solution should be saturated with CO_2 after time of 2τ.

Then the amount of absorbed CO_2 during time τ by the amine solution (W) could be written as

$$W = \int_{t=0}^{t=\tau} \left(C_i F_i - CF \right) dt \tag{2.7}$$

where C_i is the inlet CO_2 concentration (% by volume), F_i is the inlet gas flow rate (lite/min), C is the outlet CO_2 concentration (% by volume), F is the outlet gas flow rate (lite/min) (it could be calculated by the stoichiometric of reaction).

Furthermore, The CO_2 absorption capacity in solution was calculated as

$$CO_2\,Capacity = \frac{Absorbed\ CO_2\ \ amount\ \ (g)}{MEA\,amount\ \ (g)} \times 100\ . \tag{2.8}$$

2.4 Methane adsorption on porous material

After biogas is purified to be biomethane of which methane is the main component. It is rather difficult to keep the biomethane in liquid phase in a storage tank since its critical state is at the pressure of 4.75 MPa and the temperature of -82.5°C [Kapdi *et al.* 2005]. Table 2.3 show the materials for storage of compressed biogas.

Table 2.3 Materials for compressed biogas [Kapdi *et al.* 2005].

Pressure	**Storage device**	**Material**
Low (0.138-0.414 bar)	Water sealed gas holder	Steel
Low	Gas bag	Rubber, Plastic, vinyl
Medium (1.05-1.97 bar)	Propane and butane tanks	Steel
High (200 bar)	Commercial gas cylinders	Alloy

In practice, such a supplied pressure at 6.89 MPa is used to feed biomethane into a storage tank which consumes energy around 386.85 W-h [Mital 1997]. Therefore, in this study, an approach of biomethane adsorption on porous absorbent was considered.

2.4.1 Porous Medium Material

The porous materials commonly used in adsorption process are molecular sieve, zeolite or activated carbon. Adsorption characteristic of each porous material is different that depended on its molecular weight, gas size, and other properties of the adsorbent. In addition, the porous size, and the adsorption temperature and pressure are really important factors. The suitable substance on each porous size could be shown in Table 2.4. The characteristic of porous material could be shown in Figure 2.4.

Table 2.4 The suitable substance related to adsorbent porous size [Van Lookeren Campagne 2009].

Porous Size	**suitable substance**
3 Å	NH_3, H_2O
4 Å	H_2O, CO_2, SO_2, H_2S, C_2H_4, C_2H_6, C_3H_6, C_2H_5OH. (Except on C_3H_8 and higher hydrocarbons)
5 Å	normal (linear) hydrocarbons to n-C_4H_{10}, alcohols to C_4H_9OH, mercaptans to C_4H_9SH. (Except on isocompounds)
8 Å	branched hydrocarbons and aromatics
10 Å	di-n-butylamine (not tri-n-butylamine)

Figure 2.4 Molecular Sieve, Zeolite, and Activated Carbon [Molecular Sieve, Zeolite, and Activated Carbon 2015].

From the literature review, many researchers studied methane adsorption on various absorbents. For examples, Esteves *et al*. 2008 studied on the adsorption of many gas species from natural gas on absorbent. Gas species were methane, ethane, propane, butane, CO_2, nitrogen, tert-butyl mercaptan, and tetrahydrothiophene. The activated carbon size of 2 mm was taken at controlled temperature of 0-52°C and pressure of 0-9 MPa. It was found that the activated carbon could satisfactory adsorb these gas at various conditions. A gas adsorption technique on activated carbon could apply to upgrade quality of gas species. Moreover, it could also be used to adsorb methane.

2.4.2 Adsorption equilibrium [Bansal and Goyal 2005]

1) Adsorption isotherm [Bansal and Goyal 2005]

In the adsorption process, when the temperature is kept constant, then for a given adsorbent-adsorbate system, *x/m* depends on the equilibrium pressure, and the equilibrium can be represented as:

$$\frac{x}{m} = f\left(P\right) \text{ } (T\text{=constant}). \qquad (2.9)$$

where *x/m* is the adsorbed biomethane on activated carbon at equilibrium temperature and pressure (g/$g_{(AC)}$), *P* is the equilibrium pressure (MPa), *T* is the equilibrium temperature (MPa).

Such equilibrium is called an *adsorption isotherm*.

2) Adsorption isobar [Bansal and Goyal 2005]

When pressure is kept constant and *T* is varied, we obtain an *isobar*.

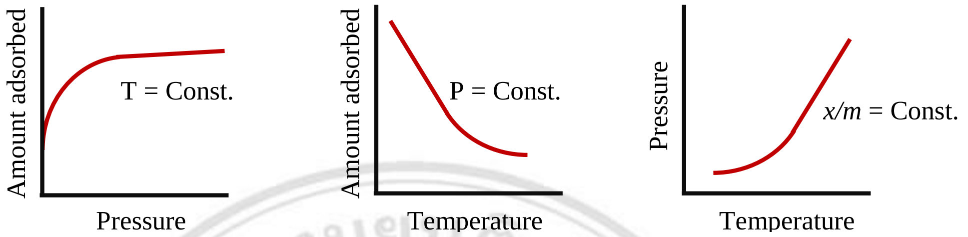
$$\frac{x}{m} = f\left(T\right) \text{ } (P = \text{constant}). \qquad (2.10)$$

3) Adsorption isostere [Bansal and Goyal 2005]

An isostere is obtained when for a constant equilibrium amount adsorbed, the temperature is varied and the pressure essential should keep *x/m* to be constant that is a function of the temperature

$$P = f(T)\ \left(\frac{x}{m} = \text{constant}\right). \qquad (2.11)$$

All adsorption processed are shown in Figure 2.5.



(a) isotherm (b) isobar (c) isostere

Figure 2.5 Adsorption process [Bansal and Goyal 2005].

2.4.3 Langmuir Isotherm Equation [Bansal and Goyal 2005]

The Langmuir isotherm equation is the first theoretically developed adsorption isotherm. The American scientist I. Langmuir derived this equation based on certain assumption which were

1) The adsorbed entitles (atoms or molecules or ions) are attached to the surface at definite localized sites.
2) Each site accommodates one and only one adsorbed entity.
3) The energy state of each adsorbed entity is the same at all sites on the surface independent of the presence or absence of other adsorbed entities at nearby sites. Thus the Langmuir model (also called localized model) assumes that the surface is perfectly smooth and homogenous and that the lateral interactions between the adsorbed entities are negligible.

The Langmuir equation is based on the assumption of a structurally homogeneous adsorbent, and is described by the following:

$$q = q_{max}\left[\frac{K_L P}{1+K_L P}\right] \qquad (2.12)$$

where q is the adsorbed biomethane on activated carbon at equilibrium temperature and pressure (g/g$_{(AC)}$), q_{max} is the limiting uptake of biomethane on the adsorbent (g/g$_{(A/C)}$), K_L is the Langmuir's constant, P is the equilibrium pressure (MPa).

From equation (2.12), the relation between the adsorbed biomethane on activated carbon at equilibrium temperature and pressure (q) with the equilibrium pressure (P), it could be rearranged as

$$\frac{1}{q} = \left(\frac{1}{q_{\max} K_L} \right) \frac{1}{P} + \frac{1}{q_{\max}} \quad . \tag{2.13}$$

From the above equation, q_{max} and K_L could be found out by equation fitting between $1/q$ and $1/P$ from the experimental data.

2.4.4 Dubinin-Astakhov (D-A) Equation

Dubinin theory of adsorption of vapor in microspores is commonly applied to the description of Type I isotherms [Dubinin 1966]. A fundamental difference between the Dubinin and Langmuir theories of adsorption is in the postulated mechanism of pore filling. Dubinin-Radushkevich (D-R) developed the equation as

$$W = W_{max}\, exp\left[-\left(\frac{A}{E} \right)^2 \right]. \tag{2.14}$$

Dubinin and Astakhov (D-A) [Tiansuwan *et al.* 1995, Loh *et al.* 2010] modified the D-R equation which could fit the data accurately and proposed the following model for adsorption of vapors and gases onto heterogeneous carbonaceous solids with a wide pore size distribution. This D-A model allows for the surface heterogeneity and extends to high pressure and express as

$$W = W_{max}\, exp\left[-\left(\frac{A}{E} \right)^n \right] \tag{2.15}$$

where A is the adsorption potential, W is the amount of uptake in ($cm^3/g_{(AC)}$), W_{max} is the limiting uptake of biomethane on the adsorbent ($cm^3/g_{(AC)}$), E is the characteristic energy of the adsorption system (J/mol), n is the structural heterogeneity parameter which indicated on the surface of adsorbent trended to be a heterogeneity surface.

A is the specific work done in the isothermal compression of a unit mass of vapor from P to the saturation vapor pressure P_s and is given by

$$A = \bar{R}T\, ln\left(\frac{P_s}{P}\right). \tag{2.16}$$

From the equation 2.15, it could be expressed as:

$$\frac{W}{W_{max}} = exp\left[-\left\{\frac{\bar{R}T}{E}ln\left(\frac{P_s}{P}\right)\right\}^n\right] \tag{2.17}$$

it could be written in term of adsorbed biomethane in $g/g_{(AC)}$ or $mmol/g_{(AC)}$ as [Hao *et al.* 2014, Rahman *et al.* 2010]

$$\frac{q}{q_{max}} = exp\left[-\left\{\frac{\bar{R}T}{E}ln\left(\frac{P_s}{P}\right)\right\}^n\right]. \tag{2.18}$$

Note: If the adsorbed phase volume is not taken into consideration [Hao *et al.* 2014].

The the saturation vapor pressure (P_s), at a given isotherm temperature is calculated by Dubinin's method that has been used for methane in earlier studies [Loh *et al.* 2010].

$$P_s = \left(\frac{T}{T_C}\right)^2 P_C \qquad ; \quad T > T_c \tag{2.19}$$

where P_c and T_c are the critical pressure and the critical temperature of gas.

2.4.5 Heat of Adsorption [Bansal and Goyal 2005]

The adsorption is an exothermic process. There are two methods for expressing the heat of adsorption, First of these is the integral heat of adsorption, which is defined as the total amount of heat (Q) given out when one gram of an adsorbent adsorbs x grams of a gas, it is expressed as Joules per gram of the adsorbent. The second type of heat of adsorption is differential heat of adsorption ($-\Delta H$), which can be expressed as J/mol of the adsorbate which it has already adsorbed x grams of a gas. The adsorbent is allowed to adsorb additional Δx grams of the adsorbate and the solid evolves ΔQ Joules. The differential heat of adsorption ($-\Delta H$) then becomes

$$-\Delta H = M \frac{\Delta Q}{\Delta x} \tag{2.20}$$

where Δx is infinitesimally small amount of gas and M_w is the molecular weight.

Thus, the differential heat of adsorption is expressed as J/mol of the adsorbate.

The isosteric heat of adsorption is a critical parameter for adsorptive separation processes. The heat release during the adsorption process due to the change in energy level of the adsorbate molecules could be evaluated the heat of adsorption from the adsorption uptake data assuming ideal gas-phase behavior of the adsorbate molecules in their gaseous phase. The value of changes greatly with the specific surface loading (q/q_{max}) [Luo *et al.* 2014]. It can be calculated from the Clapeyron equation with the assumption of an isotherm

$$H_{ad} = -\bar{R}T^2 \left(\frac{\partial \ln P}{\partial T} \right)_q . \tag{2.21}$$

where H_{ad} is the isosteric heat of adsorption at specific loading (J/mol), $\bar{R}$ is the ideal gas constant (8.1345 J/mol-K), T is the temperature (K), P is the pressure at specific surface loading (MPa) and q is the adsorbate surface loading (mmol/g$_{(AC)}$).

The minus shows that the progress of adsorption is exothermic process.

In this study, the biomethane adsorption and desorption was investigated. The weight of adsorbed and desorbed biomethane was measured. The Langmuir model and Dubinin-Astakhov model were considered on biomethane adsorption on activated carbon. The isosteric heat of adsorption from Clapeyron equation was calculated. In addition, the biomethane desorption on activated carbon at low temperature was presented, it could be calculated the % biomethane desorption as

$$\%desorbed\,bio-methane = \frac{amount\ of\ bio-methane\ desorption \times 100\,\%}{amount\ of\ bio-methane\ adsorption}\ . \qquad (2.22)$$