UPGRADING BIO-METHANE STORAGE BY ADSORPTION

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Thesis submitted in partial fulfillment of the requirements for the degree Master of Science

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DECLARATION OF THE CANDIDATE AND SUPERVISOR

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ABSTRACT

There is a growing global interest on bio-methane as a vehicular fuel and Europe Union (EU) has stated that this as a best well-to-wheel fuel. Commercialization of bio-methane under atmospheric conditions is limited due to its requirement on higher storage capacity. Compressed bio-methane systems have been currently commercialized in order to increase its low energy density however the process requires higher capital and maintenance costs. Thus, adsorbed bio-methane is suggested as a better alternative to store methane under low pressure conditions.

This study is based on upgrading bio-methane storage by gas adsorption technique. Activated Carbon (AC) is selected considering its potential and suitability as commercial scale adsorbent for Sri Lanka. This study focuses on identifying adsorption potential of bio-methane on Sri Lankan commercial AC. Two types of commercial AC samples as granular & pellet forms have been used from supplier HAYCARB for the analysis. The potential on supplied AC is discussed by characterization data of the samples. Further, the pilot scale experiment set up was developed and biogas adsorption experiments were carried out for granular and pellet samples. The experiment data was analysed by Langmuir and Toth models. Extended Langmuir model was used to understand the bio-methane adsorption behaviour from biogas adsorption. Storage capacity of 71.5V/V and 82.8 V/V values were obtained from granular and pellet AC respectively proving better methane adsorption potential on commercial AC available in Sri Lanka.

Keywords: Biogas, bio-methane, Activated Carbon, Adsorption, Toth equation, Extended Langmuir equation

DEDICATION

I dedicate this thesis to my parents who have devoted their life for making me an educated and a successful person. I would like to express my love and appreciation for the encouragement and the sacrifices made by them.

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LIST OF ABBREVIATIONS

Abbreviation	**Description**
AC	Activated Carbon
STP	Standard Temperature & Pressure
CNG	Compressed Natural Gas
LNG	Liquefied Natural Gas
ABM	Adsorbed Bio-Methane
ANG	Adsorbed Natural Gas
BET	Brunauer-Emmett-Teller
DR	Dubinin-Redushkevich
PSD	Pore Size Distribution
GAC	Granular Activated Carbon
GCMC	Grand Canonical Monte Carlo
MOF	Metal Organic Framework

Notation	**Description**
n	Adsorbed moles per unit mass (mmol/g)
P	System Pressure (barg)
n_{max}	Maximum adsorption per unit mass (mmol/g)
k_L	Affinity parameter -Langmuir model (bar^{-1})
α_T	Affinity parameter -Toth model (bar^{-1})

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CHAPTER 1 INTRODUCTION

1.1 Background

Green energy production & waste management are considered as vital practices when moving towards a greener world. If energy can be produced from generated waste then it will be a massive advantage for the problems relate to both waste management and green energy production. Biogas is such a waste to energy invention which has shown considerable advantage over conventional fuel from both environmental & economical point of view.

Biogas is a result of anaerobic digestion of organic matters done by mesophilic & thermophilic bacteria. It is mainly consists of methane (CH_4) & carbon dioxide (CO_2) while it may have small amounts of some other impurities such as hydrogen sulphide (H_2S), moisture, etc. ("Biogas," 2016). The content of these impurities depend on the composition of substrates which the gas was produced ("Upgrading Biogas to Biomethane," n.d.). When biogas strips off its carbon dioxide content & other unwanted impurities, bio-methane is obtained which is equivalent to natural gas.

Methane is considered as a promising alternative solution for the vehicular fuel application. It is relatively clean burning fuel compared to gasoline which lowers the potential of producing polluting emissions (Lozano-Castelló et al., 2002). Methane has higher H/C ratio and consequently a higher octane number (A Linares-Solano et al., 2002). However, at Standard Temperature & Pressure (STP) conditions, energy density of methane is 0.038 MJ/L which is 0.11% of that of gasoline (A Linares-Solano et al., 2002). Due to its lower energy density under normal atmospheric conditions, the usage as a fuel has been limited for most of applications when compared with other conventional transportation fuels.

Compressed bio-methane systems have been commercialized as a solution to increase its low energy density. If methane needs to become competitive on an economic basis as a transportation fuel compared to other conventional fuels, it should be compressed to high pressures (up to 25MPa) & that requires costly multi stage compression (A Linares-Solano et al., 2002). The cost of storage cylinders and high pressure facilities limits the practical use of bio-methane as a compressed gas. This techno-economical problem can be overcome by introducing novel storage concept which adequate higher energy density of methane under low pressure & temperature conditions. This can be achieved by gas adsorption technique.

Adsorbed methane has shown a good potential towards methane storage under low pressure conditions (3.5-4MPa) (A Linares-Solano et al., 2002). Energy density of methane can be increased by 200 times of its STP conditions using adsorption technique, then it is comparatively similar to compressed natural gas (CNG) at 20MPa ,298K (A Linares-Solano et al., 2002).

As a country, Sri Lanka has also set their own renewable energy targets for reducing environment pollution which is currently happening by conventional fuels during energy generation & transportation. The country is planning to contribute 10% of renewable energy fuels for electricity generation by 2016 and to develop the usage of bio-fuel in transportation sector up to 20% by 2020 (":: Sri Lanka Sustainable Energy Authority ::," n.d.). Hence bio-methane can be beneficial as environmental & economical advantageous alternative energy source for Sri Lanka, similarly its upgrading techniques.

As initiation of the concept, Department of Chemical and Process Engineering, University of Moratuwa has developed a pilot scale biogas unit, targeting utilization of bio-methane as a transport fuel. The initial research study has proven that LPG three-wheeler (without any modification) can be operated successfully by upgraded biogas (85% bio-methane). However biogas storage limits commercial usage of the application. Thus, the concept of upgrading biogas storage is proposed as the continuation of the study.

1.2 Objectives of the Research

- Identify a suitable adsorbent to upgrade bio-methane storage, considering techno-economic situation of Sri Lanka
- Adsorption reactor system development to identify bio-methane adsorption capability of the selected adsorbent
- Characterize the adsorbent and evaluate its potential for the application with globally published details

1.3 Thesis Structure

The first chapter of the thesis gives an introduction for the topic and states the objectives of this research project. Chapter two is the literature review. Potential in biogas as a commercial scale fuel for Sri Lanka and capabilities in activated carbon as a methane adsorbent are discussed under this chapter. Chapter three focuses on material selection and characterization section of the research study. Selection of a suitable adsorbent and evaluation of its potential by using characterization data are discussed under this chapter. Chapter four focuses on pilot scale study on biogas adsorption. This chapter includes development of pilot scale set up, results analysis, adsorption model development and limitations of the study. It discusses the current capacity in upgrading bio-methane storage via gas adsorption in Sri Lanka. Finally the chapter 6 gives the conclusion of the research and suggestions for future directions.

CHAPTER 2 LITERATURE SURVEY

2.1 Introduction

Renewable energy & energy storage are highly discussed topics in this decade due to environmental concerns and limitations in conventional fossil fuel. Biogas with upgraded methane composition and increased energy density shows high potential as an alternative energy source for conventional fuel. There are many commercially established upgrading techniques available to enhance methane content of biogas. Adsorbed methane is showing potential in increasing energy density of the gas which facilitates its usage as a transportation fuel. However development of proper adsorbent with optimum pore structure and bulk density is crucial.

The chapter includes the background analysis of the topic "bio-methane adsorption"; the data gathered from globally publish studies. The Scival ("SciVal - Welcome to SciVal," n.d.) Analysis carried out (refer the appendix A), has been proven that methane adsorption is a growing research area with nearly 150 publications around the world since 1996 to present.

2.2 Potential in Biogas as a Renewable Energy Source

2.2.1 Introduction to biogas

Biogas is a natural product that occurred as a result of anaerobic digestion of organic matters by mesophilic & thermophilic bacteria. It consists of combustible gas methane (50- 75%), carbon dioxide (45-25%), water (7-2%) & some other trace gasses (table 2.1). Biogas is a flexible energy carrier which can be directly used for cooking & lighting. The produced biogas can be upgraded by removing its non-combustible gas compounds. The upgraded biogas can be then used as a household energy generator, vehicular fuel or most frequently as an onsite industrial heat & electricity generator by using a combined heat & power unit (CHP)("Upgrading Biogas to Biomethane," n.d.).

Table 2.1: Biogas components

Compound	**Symbol**	**Content (Vol. %)**
Methane	CH_4	50-75
Carbon Dioxide	CO_2	25-45
Water vapour	H_2O	2(20°C)-7(40°C)
Oxygen	O_2	<2
Nitrogen	N_2	<2
Ammonia	NH_3	<1
Hydrogen	H_2	<1
Hydrogen Sulphide	H_2S	<1

Source: (“Upgrading Biogas to Biomethane,” n.d.)

Biogas is a green energy source which is capable of generating environment & socioeconomic benefits for the society as a whole. Biogas production enhances local economic capabilities, increases regional purchasing power while safeguarding jobs in rural areas (Al Seadi et al., 2008). Hence biogas as energy source, will improves the energy balance of a country while contributing to natural resource preservation & environmental protection (Al Seadi et al., 2008). Since biogas is not like other conventional energy sources which are limited in amount & concentrated into few geographical areas of the planet, it will increase the national energy security while diminishing the dependency of imported fuels of a country (Al Seadi et al., 2008).

As same as other conventional energy sources, combustion of biogas also releases CO_2 but the carbon in biogas was recently up taken from atmosphere by photosynthesis activity of plant thus the carbon cycle of biogas is closed within very short time period which won’t be happening when using conventional fuels (Al Seadi et al., 2008). Biogas production is an excellent technique for waste reduction while obtaining energy source as by product followed by fertilizer from digested substrate. It contributes to reduce the volume of waste & cost of waste disposal while providing closed nutrient & carbon cycle (Al Seadi et al., 2008). Thus, the production & utilization of biogas has the potential to comply with all three EU energy & environment targets as renewable energy production, GHG emission reduction & sustainable waste management.

2.2.2 Biogas production and utilization

Since biogas as an energy source, came up with waste to energy concept, most of biogas applications are found in waste treatment areas. Basically biogas producing plants are categorized into agricultural, wastewater treatment, municipal solid waste treatment, industrial plants and landfill gas recovery plants.

There are numerous energy utilizations which depend upon biogas source & local demand. Direct combustion of biogas can be used for heat production in both industrial & household applications while electricity generation from biogas can be done via fuel cells or micro turbines. Upgraded biogas can be used as alternative renewable vehicular fuel application over conventional fuel (Al Seadi et al., 2008).

Combined heat & power generation technique is used as a standard biogas utilization method in the countries with a developed biogas sector, as it is considered as a very efficient way for energy production via biogas (Al Seadi et al., 2008). Engine base CHP plants are efficient up to 90% with 35% electricity and 65% heat generation (Al Seadi et al., 2008). Biogas micro turbines are operated by flue gas produced from burning compressed air – biogas mixture for power generation (Al Seadi et al., 2008). Fuel cell which is currently an emerging technique uses biogas for its several applications as Polymer-Electrolyte-Membrane (PEM), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC) (Al Seadi et al., 2008). In internal combustion engines biogas is operated the range of 11:1 to 16:1 compression ratios (Krich et al., 2005). Though biogas has a major potential in vehicular fuel application, overcoming its less energy density and corrosiveness are essential to compete with current conventional fuels.

2.2.3 Upgrading biogas to bio-methane and storage

Methane is a clean burning fuel with low potential of producing polluting emissions compared to gasoline (A Linares-Solano et al., 2002). Although its higher octane number makes it as a promising alternative solution for current non-renewable energy usage (A Linares-Solano et al., 2002), its low energy density comparatively 0.11% of gasoline, limits its usage as a substitution of conventional fuels. Inert gas, which is relatively consists of 30-45% in biogas with methane, reduces its energy density further while creating corrosiveness from its H_2S composition. Hence creation of biogas as a competitive renewable energy solution for commercial applications needs improvement in energy density component and reduction in its corrosive nature.

Converting biogas into bio-methane includes the removal of non-combustible matters of the gas as CO_2, water vapour, H_2S, and other impurities. Removal of these impurities can be done by the techniques such as organic physical scrubbing, pressure sewing adsorption, chemical scrubbing, membrane separation , cryogenic separation and biological filters (Danish et al., 2011; Krich et al., 2005). Figure 2.1 refers the usage of each upgrading technique of commercially operating biogas plants in 2012. In globally, the purification technology have improved in commercial scale to obtain 98-99% bio-methane from raw biogas (Danish et al., 2011).

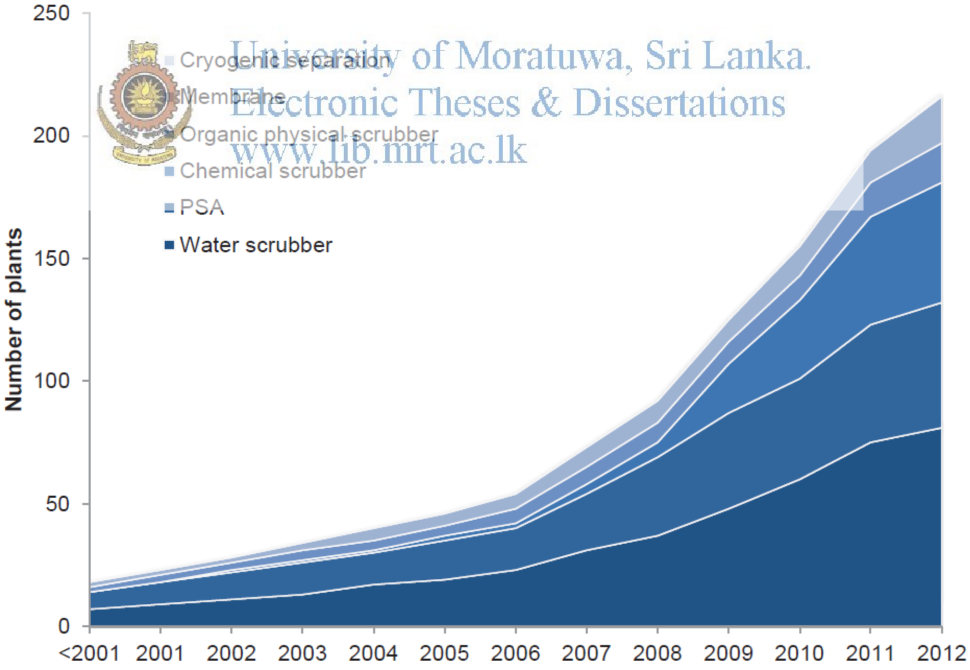


Figure 2.1: Visualization of technologies used in biogas upgrading plants

Source: (Baucer, Hulteberg, Persson, & Tamm, n.d.)

Currently, there are several techniques, identified for methane storage in order to increase its energy density such as compressed gas, adsorbed gas or liquefied gas. Natural gas which is approximately 98% of methane is being used in commercial applications in world by upgrading its energy density as liquefied natural gas (LNG) or Compressed Natural Gas (CNG). LNG, stored at 112 K temperature and atmospheric pressure, delivers high storage value as 600 volumes of gas per volume of storage (V/V) with energy density of 23 MJ/l. This increased energy density is comparability low with diesel fuel (37 MJ/l) or gasoline (32 MJ/l). Additionally, higher operational cost and potential fire hazard of LNG restricts its usability in commercial scale. As, the second option, CNG is fuelled to vehicles at high pressures up to 20MPa and room temperature. CNG at 20MPa is capable to deliver about 220 V/V value with 10MJ/L of energy density. Thus technical and economical difficulties attached to high-pressure facilities and storage containers make the system unfeasible in wide scale (Marsh & Reinoso, 2006). The Alternative option came as storing natural gas by adsorbing into suitable porous material at relatively low pressure. The system is usually evaluated in terms of volumetric methane storage capacity (Vm/Vs), where Vm is methane volume at STP, and Vs is volume of the storage container (Gottipati, Adiraju, & Mishra, 2012).

Table 2.2: Comparison on different methane storage methods

Storage method	**Temperature**	**Pressure**	**Density**	**Relative Density**
	K	**MPa**	**g/cc**	
LNG	113	0.1	0.4	600
CNG	298	20	0.15	230
CNG	298	3.5	0.023	36
ANG	298	3.5	0.13	200
Natural gas	298	0.1	0.00065	1

Source: (A Linares-Solano et al., 2002)

Adsorbed bio-methane (ABM) systems are capable of storing high energy density methane under quite low pressure when compared with compressed bio-methane system (A Linares-Solano et al., 2002). It has been proven that Adsorbed Natural Gas (ANG) at pressures ranging from 3.5 to 4.0 MPa gives a decent energy density. It is possible to reach the same delivery (V/V) of compressed gas at 20MPa, at relatively low pressures (3.5 MPa) through an appropriate adsorbent (refer Table 2.2). The system will reduce the technical & economic barriers attached with high pressure application over LNG & CNG systems (Marsh & Reinoso, 2006).

Selection of a proper adsorbent is the most crucial step in ABM system. Currently scientists are more interest in studying activated carbon compounds and metal organic frameworks as the main adsorbents for the ABM system to make it commercially viable application.

2.2.4 Biogas in Sri Lanka; production vs. utilization

Initial introduction of biogas technology to Sri Lanka was happened in 1970s (“Biogas Technology Utilization in Sri Lanka,” n.d.). Since then, many state and non-state organizations were active in this area at various periods of time. Thus, the technology didn’t immerse as a viable green energy solution for the country due to lack of proper systematic maintenance. The technology was initially promoted by state sector as a cooking and lighting energy source for rural community. Lately its utilization was expanding to water pumping, heating, electricity generation, etc. with the non-government sector participation and that facilitate to look at biogas technology in an integrated manner to reap the multiple benefits (“Biogas Technology Utilization in Sri Lanka,” n.d.; Ghimire, 2011).

Currently there are several state and non-state organizations involve in constructing biogas plants such as NERD, Sustainable Energy authority (SEA), Practical Action, Human Environmental Links Progressive Organization (HELP-O), Energy forum, Bio fuel Lanka, etc. Most of the constructed biogas plants are focusing on treating agricultural and veterinary farms waste and domestic food wastes. Still Sri Lanka is lack of experience in large scale biogas units come from municipal solid waste, market garbage, community based sewerage treatment plants, industrial wastewater treatment plants etc.(Y. Pathiraja et al., 2013).

The national survey conducted by Energy Forum indicated that the contribution of biogas energy towards the total energy production of the country was insignificant. Even though state and non-state organizations had been involved in this sector from a while ago, the country had not benefited significantly from these activities (Ghimire, 2011). The major reasons behind the failure of biogas projects were mainly lack of long-term vision, lack of organized service delivery mechanisms and lack of community awareness building activities on beneficiaries of the projects (Ghimire, 2011).

There are many researches carrying out on biogas production and utilization under solid waste management and renewable energy generation sections in the country. Scival analysis has been conducted to compare the research interest on biogas in Sri Lanka with the world during 2009 to 2014 period (refer appendix A). The results are presented in below table. It is shown that the developed countries still consider biogas as a good renewable energy solution for future applications.

Table 2.3: Scival analysis (2009-2014) on country-wise biogas related publications

Country	**Publications**
China	1501
Germany	749
United States	670
Italy	428
India	445
Spain	347
United Kingdom	251
Sweden	248
Canada	241
Brazil	201
Japan	202
Sri Lanka	3
Total publications	7804

There is a clear potential for commercialization biogas as renewable energy source in the country, but the establishment of proper long term mechanism targeting large scale biogas production units are vital. These projects can be targeted on large scale waste management plans such as municipal solid waste treatment, sanitary landfills, wastewater treatment plants, farm waste, etc. The biogas utilization is still laid in primary stage and need more focus to apply on power generation, internal combustion engines, combined heat and power, etc.

2.3 Gas Adsorption

Adsorption phenomenon can be expressed as attaching fluid phase molecules; gases, vapours and liquids to the surface of solid material at any temperature and pressure as a result of the unsaturated and unbalanced molecular forces, present on the solid surface (Bansal & Goyal, 2005; Keller & Staudt, 2005). The solid material is called as adsorbent and fluid molecule is called as adsorbate. The adsorbate may return to the gas phase which is called as desorption, due to the same unbalanced molecular forces

The interactions between a certain fluid to solid material is fairly complex due to size, structure and electric property (dipole and quadrupole moments) variation in fluid molecule and difference in adsorption sites of solid material (Keller & Staudt, 2005). There are two types of adsorption as chemisorption and physisorption which is depending upon the nature of the adsorbate & adsorbent, the reactivity of the surface, the surface area of the adsorbate, and the temperature and pressure of process (Bansal & Goyal, 2005).

2.3.1 Chemisorption

Chemisorption is an irreversible surface adsorption process occurred due to exchange or sharing of electrons between the adsorbate molecules and adsorbent surface resulting of a chemical reaction (Bansal & Goyal, 2005). Since the adsorbate and adsorbent is attached with a chemical bond, it is much stronger than physisorption and the enthalpy change is generally 40 to 800KJ per mole (Stadie, 2013). This is a specific uni-molecular thickness process occurred in between certain adsorbate and adsorbent (Bansal & Goyal, 2005; Stadie, 2013).

2.3.2 Physisorption

Physisorption is a reversible surface adsorption process occurred due to relatively weak van der waals forces, which are similar to the molecular forces of cohesion and are involved in the condensation of vapours into liquids (Bansal & Goyal, 2005). Physisorption is non-specific multi-molecular thickness process and exceedingly dynamic (Stadie, 2013). In adsorption equilibrium, the dynamic behaviour of adsorption and desorption can be observed in surface of the solid material. Additionally in highly porous solids, the equilibrium is tending to adsorption side due to the internal diffusion of adsorbate molecules in to the porous structure of the adsorbent (Keller & Staudt, 2005).

The enthalpy of adsorption is of the same order as the heat of liquefaction and does not usually exceed 10 to 20 KJ per mole (Bansal & Goyal, 2005). The adsorbed state of the molecule is more stable than the gaseous state at 273 K and 0.1 MPa pressure (Marsh & Reinoso, 2006). Desorption of adsorbate is possible by lowering gas pressure or increasing the temperature due its reversibility (Bansal & Goyal, 2005).

2.3.3 Adsorption Isotherm

Adsorption isotherm is the most extensively employed method for representing adsorption equilibrium in between adsorbate and adsorbent (Bansal & Goyal, 2005).This provides useful information regarding the adsorption process such as the surface area of the adsorbent, the volume of the pores, pore size distribution and magnitude of the enthalpy of adsorption, etc. Generally it gives the relative adsorption of a certain gas or a vapour on a given adsorbent with respect to chosen standards (Bansal & Goyal, 2005).

Desorption isotherm is overlay on adsorption isotherm however the process is slower than the adsorption as the activation energies of desorption are higher (Marsh & Reinoso, 2006). In some cases where mesopores are present, desorption isotherm is deviate from adsorption isotherm at high pressure which is being called as hysteresis (Marsh & Reinoso, 2006).

There are several isotherm equations which have been developed to represent the adsorption data; among Langmuir, the Freundlich, the Brunauer-Emmett-Teller (BET), and Dubinin equations are significant (Bansal & Goyal, 2005). Langmuir, Freundlich equations are being equally applied for both physisorption and chemisorption whereas BET and Dubinin equations are used to analysis physical adsorption of gases and vapours on porous carbon (Bansal & Goyal, 2005).

2.3.4 Adsorption Isotherm Developments

Langmuir Isotherm is developed by considering monolayer adsorption on homogeneous, non-porous, flat surface under certain idealistic assumptions. Thus the interpretation of adsorption data is significantly limited and equation remains of basic importance for expressing dynamic adsorption equilibrium (Bansal & Goyal, 2005). However the equation provides a good basis to derivate more complex models.

The BET equation for multi-molecular adsorption is developed by generalization of the Langmuir model for single molecular adsorption. BET equation represents the shape of the actual isotherms and is capable of providing average enthalpy of adsorption in the first layer, satisfactory values for adsorbed gas volume and monolayer capacity of the adsorbate which can be used to calculate the specific surface area of the solid adsorbent (Bansal & Goyal, 2005).

The DR equation is a derivative of the mathematics of Rayleigh, Gaussian or Lorenztian distributions and directly relates to micropore distribution in adsorbent. Out of the three equations available to interpret adsorption isotherms, the Langmuir and BET equations are based on general models of adsorption and are not derived from concepts of porosity. It has been stated by (Marsh & Reinoso, 2006) that DR equation is more relevant to the adsorption process than the other two equations.

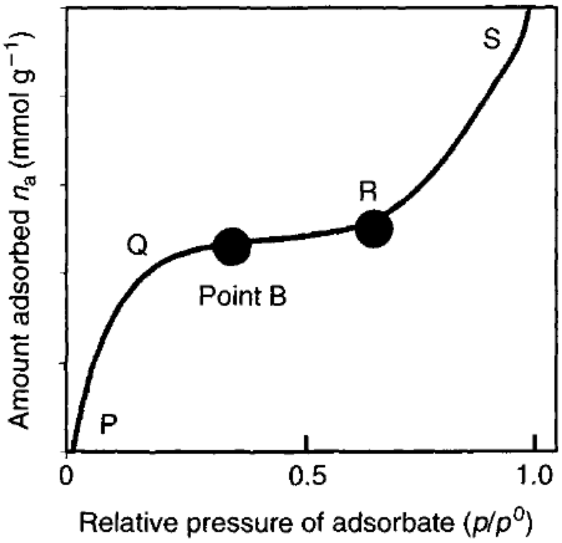


Figure 2.2: A typical adsorption isotherm

Source: (Marsh & Reinoso, 2006)

Figure 2.2 represents a typical adsorption isotherm for gas adsorption. The segment PQB indicates Langmuir equation for monolayer coverage whereas QRS dealing with pore filling and capillary condensation processes, forms the basis for the BET equation for porous solids (Marsh & Reinoso, 2006).The line PQ describes adsorption in microporosity , the smaller the micropore size, steeper the PQ line (Marsh & Reinoso, 2006). The DR equation extrapolates low relative pressure segment (PQ) of the isotherm. At the Point B, which is the point of inflection, it is assumed that the monolayer formation is complete hence it is the limit of application of the Langmuir and DR equations (Marsh & Reinoso, 2006). The curved section of isotherm, in higher relative pressure region, is usually interpreted by the BET equation (Marsh & Reinoso, 2006).

The experimentally observed isotherms have being classified into 6 different types as per IUPAC-recommendations (Figure 2.3). Type I isotherm can be expressed by Langmuir equation. This isotherm illustrates microporous materials showing micropore filling with no multilayer adsorption (Keller & Staudt, 2005; Marsh & Reinoso, 2006). The gradient of the initial part of the isotherm where P/P^0 value from

0 to 0.05 range indicates the dimensions of microporosity. Steeper the gradient, narrower are the micropores (Marsh & Reinoso, 2006).

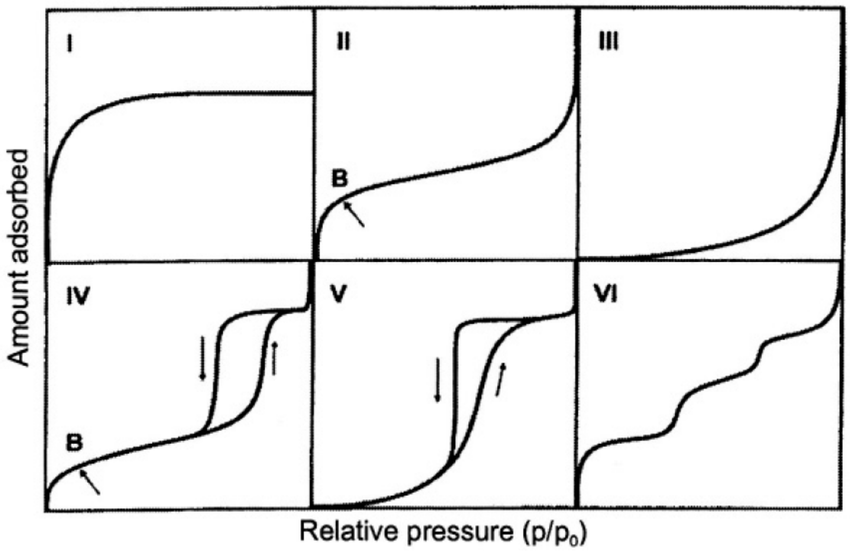


Figure 2.3: IUPAC classification of Isotherms

Source: (Marsh & Reinoso, 2006)

Type II isotherm shows two inflections, 1st in the region of $P/P^0 < 0.1$ and 2nd in the region of $P/P^0 > 0.9$ (Marsh & Reinoso, 2006). At low pressure monolayer adsorption is happening on mesoporous material. At high pressure region, isotherm indicates multilayer adsorption and pore condensation but without hysteresis. This is assisted condensation (Marsh & Reinoso, 2006) that isotherm describes adsorption, happening in both micropores and mesopores or open surface (Marsh & Reinoso, 2006). Type II isotherm can be described by the BET equation (Keller & Staudt, 2005).

Type III isotherm occurs when the adsorbate to adsorbent interactions are small compared to the adsorbate to adsorbate interactions (Keller & Staudt, 2005). This characterizes low potential of adsorption (Marsh & Reinoso, 2006). Type IV resembles type II isotherm with hysteresis loop. The filling mechanism of mesopores by capillary condensation differs from that of mesopore emptying which create hysteresis loop in adsorption and desorption branch of the isotherm (Marsh &

Reinoso, 2006). Type V isotherm also shows hysteresis loop indicating mesoporous adsorption with pore condensation. The shape of the loop and the shape of the isotherm at low pressure is the difference between Type IV and V isotherms (Marsh & Reinoso, 2006).Type VI represents step wise multilayer adsorption (Keller & Staudt, 2005; Marsh & Reinoso, 2006). This represents extremely homogeneous surface of the adsorbent (Marsh & Reinoso, 2006).

However, it is not possible to describe all physisorption phenomena occurring when pure or mixed gas contact the surface of a porous solid by a single isotherm due to complexity of the process. This complexity is a consequence of energetic heterogeneity of the adsorption sites, variety pore spectrum of the adsorbent, various properties of the adsorbate, etc. (Keller & Staudt, 2005).

2.3.5 Adsorbent

The adsorbent material is simply classified in to narrow pore material or wide pore material according to adsorbent pore spectrum. Narrow pore material mainly consists of microporous structure while all micro, meso, and macropores are visible in wide pore material (Keller & Staudt, 2005). The primary adsorption sites of the adsorbent i.e. meso, and macropores are capable of directly adsorb molecules from the gas phase. The secondary sites i.e. micropores, are filled by diffusion processes of primary adsorbed molecules, reaching eventually by open end of the pore (Keller & Staudt, 2005).

Selection of a proper adsorbent for a certain adsorbate is crucial and proper characterization of the material is necessary to figure out the compatibility of the adsorbate with adsorbent according to the requirement.

2.4 Activated Carbon as an Adsorbent

The most crucial parameters of the adsorbent are high adsorption capacity, high packing density, high adsorption/desorption rates, stability in cyclic operations and the ratio between amount adsorbed at higher pressure (as 4MPa) to amount desorbed at 0.1MPa which needs to be as close as possible to one (J. Alcañiz-Monge, M. A. De La Casa-Lillo, Cazorla-Amorós, & Linares-Solano, 1997). Activated Carbon (AC) has been shown positive results towards above points with higher storage capacities.

2.4.1 Introduction

There are two types of carbon as graphitizable and non-graphitizable carbon. Graphatizable anisotropic carbon show X-ray diffraction lines of three-dimensional graphite or become graphitic on heating to beyond 2000 °C (Marsh & Reinoso, 2006). These are consists of considerable plane and stacked graphene layers. Non-graphitizable, isotropic carbon contains micro-graphene layers and never exhibit three-dimensional XRD lines. The all porous carbons belong to non-graphitizable category (Marsh & Reinoso, 2006).

Activated carbon is a porous structure, created due to defective micro-graphene layers. This can be expressed as a three dimensional network of imperfectly joined, ring structured carbon atom layers which are being stacked, roughly parallel to each other in groups of two, or three. The resulting space of bonding arrangement creates interconnecting three dimensional passageways named as pores (Marsh & Reinoso, 2006).The existence of a PSD is a result of disordered array of imperfect, non-planar micro-graphene layers (Marsh & Reinoso, 2006).

The porosity is mostly slit-shaped and size of molecules. Activated carbon exhibits extreme specificity of application via variations in its structure which is being used in industrial applications such as water and air purification, gas mixture separations etc. Carbonizing of natural organic material creates porous carbon thus its porosity depends upon parent material structure and activation conditions. Hence the commercial value of activated carbon sample depends on its pore characteristics (Marsh & Reinoso, 2006). Currently, synthetic carbon precursors mainly of polymeric type and conventional precursors, such as lignocellulosic materials are being used to prepare activated carbons, with micropores and controlled pore-size distribution (Marsh & Reinoso, 2006).

2.4.2 Manufacturing and Activation

There are two processing steps in AC manufacturing as carbonization and activation. Carbonization is a process of converting a three-dimensional organic macromolecular system to a three-dimensional "macro-atomic" network of carbon atoms. This is a heat treatment process applied in inert gas atmosphere. During the process, small molecules such as water, methanol and carbon dioxide, are eliminated from the organic system. Movement of resultant atoms over short atomic distances creates an intermediate stable phase of higher carbon content which produces spaces in nanometer dimensions (Marsh & Reinoso, 2006). Different parent materials decompose in their own unique ways to produce a specific type of carbon with considerable microporosity (Marsh & Reinoso, 2006). The activation process open up the pores by removing the residual tarry material (Marsh & Reinoso, 2006).

There are two methods for manufacturing activated carbon as physical activation or chemical activation. In physical activation method, precursor is first carbonized and then activated using gasifying agent (Danish et al., 2011; Marsh & Reinoso, 2006). Physical activation uses two gasifying agents, carbon dioxide and water vapour either singularly or together. Carbon dioxide develops narrow microporosity, with a narrow pore size distribution whereas steam produces wide microporosity with wider micropore size distribution (Marsh & Reinoso, 2006). Controlled temperature condition is important in the process (Marsh & Reinoso, 2006). Chemical activation use phosphoric acid (H_3PO_4), Zinc chloride ($ZnCl_2$), Potassium hydroxide (KOH), Potassium carbonate (K_2CO_3) as activating agents (Danish et al., 2011; Marsh & Reinoso, 2006). The process consists of two steps; first impregnation of precursor is carried out with activating agent and then carbonization is conducted under inert gas atmosphere (Marsh & Reinoso, 2006).

Activated carbon is produced from carbon-containing organic materials as wood, sawdust, nutshells, fruit stones, peat, lignite, coal, petroleum coke, etc. Selection of precursor depends on factors like content of inorganic matter, ease of activation, degradation upon storage, volatile content, availability and cost, etc. Low inorganic matter content in precursor produces low ash content. Relatively high volatile content is needed to control the manufacturing process (Marsh & Reinoso, 2006).

Burn off value is a measurement used in activated carbon manufacturing process to identify the pore development of the materials according to activation conditions. Burn off value of AC sample is determined from the dry basis weight difference between precursor and activated carbon divided by the dry basis weight of precursor biomass (Danish et al., 2011; Mahboub, Ahmadpour, Rashidi, & Jahanshahi, 2012).

Table 2.4: Properties of materials used in the manufacture of AC

Raw material	**Carbon (wt %)**	**Volatiles (wt %)**	**Density (cc/g)**	**Ash (wt %)**	**Texture of AC**
Soft wood	40-50	55-60	0.4-0.5	0.3-1.1	Soft, large pore volume
Hardwood	40-42	55-60	0.55-0.8	0.3-1.2	Soft, large pore volume
Lignin	35-40	58-60	0.3-0.4	NG	Soft, large pore volume
Nutshells	30-45	55-60	1.4	NG	Hard, large micropore volume
Lignite	55-70	25-40	1-1.35	5-15	Hard, small pore volume
Soft Coal	65-80	20-30	1.25-1.5	2-12	Medium hard, medium pore volume
Petroleum coke	70-85	15-20	1.35	0.5-0.7	Medium hard, medium pore volume
Hard coal	70-75	10-15	1.45	5-15	Hard, large pore volume
Anthracite	85-95	5-10	1.5-1.8	2-15	Hard, large pore volume

Source: (Marsh & Reinoso, 2006)

Coconut shells are popular precursors for manufacturing hard granular activated carbon due to its relatively high density, hardness and high volatile content (Marsh & Reinoso, 2006) and are currently using in commercial scale microporous activated carbon production. Table 2.4 shows few properties of material used in AC manufacturing

2.4.3 Activated Carbon applications

Activated carbon is used commercially in many industries for liquid and gas phase applications for purification and storage processes (refer Table 2.5). The porous carbon is also used in catalytic processes (Marsh & Reinoso, 2006). There are two forms of AC which are commonly used in the industry as Granular Activated Carbon (GAC) and Activated carbon pellets.

Table 2.5: Activated carbon Applications

Liquid Phase	**Gas Phase**
Water and wastewater treatments	Gas Purification
Food and Beverage Processing	Separation of Gas Mixtures
Chemicals and Pharmaceutical processing	Methane Storage
Adsorption of Dyes	Solvent Recovery
	Adsorption of Dyes

Source: (Marsh & Reinoso, 2006)

2.2.4 Characterization

Characterization of activated carbon is a prerequisite in its industrial application which conveys detail analysis of carbon pore structure. Porosity in solid material provides accessibility to gas, vapour or liquid molecules into atomic network. In activated carbon porous structure, there are three types of pores available as maco, meso and micro. And the characterization of micro and meso porosities is important in adsorption process. Pore dimensions less than 2.0 nm are considered as micro pores and the dimensions in between 2.0 and 50 nm are called as mesopores which facilitates the access to the micropores (Marsh & Reinoso, 2006). Microporosity is further divided as ultra or narrow microporosity where the dimensions less than 0.7 nm and super or wider microporosity where pore dimensions nearer to the limit of 2.0 nm (Marsh & Reinoso, 2006).

For applications like gas storage, it is important to calculate the volume of the carbon skeleton, micropore volume and the non-microporous volume under the characterization process. Dubinin-Radushkevich (DR) equation is used to calculate micropore volume of the carbon sample by interpreting adsorption isotherm data of N_2 (at 77 K), CO_2 (at 273 K). Volume of mesopores are evaluated by subtracting total micropore volume from the amount of nitrogen adsorbed at $P/P^0 = 0.95$ (Marsh & Reinoso, 2006).

Densities of adsorbed molecules vary according to the dimensions and surface chemistry of the porosity (Marsh & Reinoso, 2006). Intermolecular structures of gases within microporosity are a function of the adsorbent micropore dimensions (Marsh & Reinoso, 2006). Adsorption processes in ultra microporous region where intense dispersion forces are applied to adsorbate in confined volumes; influence to the physical state of the adsorbed phase (Marsh & Reinoso, 2006). The entrance dimension of pores are varying hence there is a closed porosity for a given adsorbent (Marsh & Reinoso, 2006).

Except to the pore structure, physical properties of the adsorbent are also essential when selecting for an application. Under the physical properties, there are several properties evaluated as density (bulk, apparent, real), particle size, moisture content, ash content, etc. of AC sample. The details are described below (Marsh & Reinoso, 2006).

- Bulk Density –Mass of a unit volume of the sample including both pore and system voids among the particles, granular carbon used in gas adsorption have a bulk density around 0.40-0.50 g /cm^3. Standard test method is ASTM D2854-70.
- Apparent Density – Mass of unit volume of the carbon particle, including its pore system; also known as particle or mercury density. It is used to obtain the bed porosity.
- Real Density –Mass of a unit volume of the solid carbon skeleton, inaccessible to helium; also called as absolute and helium density

- Moisture content – It is estimated by measuring the evaporated water vapour after heating up to 100 °C. Standard test method is ASTM D 2867099.
- Ash content – It can be used to determine the raw material used to produce the activated carbon. AC from coconut shell contains 1-3 wt% ash, whereas AC from coal-based shows 6-20 wt% ash content. Standard test method is ASTM D 2866-70
- I_2– This is the most fundamental parameter used in AC characterization process to measure the degree of activity of the sample. Iodine number indicates the adsorption capacity in micropores. Thus, higher number implies higher adsorption capacity of the sample. Standard test method is ASTM D 4607-94 (Danish et al., 2011).

2.4.4.1 Isotherm evaluation

A pragmatic characterization of an activated carbon can made from three isotherms as N_2 at 77 K, CO_2 at 273 K and H_2O at 298K or enthalpy of immersion in water. Isotherm of nitrogen at 77 K represents the micro and meso-porosity of the sample while carbon dioxide isotherm at 273 K represents narrow microporosity which is not accessible by nitrogen at 77 K due to kinetic restrictions at low temperature (Marsh & Reinoso, 2006; Sapag et al., 2010). And Isotherm of water vapour at 298K or the enthalpies of immersion in water is the indicator of the surface polarity (Marsh & Reinoso, 2006). However, there is no special gas that characterizes the adsorbent with absolute accuracy hence several gasses should be used to obtain an adequate characterization of the material (Solar, Blanco, Vallone, & Sapag, 2010).

The experimental isotherms of nitrogen, carbon dioxide and water vapour are capable of providing significant analytical data to quantitatively describe activated carbon structure (Marsh & Reinoso, 2006). The data includes;

- Adsorption capacity of the material
- Pore size distribution of material porosity
- The presence of pores with entrance dimension less than 0.7nm diameter
- The presence of high adsorption potential sites which effective at low relative pressures of the adsorptive

- The polarity of the material surface

When analyzing activated carbon porous structure with nitrogen and carbon dioxide isotherm data, a relationship of adsorbed volume of nitrogen & carbon dioxide with porosity structure can be found. Activated carbons with <5 wt% bum-off are showing less adsorption ability towards nitrogen than to carbon dioxide. The restrictive activated diffusion of the nitrogen at 77 K into narrow micropores is responsible for this phenomenon (Marsh & Reinoso, 2006).

The activated carbon which possesses relatively narrow microporosity (about 1 nm dimension) and narrow PSD shows more or less in equal amounts nitrogen and carbon dioxide adsorbed volumes. This behaviour is mostly shown in Activated carbons with <35 wt% bum-off which only provides monolayer adsorption space for either adsorbate. Predicted micropore volumes by DR equation are mostly identical in these types (Marsh & Reinoso, 2006).

Activated carbon with >35 wt% bum-off shows much greater nitrogen adsorption volume than to carbon dioxide. This is due to its wider microporosity and a broader PSD with some mesoporosity (Marsh & Reinoso, 2006). It is stated in the literature ,(Marsh & Reinoso, 2006) when increasing burn off value of the adsorbent, micropore volume obtained by nitrogen adsorption has shown linear increment while volume of carbon dioxide adsorption reach maximum at about 60 wt% burn off and remained constant. This concludes the activation of carbon initial develops narrow micropores followed by widening of its porosity (Marsh & Reinoso, 2006). Multilayer adsorption and volume filling effects are happening in wider micropores and measopores at high pressures (Marsh & Reinoso, 2006). This leads excessively high values of estimated surface area when using the methods developed by monolayer adsorption base (Marsh & Reinoso, 2006).

The quadrupole of adsorbate molecule establishes the structure of the adsorbate monolayer by interacting the polarity of carbon pore surface. The mechanisms of filling of porosity by each type of adsorbates are different (Marsh & Reinoso, 2006).

At low relative pressure carbon dioxide adsorption at 273K are higher than the nitrogen adsorption at 77K which explains by two factors as,

- Larger quadrupole moment with the Carbon dioxide molecule, compared with Nitrogen,
- Nitrogen adsorption has diffusion restrictions into narrow microporosity at 77K temperature which makes the process impossibly slow and cannot be detected within the certain time (Marsh & Reinoso, 2006; Sapag et al., 2010).

At highest of relative pressures, nitrogen fills the mesoporosity but, due to the larger quadrupole moment of carbon dioxide, it only facilitates monolayer adsorption and reduces volume-filling effects in wider micropores. Hence nitrogen exceeds that of carbon dioxide adsorption volume. (Marsh & Reinoso, 2006).

In high pressure and relevant temperature conditions, filling mesoporosity can be occurred as capillary condensation for certain adsorbates. Nitrogen is one example for the process. And it will leads to visibility of a hysteresis loop in nitrogen adsorption and desorption isotherms (Marsh & Reinoso, 2006). In mesopores, nitrogen adsorption and desorption processes are following two different routes with condensation and evaporation effects due to wide pore diameter of the adsorbent and multilayer adsorption process of nitrogen molecule. Adsorption line describes the equilibrium of gaseous adsorbate over a curved meniscus on the internal surface of a cylinder shaped pore whereas the desorption line describes equilibrium of gaseous adsorbate over a curved semi spherical meniscus at the end of a cylinder filled with liquid nitrogen (Marsh & Reinoso, 2006). This leads hysteresis loop in the isotherm

There are IUPAC classified four types of hysteresis loop available (refer Figure 2.3). Carbon resembling the type IV with zero amounts adsorbed at zero relative pressure (Marsh & Reinoso, 2006). When the adsorption line of the loop is vertical then it indicates that all the mesoporosity is one of size (Marsh & Reinoso, 2006).

Combination of both nitrogen and carbon dioxide adsorptive data helps to understand the activation process of the material and provides satisfactory characterization data for better applications

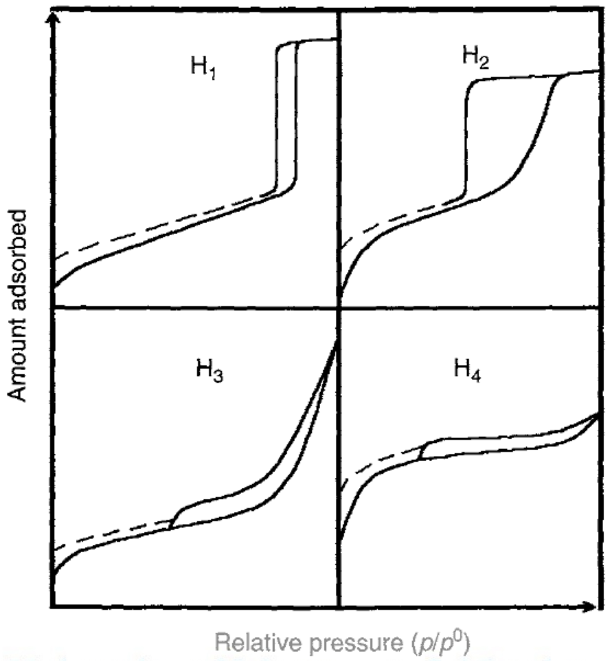


Figure 2.4: Hysteresis loop- IUPAC classification

Source: (Marsh & Reinoso, 2006)

2.4.4.2 Pore structure analysis

Several methods have been proposed in literature to evaluate different characteristics of adsorbent pore structure. The BET equation conveys the surface area of the adsorbent in physisorption phenomena by converting multilayer adsorption into monolayer adsorption. This is done by calculating required non porous monolayer surface area of adsorbent which will be equivalent to multilayer adsorption amount of the adsorbate (mmol/g). The physisorption phenomenon of nitrogen at 77 K, on porous surfaces is a multilayer adsorption process. The calculated BET surface area of the process gives monolayer coverage on non-porous surface assuming that the internal surface of porous material is identical to the external surface of the non-porous material (Marsh & Reinoso, 2006).

Adsorption may occur such that several layers of adsorbate molecules adsorb together which is termed as volume filling in large micropores and as capillary condensation in mesopores. Theoretically, the maximum surface area (both sides) of 1g of single graphene layer of graphite is considered about 2600 m^2/g surface area in nitrogen adsorption. Thus any value beyond about 1000 m^2/g must be associated with micropore volume filling and capillary condensation (Marsh & Reinoso, 2006). In literature it is been reported that higher BET surface areas than $1000m^2/g$ even up to $5000m^2/g$ which can be termed as apparent, or equivalent or effective surface area (ESA) (Marsh & Reinoso, 2006).

The DR equation can be used to characterize the microporosity and analyze the mechanisms of porosity development during activation processes. The data obtained at low relative pressure of both nitrogen and carbon dioxide isotherms are used for the calculations (Marsh & Reinoso, 2006). The micropore volume is obtained by extrapolation of the linear portion of the DR plot (from right to left) to the zero value of log (P/P^0) without considering high relative pressure data (Marsh & Reinoso, 2006). For most activated carbons DR or Langmuir application range is < 0.15 P/P^0 (Marsh & Reinoso, 2006).

The DR plot of nitrogen adsorption data shows higher range of linearity for low activation carbon samples. Hence the extrapolation to calculate micropore volume of the material is straight forward. With increase of activation, the linearity decreases and the plot starts showing a clear upward deviation. This indicates the existence of wider microporosity and small mesoporosity. When higher the activation, linear portion of the plot starts to get shorter which leads miscalculations in absolute micropore volume of the material. Thus, DR plot of nitrogen isotherm yield low values for materials with wide micoporosity (Marsh & Reinoso, 2006). It has been concluded that α plots for N_2 isotherm provides total micropore volume of the material and DR plots of the adsorption of CO_2 at 273K provides the narrow micropore volume (Marsh & Reinoso, 2006).

The pore volume calculated by BET equation is usually higher than the value derived from DR plot since the volume filling on measopores in higher relative pressure region is also considered in BET calculations (Marsh & Reinoso, 2006).

Pore Size Distribution (PSD) describes the pore structure of the material usually based on adsorption isotherm details of adsorbate. Most common methodologies for PSD analysis are the density functional theory (DFT) and the Monte Carlo (MC) simulations (Sapag et al., 2010). Nitrogen isotherm provides a broadest PSD for the material. However, most microporous material with narrow microporosity would be underestimated by diffusion limitations at low temperature (Marsh & Reinoso, 2006; Sapag et al., 2010). Thus PSD analysis by CO_2 adsorption at 273K is effective for more accurate analysis in material characterization phase (Sapag et al., 2010).

2.5 Bio-methane Storage on Activated carbon

The adsorbent for methane storage should be high in microporosity & density with minimum inter-particle space. AC is a porous material with very high micropore volume. Furthermore its low heat of adsorption prevents the excessive heating or cooling of the storage vessel during the adsorption-desorption cycles (Marsh & Reinoso, 2006). AC is mainly hydrophobic which reduce the competition between water and methane for the adsorption sites (Marsh & Reinoso, 2006). And It is consists of slit-shaped pores which creates higher packing density for spherical molecules such as methane (refer figure 2.4) (Marsh & Reinoso, 2006). These facts makes AC promise for the application and its high potential in methane storage has been published in literature studies (Burress, 2009; Ginzburg, 2006).

Except to AC, many research studies are being done to evaluate the potential of various adsorbents for methane storage capabilities. However, the study carried out by Karim Sapag, 2010 has shown that zeolite as the adsorbent has the less potential while carbon nanotube and pillared clay are not capable for this purpose. The Metal Organic Frameworks (MOF) which is a polymeric framework of metal ions shows competitive values with AC. However, its heat requirement (100^{o}C at 1atm) in desorption process, stability and less ability to tolerate impurities in methane, limits

its usage in commercial applications as presented by Wang, Ercan, Khawajah, & Othman, 2012.

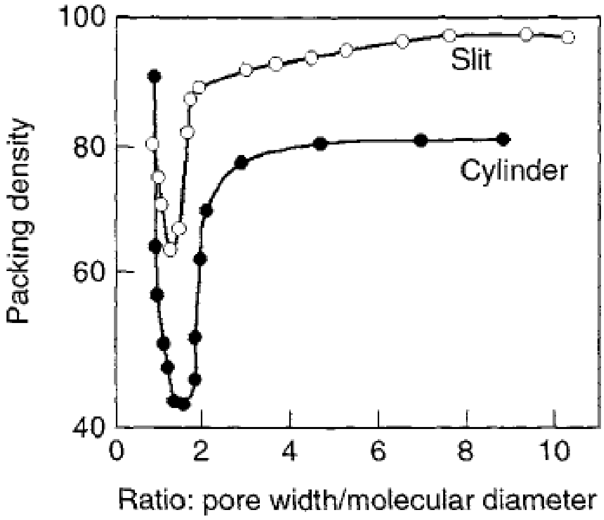


Figure 2.5: Packing mechanism of spherical molecules in narrow cylinder and slit shape pores

Source: (Marsh & Reinoso, 2006)

2.5.1 Material characterization on methane adsorption

Methane adsorption into AC in room temperature assume as occurring in supercritical gas stage due to lower critical temperature (191 K) of methane. It has been published that the adsorption of supercritical gases predominantly happens in pores which are less than two or three molecular diameters in width (Marsh & Reinoso, 2006). Hence, it is stated that the increment in pore width, rapidly decrease the forces responsible for the adsorption (Marsh & Reinoso, 2006). It is important to have the maximum volume of micropores and a minimum volume for other pores and voids in the carbon to achieve better methane adsorption. Thus the meso and macro pores present in AC are not useful for methane storage but it may create necessary transportation for gasses into and out of the micropores. Thus appropriate micropore size distribution is important to achieve high methane adsorption (Marsh & Reinoso, 2006).

Maximized fraction of micropore enhance methane storage though the width of micropores should be around 0.76 nm (larger than the thickness of two methane molecules) to maximize the deliverability of methane at ambient pressure (Marsh & Reinoso, 2006). The concept was demonstrated by Grand Canonical Monte Carlo (GCMC) simulations performed for natural gas adsorbed on carbon (Marsh & Reinoso, 2006).

It has been reported by Blanco et al., 2010) from their PSD analysis by GCMC simulations that methane adsorption on AC sample in low pressure is happened in micropore region, around 0.6 nm to 0.9nm. The same study stated that during the high pressure adsorption some mesoporosity near to the micropore region is also detected and adsorption has happened in the range of 1.8–2.2 nm (Sapag et al., 2010). Hence the literature (Sapag et al., 2010) suggested that methane adsorption is less sensitive to smaller micro pores and more sensitive to larger micropores assuming diffusive limitations of methane in high pressure region. Another study carried out by Sun et al., 2001 has stated that optimal pore range for methane storage is from 0.8 to 1.5 nm based on their modelling analysis. Further Sun et al., 2001 recommended that the adsorbent for methane storage should prepare with high super micropores and avoid ultra- micropores as super micropores offer high methane adsorption densities and fast adsorption/desorption kinetics while ultra-micropores collect “cushion gas which reduces deliverable storage capacity of the adsorbent.

Adsorbed methane density is not only a function of applied pressure but also of the adsorption potential of porosity or micropore dimensions of activated carbon sample (Marsh & Reinoso, 2006). It has been published in both theoretical and simulation studies that the maximum possible value of methane density is 0.37 g/cm^3 when the pore width is equivalent to the molecular dimension of methane. This is quite near to liquid density (0.42 g/cm^3) of methane and decreases rapidly with increasing width of the micropore (Marsh & Reinoso, 2006).The methane density in microspores increases with increasing pressure. And after analyzing the data obtained from N_2, CO_2 and CH_4 adsorption experiments, It is reported that methane density become highest, about 0.25 g/cm^3 at 2.5MPa in the narrow micropores and 0.09 g/cm^3 at

3.4MPa in the wide micropores (Marsh & Reinoso, 2006). In non microporous volume that is the volume of mesopores, macropores and inter-particle voids, the density of methane is low and similar to compressed methane at relevant pressure (at 3.4MPa, i.e. 0.023 g/cm^3) (Marsh & Reinoso, 2006).

Normally methane adsorption is carried out at room temperature, which is well above the critical temperature (191K) of methane. Thus methane density of the adsorbed phase is lower than that of the liquid methane (Marsh & Reinoso, 2006; Solar et al., 2010). This concept is further proven by Blanco et al., 2010 from their Grand Canonical Monte Carlo (GCMC) simulation studies.

The AC with high mass storage capacity and high bulk density is essential to achieve a high methane adsorption. However, as the adsorbent is gone through an activation process, the two properties are varying in opposite manner (Celzard et al., 2004; Perrin et al., 2003; Sapag et al., 2010). But achievement of satisfactory bulk density along with proper pore size distribution for favourable methane uptake is crucial to develop commercial scale application (Rios et al., 2009; Siangsai et al., 2014; Solar et al., 2010).

2.5.2 Type of AC sample

Methane adsorption on AC is varying with the type of AC. It is preferred to have pellet or monolithic activated carbon over granular activated carbon, without loss of micropore volume by considering its higher bulk density and adaptability to the shape of the container in commercial scale applications (Sapag et al., 2010).

From Grand Canonical Monte Carlo simulations, it was predicted that the theoretical maximum methane storage capacity of carbon at 3.5 MPa is 209 V/V value for monolithic carbon and 146 V/V value for pelletized carbon, both with minimum amount of macropore volume and no external void space. The adsorption of AC pellets shows considerably lower value than monolith form as the volume fraction distributions in the two physical forms are different (Marsh & Reinoso, 2006). Further the characterization study carried out by (Marsh & Reinoso, 2006) stated that

GAC has higher void percentage and lower micropore percentage compare to tested monolithic samples.

The above reported results convey difference in obtained results due to variability of AC type. However, adsorption capacity of AC differs due to its variety in appearance as pellet, monolith, granular, etc except to its parent material structure and activation process. The reason behind the variation is difference in its pore structure and packing density obtained from its manufacturing conditions and parent material.

2.5.3 Bio-methane adsorption isotherm development

Methane adsorption into microporous AC delivers type I isotherm in room temperature (Cavalcante et al., 2007; Gottipati et al., 2012; Mota et al., 2008). The isotherm obtained directly from experimental studies is defined as absolute adsorption isotherm (Stadie, 2013). This includes the adsorbed gas amount and free gas amount trapped in both void spaces and macropores in adsorbent material. The adsorbed gas which is named as excess uptake is approximately equal to absolute quantity at low pressure, but the difference between excess to absolute value increases with increasing pressure (refer figure 2.6)

2.5.4 Model developments

Development of appropriate adsorption equilibrium correlation is essential for a reliable prediction of adsorption parameters and quantitative comparison of adsorbent behaviour with different adsorbent systems. This equilibrium relationship or isotherm model expresses the surface properties and capacities of adsorbents thus it can be used for optimization of the adsorption mechanism pathways and effective design of the adsorption systems (Hameed & Foo, 2010).

Wide variety of equilibrium isotherm models have been formulated based on three fundamental approached as kinetic consideration of the dynamic behaviour of the process, thermodynamic behaviour of adsorption systems and potential theory which conveys main idea in generation of characteristic curve (Hameed & Foo, 2010).

Langmuir and Toth models have been mostly used to analyse methane and carbon dioxide adsorption systems in literature.

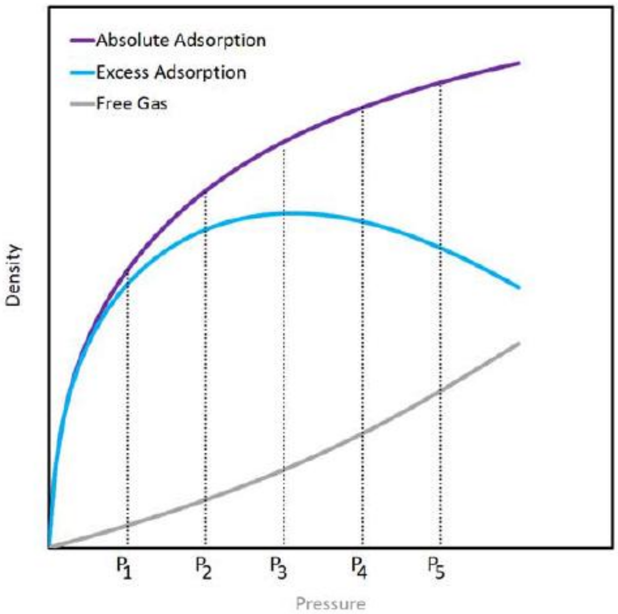


Figure 2.6 : Gas – Solid Adsorption Isotherm

Source (Stadie, 2013)

Langmuir model is originally developed to describe gas solid phase adsorption on AC assuming monolayer homogeneous adsorption process (Hameed & Foo, 2010). Toth model is a modified version of Langmuir model with minimum deviation errors between experimental data and calculated values and describe the adsorption equilibrium on heterogeneous systems and multilayer adsorption (Goldberg & Brown Jr., 2005; Hameed & Foo, 2010). Thus, toth equation is suitable for forecasting methane adsorption potential of a certain adsorbent in high pressure (Mota et al., 2008; Waltson et al., 2006; Zheng et al., 2015). The reported relative errors between the experimental and predicted data are less than 0.07% (Zheng et al., 2015).

2.5.5 Process limitations

In early 1990s, US Department of Energy set a target figure for methane as 150V/V value at 3.5MPa pressure and 25 °C temperature for an operational ANG vehicle system. The target was demanding and several researchers were able to achieve the goal (Marsh & Reinoso, 2006). However, still researches are going on globally under this area to develop better AC adsorbent to overcome current limitations.

Development of a proper pore structure using correct activation process is the crucial step when developing AC for methane storage. In Physical activation methods microporosity is developed by widening the rudimentary porosity of the parent char. The process variables as temperature, pressure, heating rate, etc. are unable to influence the micropore size distribution greatly. However, a well-controlled chemical activation is capable to modify the porosity development of the carbon substantially (Marsh & Reinoso, 2006). Hence it is proven that chemically activated samples have more capacity in methane storage over physically activated carbon (Solar et al., 2010). However, currently major AC suppliers of the country are following physical activation method in their commercial scale manufacturing.

If we are heading towards commercial applications, it is essential to figure out optimum parameters in methane adsorption process. Most of previous studies were carried out in room temperature with increased pressure. Though, the compaction decrease the inter-particle voids space and increase the bulk density of the material, the process is unable to create a significant effect on adsorption capacities. It is reported that AC at compaction pressure of 100 MPa shows maximum storage capacity of 193 V/V and the same sample shows 163 V/V value of methane storage capacity at 3.5 MPa gas pressure at 30 °C (Marsh & Reinoso, 2006). Hence the optimal pressure range is selected as 3.5-4 MPa for most researchers in their studies.

The temperature is a key parameter in adsorption and desorption process. The exothermic nature of adsorption process and endothermic nature of desorption process creates negative impact on charge and discharge cycle of the storage vessel (Cavalcante et al., 2007; Walton & LeVan, 2006). This significant temperature fluctuation in adsorption bed controls its adsorption capabilities (Gottipati et al., 2012; Sapag et al., 2010; Walton & LeVan, 2006). Thus, the development of better carbon adsorbents wouldn't be the solution but improving the heat transfer mechanism within the adsorption bed is also essential for the advance in ANG technology in commercial scale (AZIMI & MIRZAEI, 2012).

The minimization of thermal effect by different methods has been discussed in literature (AZIMI & MIRZAEI, 2012; Sapag et al., 2010). The arrangements as maintaining a lower flow rate of charge, using a perforated tube to direct the transfer path in radial direction rather than axial direction etc., are suggested for a successful design of a storage vessel for better performance in commercial scale applications (Zheng et al., 2015). The simulation studies carried out by AZIMI & MIRZAEI, 2012 has proven that rate of temperature rising and the filling time in radial model are smaller than that of axial model by comparison studies. It also facilitates to overcome transportation restrictions in regular packed bed system. Thus, radial gas flow through adsorption bed is more advantageous over axial flow. However, optimization design of the vessel need to be carried out by considering storage density, heat and mass transfer of the adsorbent and compatibility with the relevant application (Zheng et al., 2015).

Methane storage on AC vessel is a cyclic process. It has been reported in certain literature that the adsorption capacity of the adsorbent deteriorates on extended cyclic operations due to the presence of higher molecular weight hydrocarbons and sulphur based odorants (Mota, 1999; Mota et al., 2008; Walton & LeVan, 2006). These impurities decrease the methane adsorption capacity by accumulating in the bed during cyclic operations (Walton & LeVan, 2006). This can be overcome by regenerating the adsorbent however the process is usually prohibitive (Mota, 1999; Mota et al., 2008). However, cleaner methane reduces the impact.

It has been found out by model simulations (Walton & LeVan, 2006) that temperature effects can be more detrimental to cyclic performances of methane storage than presence of impurities in feed gas Thus, maintain correct temperature is essential. Maintaining low temperature during filling process will be more similar to acetylene filling process but the commercially viability of the process needs to be further evaluated. There are several studies found in literature proves that wet AC shows higher potential than dry AC, however the optimum temperature and pressure conditions used for the process ($2^{o}C$ & 8MPa) are not viable for commercial usage (Mahboub et al., 2012).

2.6 Conclusion

Biogas is a technologically viable renewable energy source for Sri Lanka and capable of fulfilling country's energy needs while providing solution for the current solid waste problem of the country. The less energy density of the gas can be avoided by increasing its methane content up to 99% and upgrading storage capacity via adsorption techniques.

As per the literature, activated carbon with higher micropore volume, optimum pore size distribution and higher bulk densities are suggested as a suitable adsorbent for methane storage by adsorption. Micropores are favourable for methane storage while macro and mesopores are also essential to provide proper transportation to the micropores. Higher bulk density is important to maintain higher gas amount per storage cylinder.

It has been published in previous studies that optimum pores for methane adsorption are found in wide micopore range by their PSD simulation analysis and higher methane densities are found in narrow micropores by experimental result analysis. However, it is also essential to note that AC found in these published work based on different parental material. Thus it is hard to ensure the most suitable pore characteristics for our own AC as the variations in three dimensional pore arrangements due to different parental molecule structures may affect the expected out come. Hence it is more suitable to characterize the sample and identify its favourable pore ranges in initial stage of the study.

There are some process limitations which need further attention in order to establish the process in commercial scale. Since adsorption is temperature dependent process, it is also essential to minimize thermal effects during adsorption desorption processes. Usage of highly purified bio-methane is important to extend the cyclic operation of the adsorbent.

However, Sri Lanka is a leading producer of AC using coconut shell charcoal. And there is a clear potential for commercialization biogas as renewable energy source in the country.

CHAPTER 3 MATERIAL CHARACTERIZATION

3.1 Introduction

Selection of a suitable adsorbent and evaluation of its potential by using characterization data are discussed under this chapter. Adsorbent was selected to enhance bio-methane storage by considering technical and economic aspects of the country. Under material characterization step, the main raw materials, i.e. adsorbent and adsorbate were analysed to identify the storage capacity by adsorbent pore structure and adsorbate composition. A proper characterization study would support to recognize future requirements of adsorbent pore structure developments and biogas purification to achieve high density methane storage.

3.2 Material Selection

The main raw materials for the process are adsorbent and adsorbate. According to the published literature, it is stated that MOF and AC are showing promising adsorption results on methane. However, MOF has shown adsorption constrains when presence of impurities in adsorbate and desorption restrictions in atmospheric temperature conditions (Ercan et al., 2012). And AC has shown potential in commercial scale application considering the economical background of Sri Lanka and is currently viable in the country. Thus, AC has selected as most suitable adsorbent for this study.

Sri Lanka is a leading producer of AC using coconut shell charcoal. Current production of AC of the country is targeted on applications like gas & air purification, water treatment, gold extraction, food & beverage industry etc. Analysing on commercial scale AC as the methane adsorbent was conducted under this study as considering the initial step on upgrading bio-methane storage by Sri Lankan AC through adsorption.

Commercial AC from HAYCARB PLC, the global leader in manufacturer of AC from a renewable source (coconut shell), was analysed to identify the methane adsorption potential with biogas storage in view.

As adsorbate, it is important to use highly purified methane to understand the actual capability of the adsorbent in energy storage. However, biogas was used instead of bio-methane due to unavailability of proper biogas upgrading facilities during the research time frame.

3.2 Activated Carbon Characterization

3.2.1 Sample preparation

Commercial AC manufactured by HAYCARB PLC was used for the study. Two forms of AC were used as pellet and granular (figure 3.1). HAYCARB is using coconut shell as the raw material for AC manufacturing. Prepared coconut shell charcoal is physically activated by steam in their commercial scale manufacturing process. Granular AC is manufactured by direct activation of coconut shell charcoal by steam but in pellet form, charcoal is first converted in to pellet and then steam activation is carried out. The basic AC property details of the samples, supplied by HAYCARB are stated in table 3.1. The cumulative distribution of particles of provided samples are presented in figure 3.2 and 3.3.

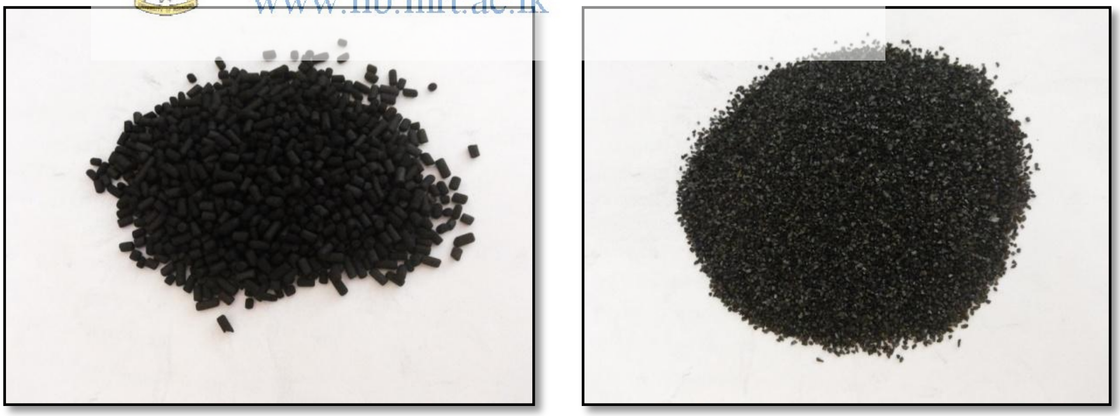


Figure 3.1: AC pellets (Left) and granular AC (right) samples used for the study

Table 3.1: AC Properties

Sample Property	Sample Type	
	Granular AC (PHO 18X40 DDH)	AC Pellet (PHO 2S)
Moisture Content (%)	3.6	0.4
Ash Content (%)	NG	9.1
Dry Bulk Density (g/cc)	0.56	0.477
I_2 (mg/g)	1150	1070
Ave. Length (mm)	NA	4.68
Ave. Diameter (mm)	NA	2.11

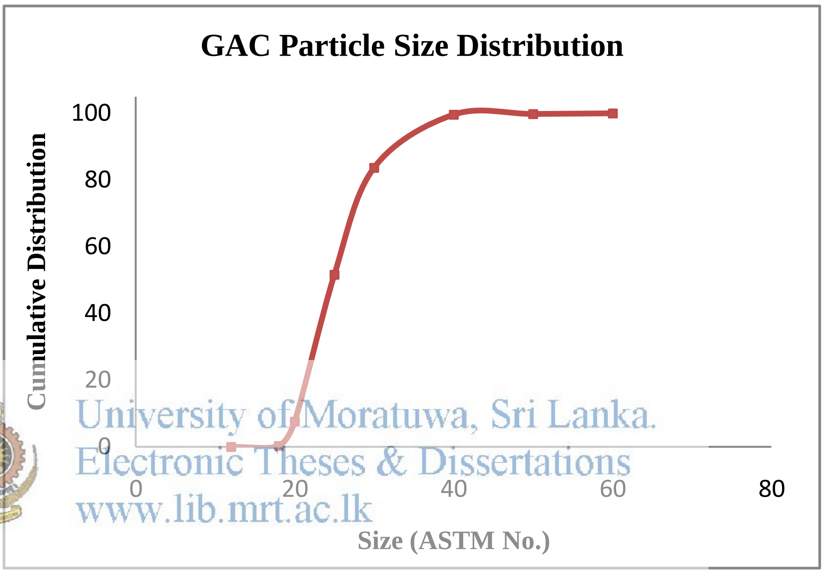


Figure 3.2 : Particle size distribution of GAC

3.2.2 Characterization methodology

The study mainly focuses on pore structure evaluation of provided AC samples under the characterization step. Usually N_2 at 77K and CO_2 at 273K adsorption isotherm studies are conducted to analyze pore characteristics in sensible manner (Marsh & Reinoso, 2006).

N_2 adsorption experiment was carried out Quantachrome Autosorb iQ-1 apparatus at 77K by HAYCARB PLC for supplied samples. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}), BJH surface area (S_{BJH}), total pore volume, micropore volume (V_{DR}), average pore diameter and pore size distribution data (PSD) were calculated using Quantachrome software. The DR equation was used to calculate micropore volume. Surface areas of the samples were determined using BET equation & mesopore surface areas of the samples were determined by BJH equation. Total pore volume was estimated from the liquid volume of the adsorbate (N_2) at a relative pressure of 0.95 (Zhang, Walawender, & Fan, 2010).Average pore diameter was calculated using BET surface area (S_{BET}) & total pore volume data, assuming cylindrical pore geometry (Zhang et al., 2010)

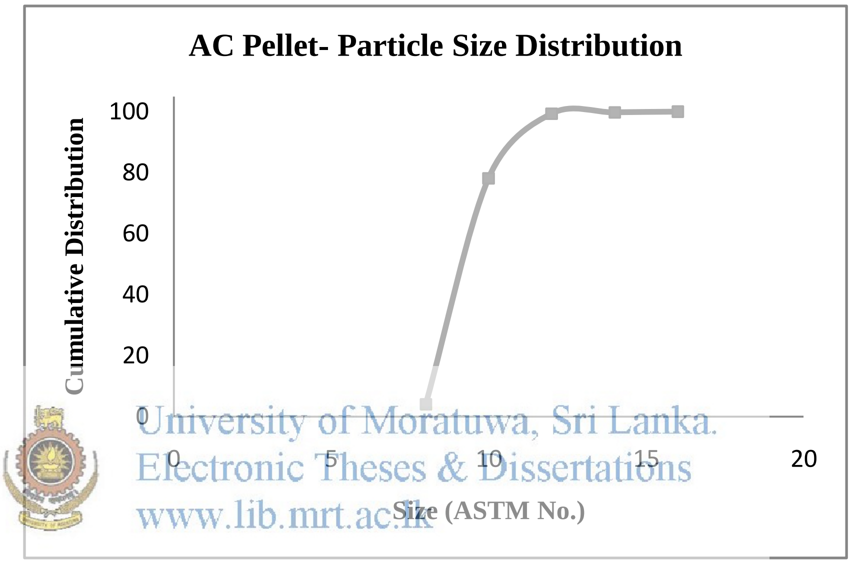


Figure 3.3 : Particle size distribution of AC Pellets

The PSD was determined using Density Functional Theory (DFT) method (Zhang et al., 2010). Dry bulk densities of the samples were determined as per American Society for Testing & Materials (ASTM) standard test method D2854-09.

3.2.3 Sample characterization

The isotherm obtained from N_2 adsorption at 77K is presented in figure 3.4. Granular sample shows higher adsorption towards N_2 than pellet sample. The shape of both isotherms illustrates type I isotherm with & type IV hysteresis loop. This explains micropore structure of material with presence of mesopores. Steeper line is visible in the first section (0-0.05 range) of both isotherms thus presence of smaller micropores in the sample can be assured. Table 3.2 presents the results obtain from isotherm data by Quantachrome software. As per analysed data presented in Table 3.3, both granular & pellet AC samples show low mesoporosity & high microporosity with similar mesoporosity & microporosity values.

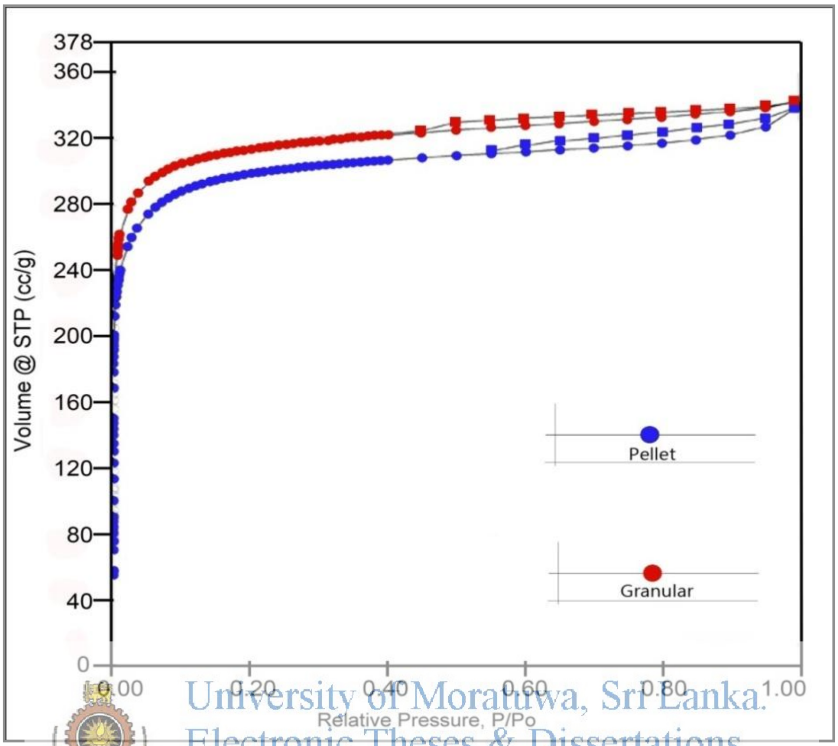


Figure 3.4 : N_2 adsorption isotherm at 77K

Adsorption capacity measured by iodine number shows similar results for both granular and pellet from. Dry bulk densities of both samples are found similar to the bulk density of commercial AC tested in literature (Ercan et al., 2012). PSD details of granular & pellet forms obtained from N_2 gas adsorption are presented in figure.3.5. PSD of both samples are narrow, but granular sample shows much wider distribution than pellet AC sample. The peak is obtained around 1.1-1.3 nm range for both samples.

Pore distribution (figure 3.5) is mostly visible in wide microporous range in both samples which explains the inaccessibility of N_2 gas at 77K into narrow micropores as discussed in literature. Hence the micropore volume obtained from the isotherm (table 3.2) mostly indicates wide micropores of the sample. Some mesopores are visible similarly in both samples.

Table 3.2: AC characterization details obtain from N_2 adsorption at 77K

Parameter	Sample type	
	Granular AC (PHO 18X40 DDH)	AC Pellet (PHO 2S)
Surface Area		
BET Surface Area (Multi point)	1232 m^2/g	1155 m^2/g
BJH Cumulative Surface Area	30.63 m^2/g	28.27 m^2/g
t-method Micropore Surface Area	1211 m^2/g	1128 m^2/g
DR method Micropore Surface Area	1285 m^2/g	1203 m^2/g
Pore Details		
Total Pore Volume	0.53 cc/g	0.525 cc/g
t-method MicroporeVolume	0.49 cc/g	0.464 cc/g
DR method MicroporeVoume	0.456 cc/g	0.427 cc/g
Average Pore Diameter	17.25 A	18.17 A
DR method Micropore Pore Width	10.32 A	10.94 A

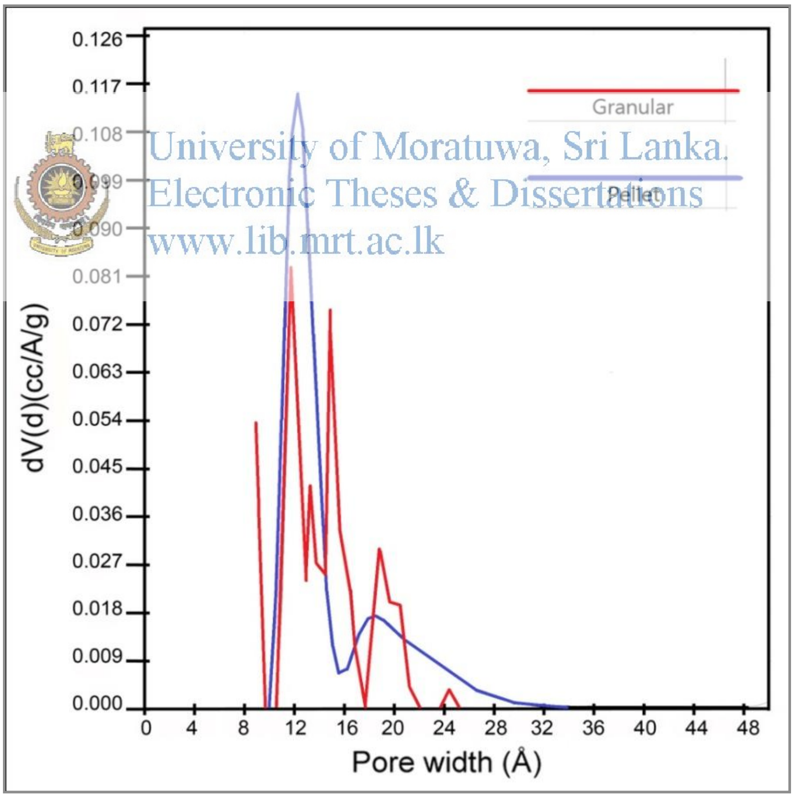


Figure 3.5: Pore size distribution, N_2 adsorption at 77K

3.2.4 Adsorbent comparison

The characterization details of commercial AC made from coconut shell charcoal by HAYCARB PLC were analysed in this section. AC properties developed in current manufacturing process is basically targeting applications like gas & air purification, water treatment, gold extraction, food & beverage industry etc. Thus, evaluation of its potential as a methane adsorbent by comparative analysis with globally tested AC data was conducted in this section. The characterization details and methane adsorption data of coconut shell AC are presented in table 3.3. The BET surface area and microporosity values are considerably similar in HAYCARB samples with literature. Thus moderate micropore volume is visible compare with other samples (refer Appendix B). However proper prediction on methane adsorption potential of HAYCARB samples aren’t possible due to different testing conditions, different physical shapes and lack of some information as apparent density, pore size distribution etc. in published samples

Table 3.3: Characterization details and methane adsorption data of coconut shell AC

AC Type	**BET Surface Area (m^2/g)**	**Micropore ratio**	**Apparent Density**	**Methane Adsorption (V/V)**	**Condition**	**Reference**
PAC	1000	0.892	0.4	107	8 MPa , 275K	(Perrin et al., 2003)
	1587	0.866	0.34	158		
	2031	0.852	0.29	121		
GAC	520	0.882	0.32	62	3.5 MPa, 303K	(Rafael B. Rios et al., 2009)
	727	0.905	NG	NG		
	783	0.878	NG	NG		
	844	0.909	0.45	95		
	536	0.865	NG	NG		
	767	0.863	0.33	67		
	779	0.880	0.35	73		
	693	0.784	0.28	59		
	1441	0.849	0.26	82		
PAC	2114	0.876	NG	80	4MPa, 298K	(Bastos-Neto, Torres, Azevedo, & Cavalcante Jr, 2005; Cavalcante et al., 2007)
	1266	0.925	NG	NG	NG	
	1091	0.806	NG			
	1699	0.867	NG			
GAC	1232	0.859	NG	Commercial sample provided by HAYCARB PLC for this study		
Pellet	1155	0.814	NG			

3.3 Biogas Characterization

Biogas produced from pilot plant located at University of Moratuwa was used for the study. Since upgrading facility of the plant was not functioning properly, biogas from reactor was directly pumped to the high pressure cylinder by scuba type four stage compressor up to 100 bars. During the compression process most of water vapour was removed due to the effect of rapid compression. Pressurized gas was characterized using gas chromatography method. The results are presented in table 3.4 and the relevant report is attached in Appendix F. The Gas analysis system was only capable in identifying CH_4, CO_2, N_2 and O_2. The rest was categorized as other which may contain hydrogen, hydrogen sulphite, water vapour, etc.

Table 3.4: Biogas composition

Gas Component	**Composition (%)**
Methane (CH_4)	55.89
Carbon dioxide (CO_2)	36.39
Nitrogen (N_2)	3.57
Oxygen (O_2)	0.89
other	3.26

It is always crucial to carry out adsorption process only with the methane component of biogas as it only contains the energy value of the gas. Carbon dioxide has higher adsorption potential with AC over methane which obviously reduces the energy efficiency of the overall process (Himeno et al., 2005; R. B. Rios et al., 2013). And other impurities like hydrogen sulphite decrease the methane adsorption capacity by accumulating in the bed during cyclic operations as per literature (Walton & LeVan, 2006).

CHAPTER 4 PILOT SCALE STUDIES ON BIOGAS ADSORPTON

4.1 Introduction

The study was conducted to understand bio-methane storage capability in commercial AC made from coconut shell charcoal in Sri Lanka. The unit was designed for pilot scale testing. Experiments were carried out in isotherm conditions for a predefined pressure range. Adsorption isotherm development for bio-methane was carried out to full fill the main objectives of this work. Methane storage by adsorption was compared with compression process which is currently practicing to upgrade biogas storage in global

4.2 Process Selection

Methane adsorption on AC is a well-recognised technology in global however it still needs further improvements to establish in commercial grade. As per records this is the first time in Sri Lanka, study on the adsorption ability of AC for bio-methane storage is happening. It is impossible to carry out the study in lab scale without automatic volumetric gas adsorption unit which isn't available in Sri Lanka for methane at the moment. Moreover methane adsorption on AC is a proven process in lab scale studies in adsorption cell concept in globally, thus pilot scale testing mechanism was developed to identify the capacity of commercial AC when used in a packed bed high pressure cylinder.

There are two approaches which have been used in literature to measure the adsorbed gas amount as gravimetric and volumetric methods. Most precision pressure gauges and gas manifold systems need to be used in volumetric method over gravimetric process. In addition to that the unit is designed in pilot scale and the volume of adsorption cylinder is nearly 2 litres in volume, thus it was more convenient to go for gravimetric approach with properly selected weighing scale over volumetric method.

4.3 Pilot Scale System Development

4.3.1 Design considerations

Pressure and Temperature are the crucial parameters to measure the adsorption behaviour. Observing adsorption behaviour with pressure under constant temperature conditions is the most common procedure practising globally. Pressure of 3.4MPa is identified in literature (Marsh & Reinoso, 2006) as the optimum value for methane adsorption on AC micropores. Thus testing pressure range was selected as 0 to 50 bar of gauge pressure range with atmospheric temperature, 303K was selected as the temperature.

According to selected pressure range, high pressure equipment was used to develop the system. Relevant equipment testing was carried out to confirm on high pressure withstand ability of the unit. Relevant calibrations were done to assure on accuracy of experimental results.

4.3.2 Unit development

The unit was mainly consists of biogas cylinder (100 bar) with gas regulator, gas manifold, adsorption cylinder and vacuum pump. 35 Litres volume, tested high pressure (250 bars) O_2 cylinder was used as initial biogas storage cylinder. Pressurized biogas by compression up to 100 bars was used for the experiment. Gas regulator with maximum 50 bars outlet pressure was connected to cylinder valve of the biogas cylinder. The importance of gas regulator is to provide controlled and smooth outlet gas line for the gas manifold system.

2050 cm^3 volume, CO_2 fire extinguisher with CO_2 cylinder valve was selected as the adsorption cylinder. During the desorption process, outlet biogas from adsorption cylinder should be filtered before entering it in to gas manifold valve system as the desorbing biogas may consists of AC particles while releasing its pressure. Thus high pressure filter bud was located within the adsorption cylinder in between AC bed and cylinder valve to clean the outlet gas line (figure 4.2). Weighing scale was used to measure the adsorbed biogas amount as per gravimetric method. The performance range of the scale is 0-30kg with precision of 1g. The calibration detail of the scale can be found in Appendix G. Vacuum pump was used to maintain vacuum conditions in system when necessary.

Figure 4.1 :Gas Manifold (Left) & Adsorption cylinder (Right)

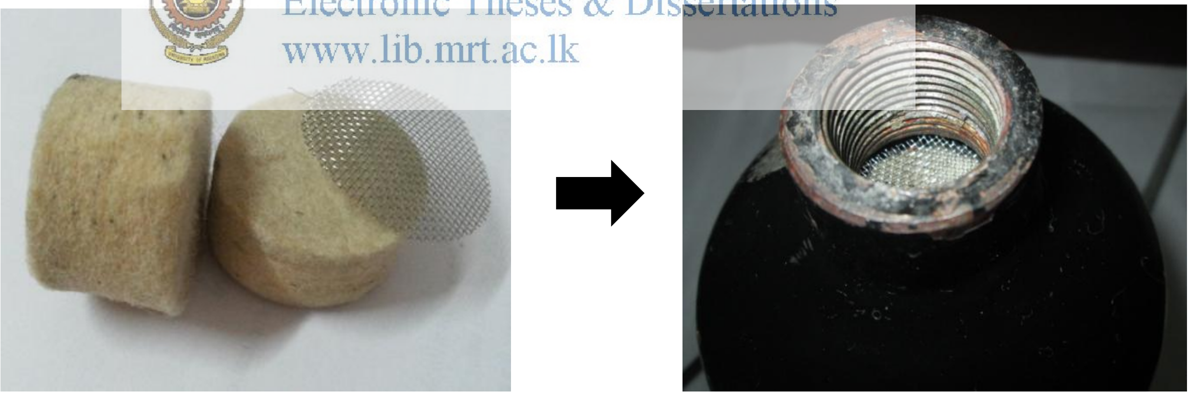


Figure 4.2 : Filter buds

Biogas cylinder with regulator, adsorption cell and vacuum pump were connected to gas manifold system by flexible hose lines. Design pressure of 225 bars, hydraulic hose, and ¼” in size was used as flexible hose. Gas manifold was ¼” in size, and was designed up to 70 bar pressure withstanding ability. High pressure needle valves, ¼” in size female tread, were connected to gas manifold system to control smooth gas line during experiments (figure 4.1). Separate gas outlet line was designed in gas manifold for desorption. The sketch of the experimental set up is shown in figure 4.3.

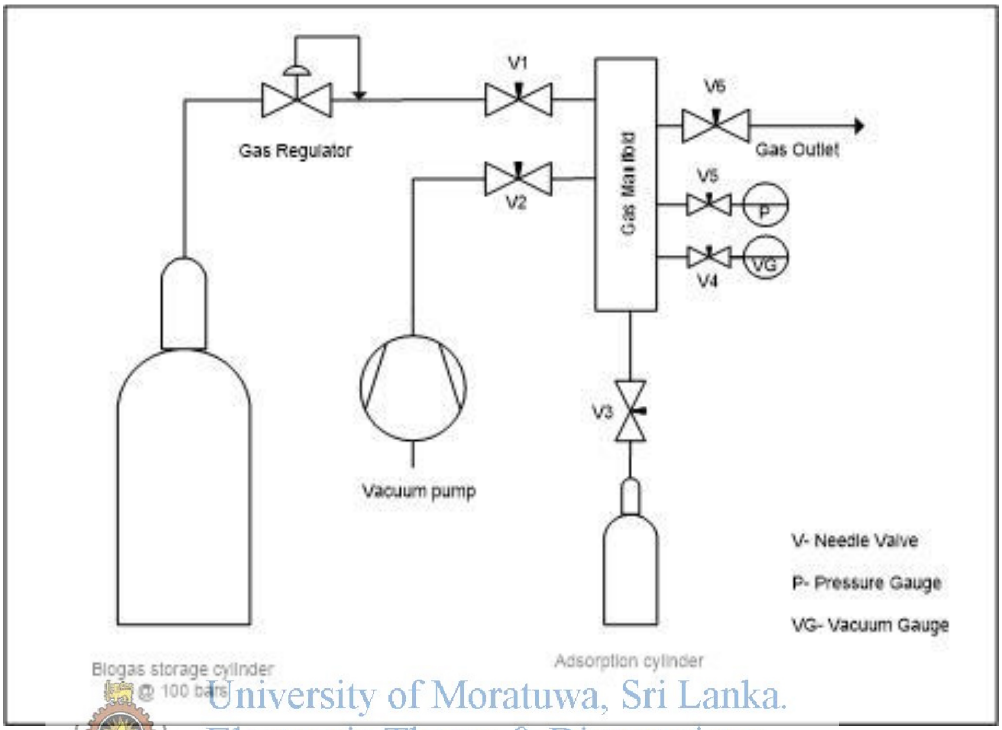


Figure 4.3 : Experimental Set up (Sketch)

4.3.3 System Operation

Supplied AC was dried in muffle furnace at 100^{o}C for 3 hrs. in order to make the samples moisture free (Zhang et al., 2010). Then sample was loaded into adsorption cylinder. Isotherm condition of the sample during the adsorption was maintained by placing adsorption cylinder in a water bath. Gas manifold system and adsorption cylinder set up was vacuum using vacuum pump. Once the system was set to vacuum conditions, biogas was released to the unit in different pressure values starting from 0 to 50 bars pressure. When unit was reached to adsorption equilibrium in certain pressure, the relevant weight values of the adsorption cylinder according to the pressure were recorded. When the unit was reached to 50 bars of pressure, the stored biogas on adsorption cylinder was realised via gas outlet valve of the manifold. Gas samples were collected at several equilibrium pressure values to analyse the individual adsorption capacity of methane and carbon dioxide in biogas mixture.

Then CO_2 composition of the collected samples were analysed by using Orsat apparatus. After system was reached to atmospheric conditions, unit was vacuumed again and the adsorption process was repeated for the 2nd cycle. The experiments were carried out for both granular and pellet forms. The experimental setup was shown in figure 4.4.

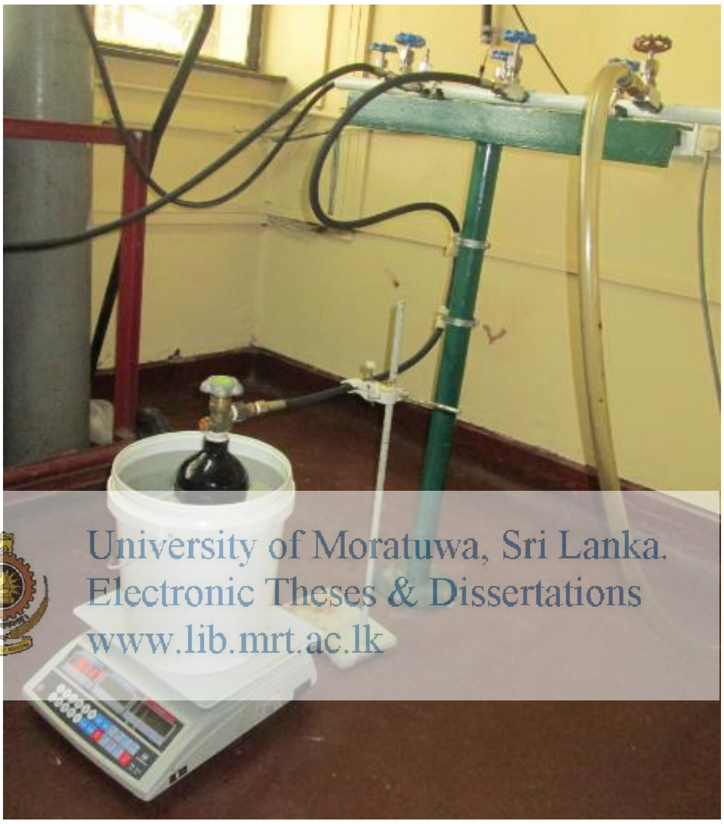


Figure 4.4 : Experimental Set up

4.4 Pilot Scale Experiment Result Analysis

4.4.1 Biogas adsorption on AC pellets

The experiment was conducted at 303K temperature for 0 to 50 bars pressure range. Weight of filled AC pellets was 1.053 kg. Weighing scale correction was negligible as weight difference is considered to find out adsorbed biogas weight in each pressure stage. Few assumptions were made as biogas composition was taken as 56% of Methane, 37% of Carbon dioxide and 8% of Nitrogen and volume of 1 mole of biogas at STP conditions was taken as 22.4 dm^3 for calculations. The adsorption results of 1st cycle and 2nd cycle are presented in table 4.1 and 4.2 respectively. The results are graphically shown in figure 4.5.

Table 4.1: Biogas adsorption into AC pellets – 1st cycle

Pressure	Adsorbed Biogas		
	per cylinder		per AC weight
(barg)	g	moles	mmoles/g
0	0	0.0000	0.0000
4	69	2.6620	2.5281
8	99	3.8194	3.6272
12	120	4.6296	4.3966
16	135	5.2083	4.9462
22	156	5.9028	5.6057
27	173	6.5201	6.1919
31	191	7.3688	6.9979
36	211	8.1404	7.7307
40	220	8.4877	8.0605
46	231	8.9120	8.4635
52	241	9.2978	8.8299

Table 4.2: Biogas adsorption into AC pellets – 2nd cycle

Pressure	Adsorbed Biogas		
	per cylinder		per AC weight
(barg)	g	moles	mmoles/g
1	2	0.772	0.7333
4	72	2.7778	2.6380
9	101	3.8966	3.7005
12	115	4.4367	4.2134
17	127	4.8997	4.6531
20	138	5.3241	5.0561
25	153	5.9028	5.6057
30	161	6.2114	5.8988
35	174	6.7130	6.3751
45	194	7.4846	7.1079
52	202	7.7932	7.4010

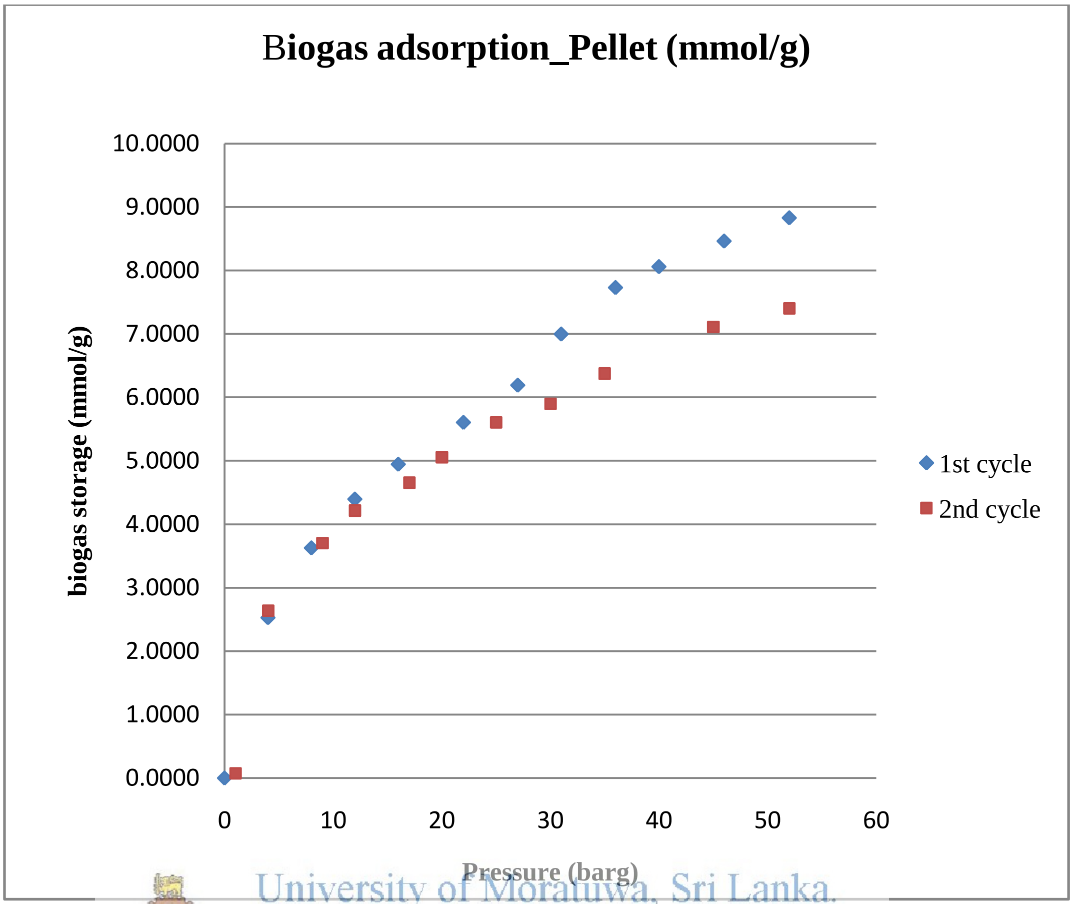


Figure 4.5 : Biogas adsorption on AC pellets

4.4.2 Biogas adsorption on granular AC

The experiment was conducted at 303K temperature for 0 to 50 bars pressure range. Weight of filled AC pellets was 1.074 kg. Weighing scale correction was negligible as weight difference is considered to find out adsorbed biogas weight in each pressure stage. Same assumptions were made. Biogas composition was taken as 56% of Methane, 37% of Carbon dioxide and 8% of Nitrogen. And volume of 1 mole of biogas at STP conditions was taken as 22.4 $dm^3$for calculations. The adsorption results of 1^{st} cycle and 2^{nd} cycle are presented in table 4.3 and 4.4respectively. The results are graphically shown in figure 4.6.

Table 4.3: Biogas adsorption into granular AC– 1st cycle

Pressure	Adsorbed Biogas		
	per cylinder		per AC weight
(barg)	g	moles	mmoles/g
0	0	0.0000	0.0000
5	87	3.3565	3.1252
9	115	4.4367	4.1310
13	142	5.4784	5.1009
18	164	6.3272	5.8912
20	172	6.6358	6.1786
25	189	7.2917	6.7893
30	201	7.7546	7.2203
34	216	8.3333	7.7592
42	234	9.0278	8.4058
46	242	9.3364	8.6931
54	259	9.9923	9.3038

Table 4.4: Biogas adsorption into granular AC– 2nd cycle

Pressure	Adsorbed Biogas		
	per cylinder		per AC weight
(barg)	g	moles	mmoles/g
5	84	3.2407	3.0174
13	128	4.9383	4.5980
18	154	5.9414	5.5320
23	175	6.7515	6.2864
28	185	7.1373	6.6456
36	205	7.9090	7.3640
43	218	8.4105	7.8310
49	219	8.4491	7.8669
52	225	8.6806	8.0825

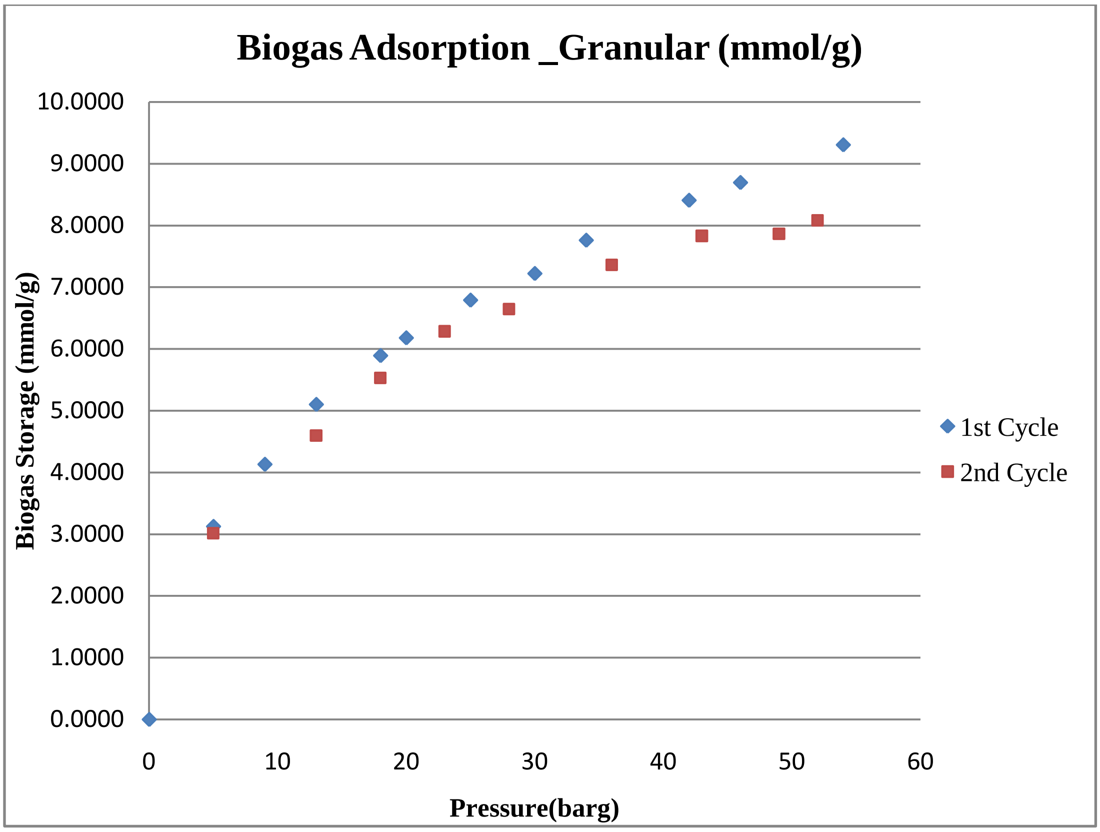


Figure 4.6 : Biogas adsorption on granular AC

4.4.3 Biogas storage as cyclic operations

The experimental isotherms shown in figure 4.5 and 4.6 are referring type I isotherm according to IUPAC classification for both granular and pellet AC types. This proves the microporous adsorption behaviour of both samples. In second cycle both samples are showing less adsorption capabilities compare to first cycle.

When comparing the results of 1st cycle and 2nd cycle, it is shown clear reduction in adsorption capacity of both granular and pellet types. There are several reasons which may cause this effect as describe in literature. The thermodynamic nature of adsorption and desorption processes can be explained as one of possible reasons for the reduction in adsorption capacity of 2nd cycle in both AC types. Water bath system was used to maintain constant temperature condition during the adsorption cycle of the cylinder but during the desorption process any particular action was not taken to maintain the same temperature condition. Since desorption is endothermic process, proper removal of gas was not happened and the rate of the process was very low in atmospheric conditions. Transportation restrictions occurred in a packed bed system can be taken as another reason. During the desorption process at atmospheric conditions, some gas molecules may trapped inside the AC bed due to restrictions in gas molecule pathways. This issue can be minimized by introducing radial flow mechanism for adsorption cylinder instead of axial flow filling process (AZIMI & MIRZAEI, 2012)

The bio-methane was used for this practical in un-purified condition. Thus it may contain water vapour and some sulphur based odorants other than to its characterized carbon dioxide, nitrogen or oxygen content. Hence the presence of impurities can be stated as another reason for visible adsorption capacity reduction in 2nd cyclic process for both AC types (Walton & LeVan, 2006).

Therefore, it is important to maintain proper thermal conditions, optimize adsorption vessel design for proper adsorbing & desorbing mechanism and usage of purified methane for better cyclic operations.

4.4.4 Biogas adsorption model development

Methane adsorption behaviour on activated carbon porous structure is explained by Langmuir and Toth models in literature (Hameed & Foo, 2010; Mota et al., 2008; Zheng et al., 2015). These pure component models have been shown less relative errors with obtained experiment values. When analysing the adsorption behaviour of gas mixture on AC, the frequently used isotherms are extended Langmuir and Sip models (Burress, 2009; García et al., 2013).

Since this study was carried out for biogas, initially Langmuir and Toth models were used to understand the behaviour of gas adsorption on AC samples with pressure by assuming biogas as a pure component. As the second part of the study, multi component Langmuir model was used to obtain a separate isotherm for methane and carbon dioxide gas components. These models behaviour were analysed according to the literature.

4.4.4.1 Langmuir model development

Langmuir equation is developed for monolayer adsorption on homogeneous surface. Equation 1 represents the Langmuir equation where n and P represents adsorbed moles per unit mass and system pressure respectively. n_{max} symbolises monolayer capacity or maximum adsorption per unit mass ("Adsorption on solid surfaces," n.d.) and k_L symbolises affinity parameter related to bonding energy of the surface (Goldberg & Brown Jr., 2005; Vargas et al., 2012)

$$n = \frac{n_{max}\, k_L P}{1 + k_L P} - - - - - - -(1)$$

Langmuir model was developed from MATLAB software for granular and pellets forms. The optimized parameters obtained from the model are presented table 4.5. The adsorption behaviour of the granular and pellet AC samples obtained from the Langmuir model for 1st and 2nd cycles are shown in Figure 4.7 and 4.8 respectively.

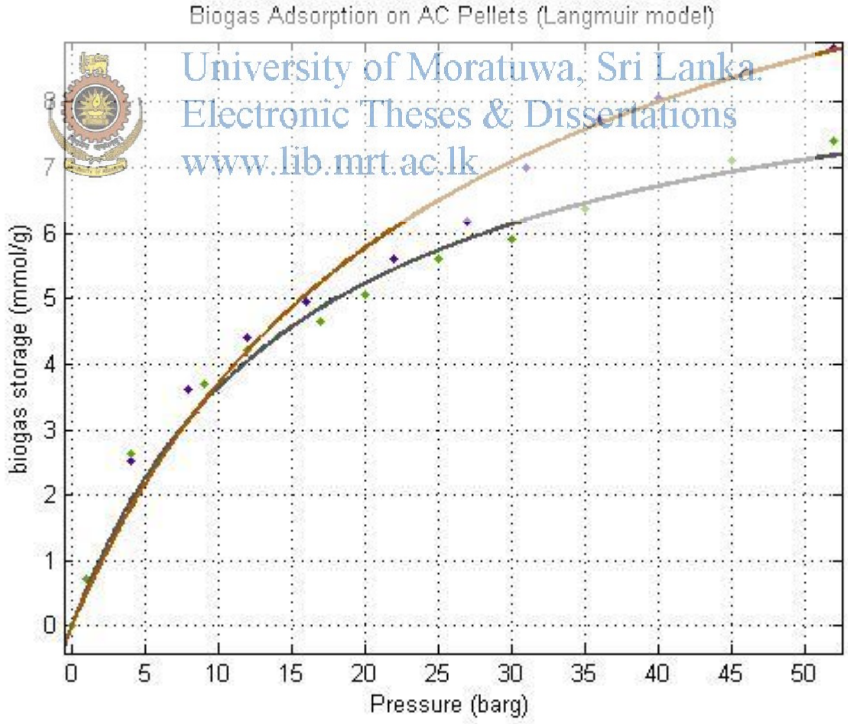


Figure 4.7 : Langmuir model for biogas adsorption on AC pellets at 303K

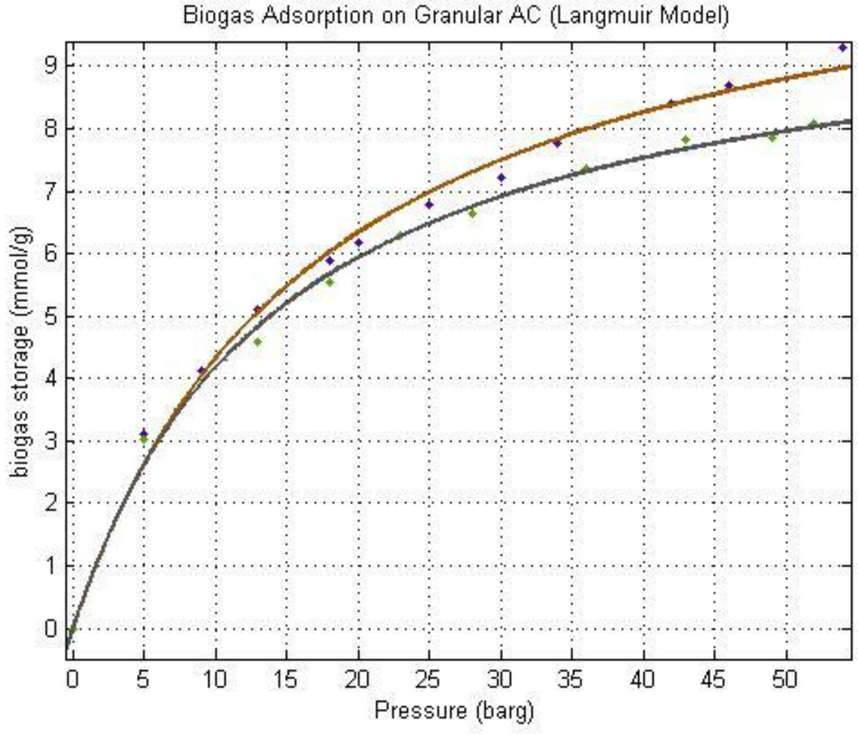


Figure 4.8 : Langmuir model for biogas adsorption on Granular AC at 303K

4.4.4.2 Toth Model development

Toth equation which is modified version of Langmuir model, is useful in describing multilayer adsorption on heterogeneous surface (Vargas et al., 2012). Equation 2 represents the Toth equation where n and P represents adsorbed moles per unit mass and system pressure respectively. α_T and n_{max} are parameters are similar to Langmuir model which symbolises maximum adsorption per unit mass ("Adsorption on solid surfaces," n.d.) and affinity parameter related to bonding energy of the surface respectively (Goldberg & Brown Jr., 2005; Vargas et al., 2012). t is an exponent related to the heterogeneity of the adsorbent surface (Vargas et al., 2012).

$$n = \frac{n_{max}\,\alpha_T P}{(1+(\alpha_T P)^t)^{\left(\frac{1}{t}\right)}} - - - - - (2)$$

The model was developed from MATLAB software for granular and pellets forms. The optimized parameters obtained from the model are presented table 4.5.The adsorption behaviour of the granular and pellet AC samples obtained for 1^{st} and 2^{nd} cycles are shown in Figure 4.9 and 4.10 respectively.

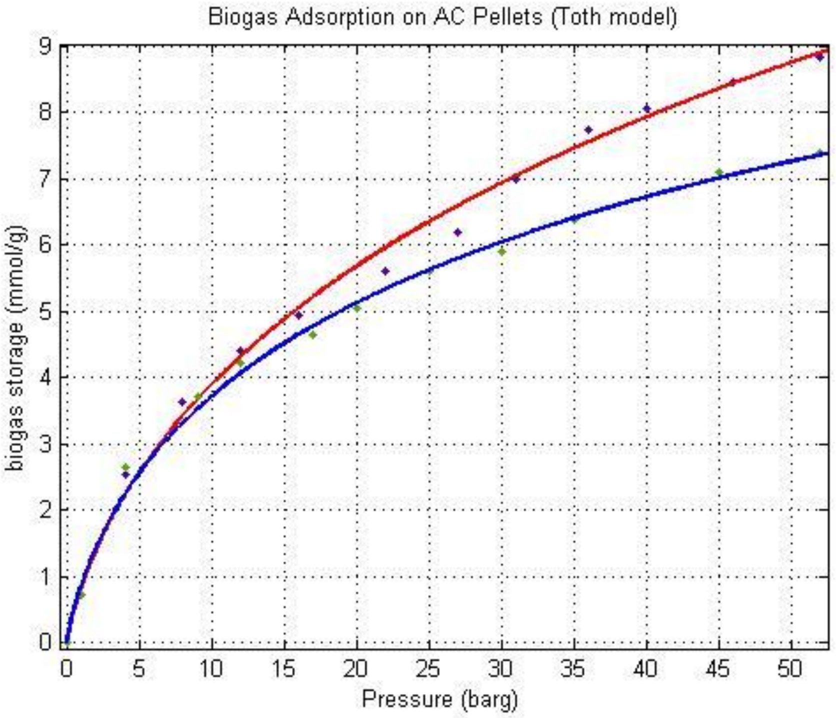


Figure 4.9 : Toth model for biogas adsorption on AC pellets at 303K

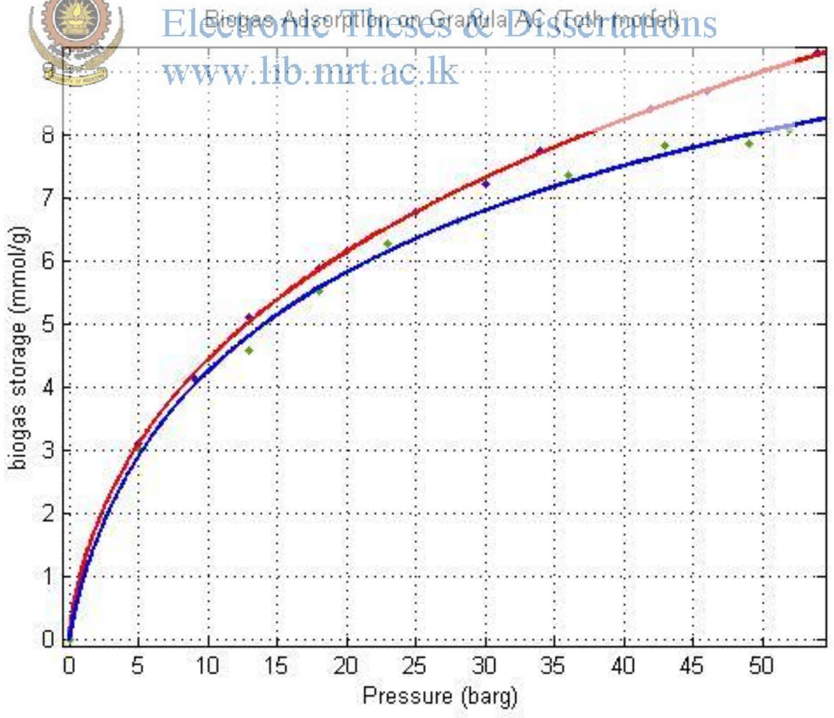


Figure 4.10 : Toth model for biogas adsorption on Granular AC at 303K

4.4.4.3 Toth over Langmuir model comparison

The optimized parameters obtained from Langmuir and Toth models are shown in table 4.5. The correlation coefficient (R^2) and average relative error (Δn) in both models have given sensible fit to experimentally obtained results for both pellet and granular AC forms.

$$\Delta n(\%) = \left(\frac{100}{N}\right)\sum_{i}^{N}\left|(n_i - n_{model})/n_i\right| \text{----------}\ (3)$$

When comparing the two models, Toth model shows better fit for both AC types by its highest correlation coefficient and lower relative error over Langmuir model. This confirms the facts found in literature (Vargas et al., 2012; Waltson et al., 2006; Zheng et al., 2015) as suitability of Toth model in forecasting methane storage potential on AC and underestimation of adsorption capacity of Langmuir model in higher pressure.

Table 4.5: Isotherm parameters obtained from Langmuir and Toth models

Parameter	AC Pellets		Granular AC	
	1st cycle	2nd cycle	1st cycle	2nd cycle
	Langmuir Model			
n_{max}(mmol/g)	13.08	9.37	11.88	10.3
k_L(bar^{-1})	0.0394	0.0632	0.057	0.068
R^2	0.9984	0.9934	0.9931	0.9953
Δn (%)	1.59	5.19	3.02	2.67
	Toth Model			
n_{max} (mmol/g)	43.6	18.26	57.4	15.8
α_L (bar^{-1})	0.0429	0.0969	0.113	0.0996
t	0.3535	0.4396	0.2426	0.5289
R^2	0.9993	0.9977	0.9996	0.9977
Δn (%)	1.05	3.46	0.62	1.72

In developed toth model, n_{max} related to maximum adsorption capacity of the gas system on solid material at the given temperature and α_L related to adsorption energy which indicates, how strongly an adsorbate molecules are attracted onto the adsorbent surface (R. B. Rios et al., 2013; Vargas et al., 2012). The data presented in table 4.5 for toth model illustrates higher adsorption capacity on granular form than pellet form in 1st cycle of adsorption. The affinity parameter of granular sample shows high value over the pellet sample which explains the strong bonding capability of granular sample over pellet sample with biogas components.

Biogas used in experiment mainly consists of 56% of methane and 36% of carbon dioxide as feed compositions. Thus, the adsorption capacity and affinity value obtained from the graph based on this gas mixture. However it has been proven in literature that carbon dioxide has higher adsorption potential on AC over methane. (Esteves et al., 2008; García et al., 2013; Himeno et al., 2005). Comparison study conducted by (R. B. Rios et al., 2013) has revealed that carbon dioxide is approximately 2.3 times higher in adsorption capacity to methane. The published results from the study are presented in table 4.6. Higher adsorption capacity and affinity values are found in carbon dioxide over methane. Thus, it can be concluded as the adsorption capacity and affinity values obtained from biogas adsorption would be reduced if the study was carried out for pure methane for same granular and pellet samples.

Table 4.6: Parameters of Langmuir and Toth models at 293K

Isotherm	**Langmuir**			**Toth**			
	n_{max}	**k_L**	**Δn**	**n_{max}**	**α_L**	**t**	**Δn**
CO_2	17.396	1.014	17.9	19.107	1.134	0.827	13.4
CH_4	7.616	0.809	9.1	8.193	0.769	0.927	9.5

Source (R. B. Rios et al., 2013)

The surface heterogeneity is expressed by t value of the Toth model. It can be stated as the surface is homogeneous when t value is equals to 1 by comparing Langmuir and Toth model assumptions. According to the table 4.5, both granular and pellets forms are showing surface heterogeneity but granular surface is more heterogeneous than to pellet type in 1st cycle results. When analysing the obtained parameters in 2nd cyclic operation in toth model, there is a clear reduction in adsorption capacity of both pellet and granular samples. The reasons behind this reduction were discussed in previous section. Surface heterogeneity has decreased and affinity value has become similar for both granular & pellet samples in 2nd cyclic operation. When analysing the parameter variation from 1st cycle to 2nd cycle, higher adsorption capacity reduction is visible in granular AC over pellet sample, affinity value has increased in pellet while has decreased in granular. And surface has become more homogeneous by cyclic operation. However, these results emphasize that surface heterogeneity favours biogas adsorption (Vargas et al., 2012) as the surface become more heterogeneous, comparatively higher adsorption is visible in both 1st and 2nd cyclic operations despite of AC type.

Biogas storage at 35 bars obtained from Toth model for granular AC is 91.7 V/V value while it is 85.9 V/V for AC pellets. However, biogas is a mixture of mostly methane and carbon dioxide, thus it is essential in understanding methane adsorption potential of supplied AC other than to biogas adsorption capability. Multi component Langmuir model development was carried out to fulfil this purpose.

4.4.4.4 Langmuir model for multi-component adsorption

The model is stated as extended multi-component Langmuir model. The predications of the adsorbed gas mixture components are carried out by using the pure component isotherm parameters as per the previous studies found in literature (García et al., 2013; R. B. Rios et al., 2013).

$$n_i = \frac{n_{max,i} k_{L,i} P_i}{1 + \sum_{j=1}^{n} k_{L,j} \,.\, P_j} ----- (4)$$

Since pure gas isotherms were not developed for the studied AC samples, bulk gas carbon dioxide mole fractions in different equilibrium pressure conditions were measured to develop the binary component Langmuir model. The equation 5 was used for the model development. Assumption was made that the biogas is only consists of bio-methane and carbon dioxide. Since the both carbon dioxide and methane have similar molecular diameters, validity of the extended Langmuir equation is fulfilled (“Sorption,” 2007).

$$n_{total} = \frac{n_{max,CH4} . k_{L,CH4} . y_{CH4} . P}{1 + k_{L,CH4} . y_{CH4} . P + . k_{L,CO2} . y_{CO2} . P} + \frac{n_{max,CO2} . k_{L,CO2} . y_{CO2} . P}{1 + k_{L,CH4} . y_{CH4} . P + . k_{L,CO2} . y_{CO2} . P} ---- (5)$$

The biogas adsorption results obtained in 1st cycle experiment for both granular and pellet AC were used for binary component Langmuir model development. Carbon dioxide mole percentages measured at different pressure equilibrium conditions were shown in table 4.7.

Table 4.7: Bulk gas CO_2 mole percentage variation in adsorption equilibrium with pressure

Granular AC		**AC Pellets**	
Pressure (barg)	**Bulk Gas CO_2%**	**Pressure (barg)**	**Bulk Gas CO_2%**
5	33.5	8	32
15	24.6	17	25.2
25	22.4	25	24.6
30	19.0	30	24
35	26.2	40	26.8
40	25.7	45	27
50	28.1		

By considering the data behaviour in table 4.7, quadratic polynomial equation was selected for the pressure range 0 to 55 bars. The parameters of the equation were determined by MATLAB software, the relevant graphs are shown in figure 4.11 for both samples and the relevant equations are presented as equation 6 and 7 for granular and pellet samples respectively.

$$y_{CO2} = 0.017P^2 - 1.019P + 37.23; 0 \leq P \leq 55\, bar - - - (6)$$

$$y_{CO2} = 0.016P^2 - 0.957P + 38.03; 0 \leq P \leq 55\, bar - - - (7)$$

Surface graphs were plotted from surface function tool in MATLAB software for total adsorbed biogas moles (n_{total}) against carbon dioxide and bio-methane partial pressure values by using binary component Langmuir equation (eq.5). Figure 4.12 and 4.14 are the screen shots of the MATLAB calculations performed using surface function tool for granular and pellet samples. The maximum adsorption capacities

(n_{max}) and affinity parameters (k_L) obtained for bio-methane and carbon dioxide are presented in table 4.8.

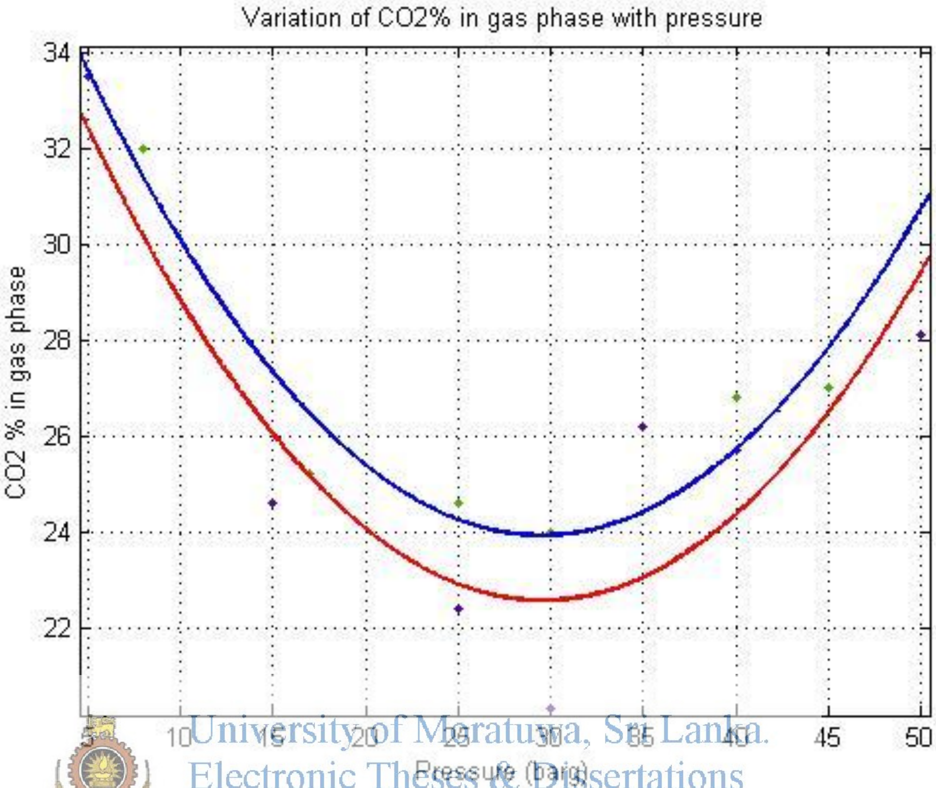
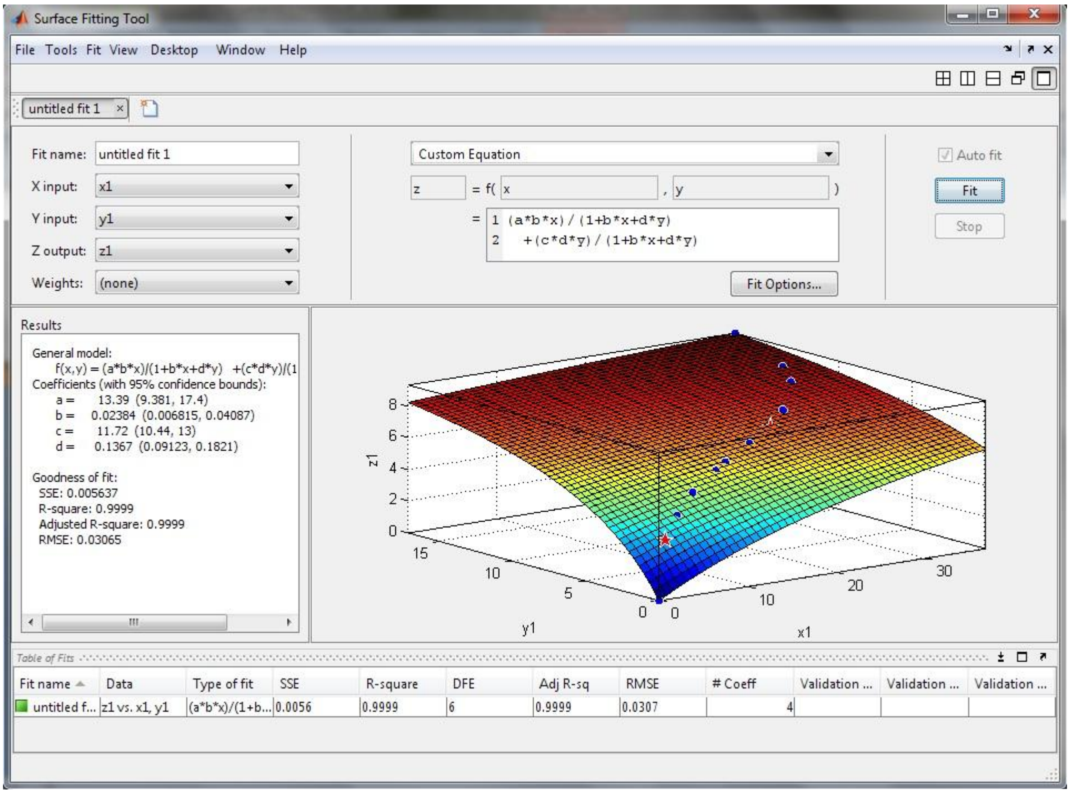


Figure 4.11 : Variation of CO_2 mole % with pressure in bulk gas for Granular (Red) and Pellet (Blue) samples

Table 4.8: Isotherm parameters obtained from binary component Langmuir model

Parameter	**Granular AC**	**AC Pellet**
$n_{max,CH4}$(mmol/g)	13.39	15.17
$k_{L,CH4}$(bar^{-1})	0.02384	0.02581
$n_{max,CO2}$(mmol/g)	11.72	11.17
$k_{L,CO2}$(bar^{-1})	0.1367	0.07819
R^2	0.9999	1



Fit name: untitled fit 1
X input: x1
Y input: y1
Z output: z1
Weights: (none)

Custom Equation

z = f(x , y)

```
= 1 (a*b*x)/(1+b*x+d*y)
  2   +(c*d*y)/(1+b*x+d*y)
```

```
General model:
     f(x,y) = (a*b*x)/(1+b*x+d*y)  +(c*d*y)/(1
Coefficients (with 95% confidence bounds):
       a =      13.39  (9.381, 17.4)
       b =    0.02384  (0.006815, 0.04087)
       c =      11.72  (10.44, 13)
       d =     0.1367  (0.09123, 0.1821)

Goodness of fit:
  SSE: 0.005637
  R-square: 0.9999
  Adjusted R-square: 0.9999
  RMSE: 0.03065
```

Fit name	Data	Type of fit	SSE	R-square	DFE	Adj R-sq	RMSE	# Coeff	Validation ...	Validation ...	Validation ...
🟩 untitled f...	z1 vs. x1, y1	(a*b*x)/(1+b...	0.0056	0.9999	6	0.9999	0.0307	4			

Figure 4.12 : Langmuir model MATLAB surface function calculations for Granular AC

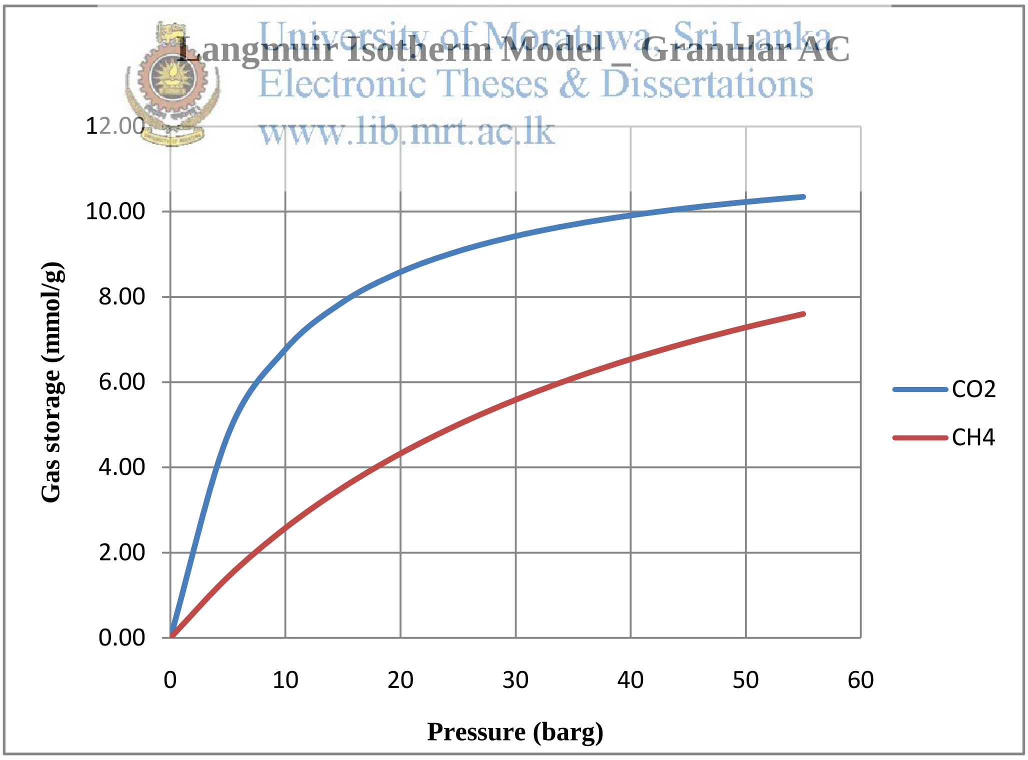
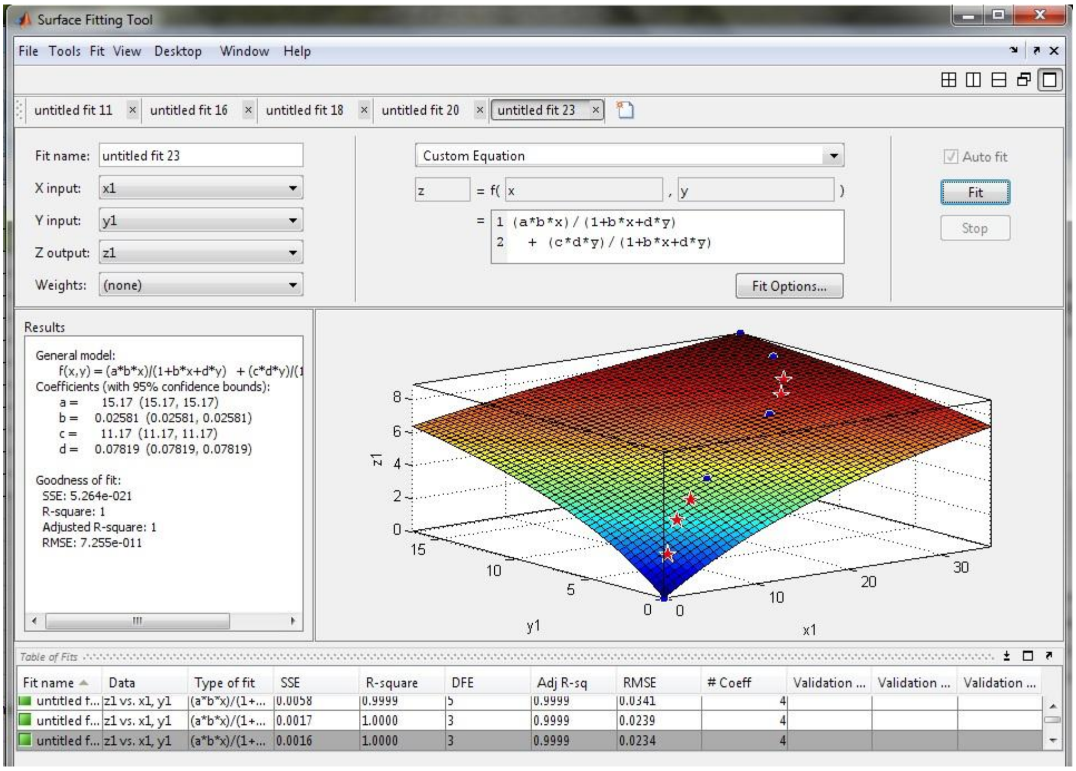


Figure 4.13 : Developed pure component Langmuir Isotherm CH_4 and CO_2 for Granular AC



Fit name: untitled fit 23

X input: x1

Y input: y1

Z output: z1

Weights: (none)

Custom Equation

z = f(x , y)

```
= 1 (a*b*x)/(1+b*x+d*y)
  2    + (c*d*y)/(1+b*x+d*y)
```

Results

```
General model:
     f(x,y) = (a*b*x)/(1+b*x+d*y)   + (c*d*y)/(1
Coefficients (with 95% confidence bounds):
     a =      15.17  (15.17, 15.17)
     b =    0.02581  (0.02581, 0.02581)
     c =      11.17  (11.17, 11.17)
     d =    0.07819  (0.07819, 0.07819)

Goodness of fit:
  SSE: 5.264e-021
  R-square: 1
  Adjusted R-square: 1
  RMSE: 7.255e-011
```

Table of Fits

Fit name	Data	Type of fit	SSE	R-square	DFE	Adj R-sq	RMSE	# Coeff	Validation ...	Validation ...	Validation ...
🟩 untitled f...	z1 vs. x1, y1	(a*b*x)/(1+...	0.0058	0.9999	5	0.9999	0.0341	4			
🟩 untitled f...	z1 vs. x1, y1	(a*b*x)/(1+...	0.0017	1.0000	3	0.9999	0.0239	4			
🟩 untitled f...	z1 vs. x1, y1	(a*b*x)/(1+...	0.0016	1.0000	3	0.9999	0.0234	4			

Figure 4.14 : Langmuir model MATLAB surface function calculations for AC Pellet

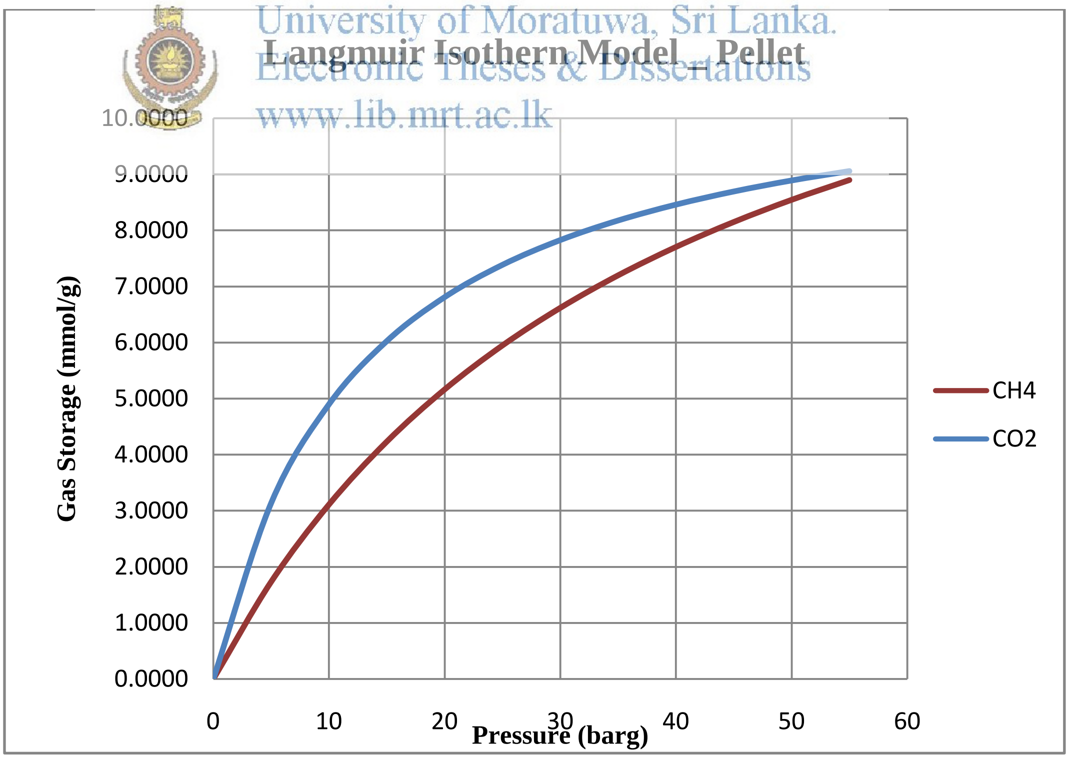


Figure 4.15 : Developed pure component Langmuir Isotherm CH_4 and CO_2 for Granular AC

The optimized parameters obtained from extended Langmuir model for carbon dioxide and methane components were used to develop pure component Langmuir isotherm by using equation 1. The developed graphs are shown in figures 4.13 and 4.15 for granular and pellet AC types respectively.

4.4.5 Adsorption Isotherm comparison - carbon dioxide over bio-methane

The obtained pure component isotherms from the extended Langmuir model in figure 4.13 and 4.15 prove the preferentially in carbon dioxide adsorption over methane for both AC types as stated in literature ("Sorption," 2007). The optimized parameters presented in table 4.8 indicates higher affinity coefficient on carbon dioxide over bio-methane. When comparing the obtained results from binary component Langmuir model with the results from Langmuir model values for biogas, it is observed that affinity coefficient of biogas laid between the values of carbon dioxide and bio-methane as expected.

However, 2-3 times of higher adsorption capacity in carbon dioxide over methane is not visible from this results as revealed by (R. B. Rios et al., 2013). The values obtained from the extended model are quite similar for both gas components. The possibility for this variation can be explained by experimental limitations of the pilot scale set up over lab scale automated adsorption set up in (R. B. Rios et al., 2013) and differences in adsorption potential on tested AC samples in both studies.

The behavior of pure component isotherms developed for pellet sample are found slight different with other similar studies found in literature (R. B. Rios et al., 2013). It shows better adsorption potential for methane while little less adsorption ability towards carbon dioxide compare to granular sample. This behavior can be explained from several aspects. Since pellet contains narrower N_2 adsorption PSD compare to granular, there is a possibility in more methane favorable pores found in pellet over granular sample in that range. And Granular sample should contain more narrow micropores which favors in CO_2 adsorption over pellet to show higher CO_2 adsorption. However, experiment results of granular study gave better fit in model development compare to pellet study. Thus experimental limitations may be another reason for this behavior.

Since heterogeneity of the system is not explained by the Langmuir model, it is unable to discuss the surface heterogeneity of each adsorbent to adsorbate under this analysis. However, according to (Vargas et al., 2012) these models are probably too simple to represent the real case of adsorption on the carbon materials of a study or amount of data fitted is not large enough.

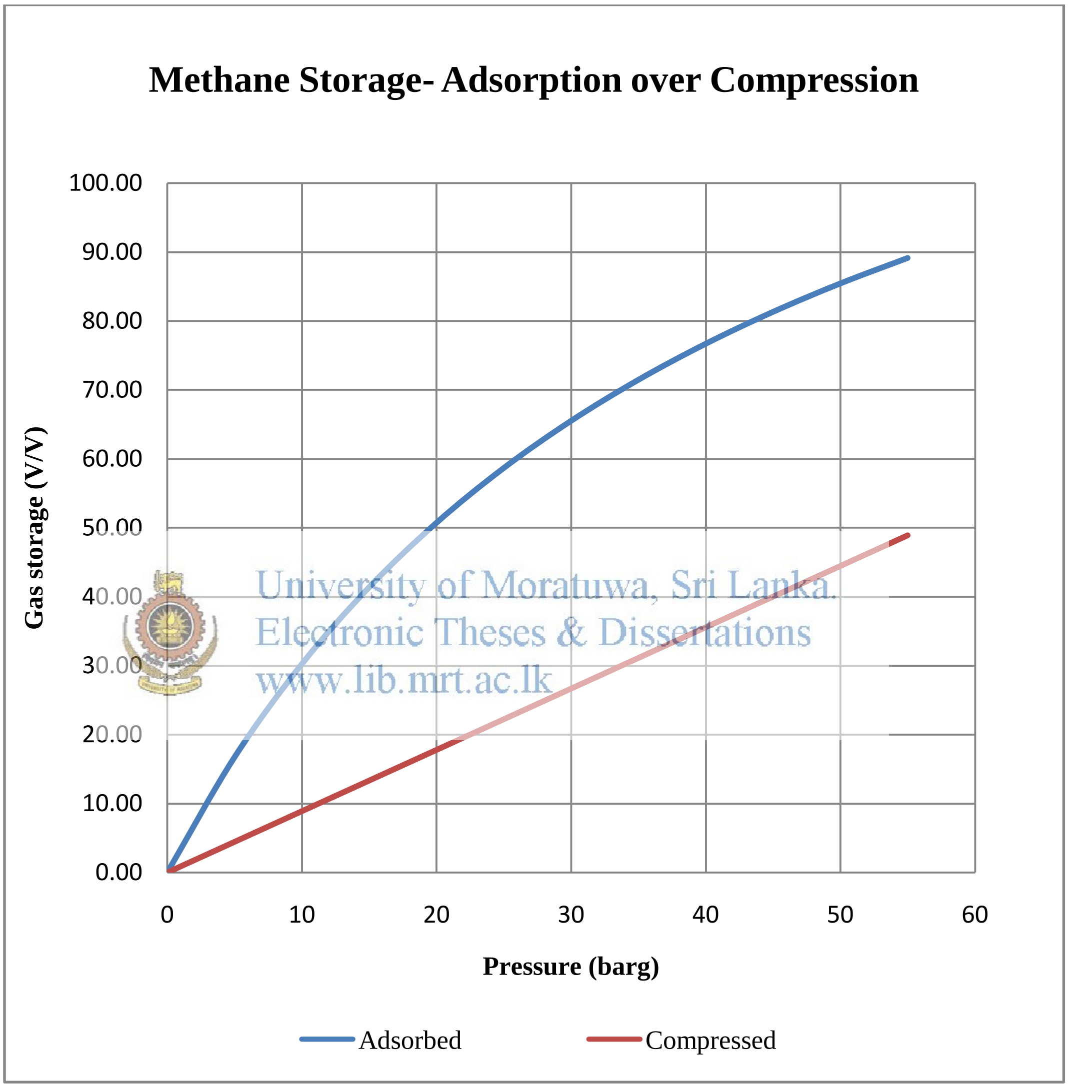


Figure 4.16 : Methane storage on adsorption over compression for granular AC

4.4.6 Bio-methane storage on commercial AC in Sri Lanka

The absolute methane isotherm obtained from extended Langmuir model shows high storage potential comparing with compressed gas storage system (refer figure 4.16). As described in literature analysis, higher methane density is found in methane adsorption system at 3.5 MPa in its excess uptake. Therefore methane storage in adsorption system at 3.5 Mpa is selected for further comparison analysis. As per developed model for bio-methane, the graph shows approximately 2 to 2.5 times of increment over compressed methane storage system. When converting the results into volume to volume storage value, granular sample shows 71.5 V/V while pellet sample gives 82.8 V/V value of methane storage. These V/V values express the competitive performing capabilities of Sri Lankan commercial scale AC on methane adsorption application over similar studies found in literature (refer Appendix C).

Importantly few assumptions have been made during the model development. N_2 and other gasses found in biogas sample were considered as negligible, and the model was developed for a binary mixture. Since extended Langmuir model was used in methane isotherm development, it was considered as adsorption surface is homogenous. Hence there may be little variations in obtained results with actual values.

The study carried out at Dept. of Chemical & Process Engineering, University of Moratuwa in 2010 (M. A. D. I. C. Kularatna, 2010), has demonstrated LPG three wheeler (15.7 liter volume gas tank of 15 bar design pressure) on compressed bio-methane concept and was capable of operating 5.3 km from 320 L (1atm , 30oC) volume of 85% pure methane gas. When applying adsorbed bio-methane concept theoretically into same system, the three-wheeler should possible to operate 12.7 km by filling 85% methane into same gas tank packed with granular AC upto15 bar pressure.

However, the target achievement on adsorbed methane is stated by Department of Energy, United States of America as 150 V/V value for light duty vehicular fuel applications (Marsh & Reinoso, 2006). Thus the current limitations in the study need to be overcome to achieve a competitive outcome for vehicular fuel application.

4.4.7 Experiment limitations and recommendations

It is important to conduct a research study with minor experimental errors; still there are possibilities in equipment unavailability, funding problems, testing facility issues and time constraints which would create limitations in final outcome.

Adsorption analysis of methane on AC is a popular study area in globally. The experiments are carried out in automated adsorption systems which specially developed for the purpose. Since this is quite new research area for the country, Sri Lanka still lacks proper infrastructure facilities for a better results analysis. Below stated the experimental limitations faced during the research.

Material characterization supports proper analysing of experimental results and it also suggests improvements in relevant characteristics for better outcome in future studies. In AC characterization, both N_2 and CO_2 adsorption analysis provide better understanding on material micropore structure. But N_2 adsorption studies were only able to perform under this study.

Un-purified biogas was used as the methane source for adsorption, due to unavailability of proper biogas upgrading facilities during the research time frame. And the obtained results for methane adsorption were based on assumptions. Hence, proper AC characterization and purified bio-methane is recommended in continuation of this work.

Several limitations were identified in developed pilot scale experimental set up. Precision weighing scale is essential for gravimetric result measuring system. The weighing scale found wasn't specific enough to use for Helium measurements thus excess adsorption amount was unable to calculate for the supplied AC samples. This excess adsorption details support in identifying the proper pressure range of higher methane densities. The pressure and vacuum conditions of the unit were measured by pressure and vacuum gauges attached to gas manifold unit. Attaching another pressure and vacuum gauge system to adsorption cylinder would effectively indicate more accurate pressure conditions in adsorption system. The water bath system was used to control temperature in adsorption cycle only. Modifying the system to adjust for both heating and cooling conditions would facilitate better thermal management system.

It has been proved in literature (AZIMI & MIRZAEI, 2012) that adsorption ability of regular packed bed AC cylinder is reduced due to transportation restrictions of gasses. Thus introducing redial flow pattern to the pilot scale adsorption vessel instead of currently conducting axial flow pattern would enhance transport facility of adsorption vessel. By inserting perforated gas tube into the packed bed AC vessel would provide redial flow pattern.

Other than to the limitations that should overcome in continuation of this work, there are some suggestions to enhance the performance of the application. Development of proper pore structural AC from Sri Lankan coconut shells, introduce better thermal management system for adsorption vessel ("| AIChE," 2015) and designing of commercial scale adsorption cylinder to facilitate better thermal management and minimize transportation restrictions in packed bed can be suggested as long term recommendations for a commercial scale application.

CHAPTER 5 CONCLUSIONS & RECOMMEDATIONS

Biogas is globally recognized as the best well-to-wheel fuel and is a technologically viable green energy solution for Sri Lanka to fulfil country's growing energy demand. Development of proper solid waste management practices and creating a proper infrastructure would facilitate biogas as a commercial fuel for Sri Lanka. Being a gas, its low energy density creates storage restrictions in commercial scale. Gas adsorption technique is being introduced to achieve adequate higher energy density of methane under low pressure & temperature conditions. And the country is a leading producer of AC using coconut shell charcoal globally. Thus upgrading bio-methane storage by AC adsorption would facilitate biogas as a commercial fuel in country.

The main objective of this study was development of experiment setup to understand the methane adsorption potential on Sri Lankan commercial grade AC. The initial set of experiments was carried out to analyze the capability of HAYCARB granular and pellet AC types as a methane adsorbent.

The characterization data shows comparative values with coconut shell AC samples in globally published adsorption studies. Biogas with 56% of methane was used for pilot scale adsorption studies. Results analyzed by toth model shows 91.7 V/V adsorption potential on granular AC while 85.9 V/V adsorption capacity for AC pellets at 35 bar pressure, 303K temperature. Granular surface was more heterogeneous than to pellet type which emphasized, surface heterogeneity favours biogas adsorption.

Adsorption capacity in both granular and pellet samples noticeably reduced in cyclic operations. Presence of impurities in biogas such as sulphites etc., gas transportation restrictions in a packed bed, less desorption due to endothermic behaviour were identified as the possible reasons for the purpose.

Multi component Langmuir model development was carried out to analyse the behaviour of gas components in biogas. The obtained pure component isotherms from the extended Langmuir model were preferential in carbon dioxide adsorption over methane for both AC types. However, higher adsorption capacity in carbon dioxide over methane was not obtained from the extended model as expected. The possibility for this variation can be explained by experimental limitations of the pilot scale set up over lab scale automated adsorption set up.

Granular sample showed 71.5 V/V while pellet sample gave 82.8 V/V methane uptakes at 35 bars from which was 2 to 2.5 times increment over compressed methane storage system. Conclusively it can be explained that Compressed bio-methane (85% methane, 320L volume at 1 atm) three wheeler operates 5.3 km can extends its operation up to 12.7 km by using same gas tank packed with granular AC.

Comparing with similar studies found in literature, obtained V/V values express the competitive performing capabilities of Sri Lankan commercial scale AC on methane adsorption application. However, the target achievement on adsorbed methane is stated by Department of Energy, United States of America as 150 V/V value for light duty vehicular fuel applications. Thus the current limitations in the study need to be overcome to achieve a competitive outcome for vehicular fuel application

Thus, in continuation of this work, it is essential to overcome the current limitations of the study by performing a proper AC characterization to analyze its pore structure, using of purified bio-methane instead of biogas and advancement of current set up to improve the accuracy of the results. As future recommendations for vehicular fuel application in long term, includes development of methane favorable pore structure in coconut shell based AC, enhancing thermal management abilities of the adsorption vessel and introducing new concepts to overcome restrictions in gas transportation with in the vessel, etc.

REFERENCES

| AIChE. (2015, August). Retrieved January 30, 2016, from http://www.aiche.org/resources/publications/cep/2015/august

Adsorption on solid surfaces. (n.d.). Department of Chemistry, National Taiwan University.

A Linares-Solano, Alcañiz-Monge, J., de la Casa-Lillo, M. A., Cazorla-Amorós, D., & D Lozano-Castelló. (2002). Advances in the study of methane storage in porous carbonaceous materials. *Fuel*, *81*(14), 1777–1803. http://doi.org/10.1016/S0016-2361 (02)00124-2

Al Seadi, T., Rutz, D., Prassl, H., Köttner, M., Finsterwalder, T., Volk, S., & Janssen, R. (2008). *Biogas handbook*. Esbjerg: University of Southern Denmark Esbjerg.

AZIMI, A., & MIRZAEI, M. (2012). MODELING OF RADIAL AND AXIAL NON-ISOTHERMAL ADSORPTION OF METHANE ON ACTIVATED CARBON IN CYLINDRICAL VESSELS, *74*(4), 113–126.

Bansal, R. ., & Goyal, M. (2005). *Activated Carbon Adsorption* (illustrated). CRC Press.

Bastos-Neto, M., Torres, A. E. B., Azevedo, D. C. S., & Cavalcante Jr, C. L. (2005). Methane Adsorption Storage Using Microporous Carbons Obtained from Coconut Shells. *Adsorption*, *11*(1), 911–915. http://doi.org/10.1007/s10450-005-6045-x

Baucer, F., Hulteberg, C., Persson, T., & Tamm, D. (n.d.). Biogas upgrading – Review of commercial technologies. Retrieved from http://sgc.camero.se/ckfinder/userfiles/files/SGC254.pdf

Biogas. (2016, January 9). In *Wikipedia, the free encyclopedia*. Retrieved from https://en.wikipedia.org/w/index.php?title=Biogas&oldid=699012899

Biogas Technology Utilization in Sri Lanka. (n.d.). Centre for Sustainable Agricultural Mechnization.

Burress, J. W. (2009). *Gas sorption in engineered carbon nanospaces* (Thesis). University of Missouri--Columbia. Retrieved from https://mospace.umsystem.edu/xmlui/handle/10355/9666

Cavalcante, C. L., Araújo, J. C. S., Bastos-Netoa, M., Torres, A. E. B., Jaguaribe, E. F., & Azevedo, D. C. S. (2007). Microporous activated carbon prepared from coconut shells using chemical activation with zinc chloride. *Microporous and Mesoporous Materials*, *100*(1), 361–364. http://doi.org/10.1016/j.micromeso.2006.11.024

Celzard, A., Perrin, A., Mareche, J. F., & Furdin, G. (2004). Improved methane storage capacity by sorption on wet active carbons. *Carbon*, *42*(7), 1249–1256. http://doi.org/10.1016/j.carbon.2004.01.039

ÇUHADAR, Ç. (n.d.). *Production and Characterization of Activated Carbon from hazelnut shell and hazelnut husk* (M.Sc. thesis). MIDDLE EAST TECHNICAL UNIVERSITY, Inonu Bulvari, Turkiye. Retrieved from http://etd.lib.metu.edu.tr/upload/12606430/index.pdf?origin=publication_detail

Danish, M., Hashim, R., Ibrahim, M. N. M., Rafatullah, M., Ahmad, T., & Sulaiman, O. (2011). Characterization of ACACIA MANGIUM wood based Activated Carbons prepared in the presence of basic activating agents. *BioResources*, *6*(3), 3019–3033.

Dilhani, J. A. T., De Alwis, A., & Sugathapala, T. (n.d.). Biogas Production Using Market Garbage. Retrieved from http://www.energy.gov.lk/pdf/special_publications/Biogas%20Production%20Using%20Market%20Garbage.pdf

Do, D. D., & Do, H. D. (2003). Adsorption of supercritical fluids in non-porous and porous carbons: Analysis of adsorbed phase volume and density. *Carbon*, *41*(9). http://doi.org/10.1016/S0008-6223 (03)00152-0

Ercan, C., Khawajah, A., Wang, Y., & Othman, R. (2012). Experimental and theoretical study of methane adsorption on granular activated carbons. *AIChE Journal*, *58*(3), 782–788. http://doi.org/10.1002/aic.12611

Esteves, I. A. A. C., Lopes, M. S. S., Nunes, P. M. C., & Mota, J. P. B. (2008). Adsorption of natural gas and biogas components on activated carbon. *Separation and Purification Technology*, *62*(2), 281–296.

García, S., Pis, J. J., Rubiera, F., & Pevida, C. (2013). Predicting Mixed-Gas Adsorption Equilibria on Activated Carbon for Precombustion CO2 Capture. *Langmuir*, *29*(20), 6042–6052. http://doi.org/10.1021/la4004998

Ghimire, P. C. (2011). *Feasibility Study of National Domestic Biogas Programme in Sri Lanka*.

Ginzburg, Y. (2006). ANG storage as a technological solution for the "chicken-and-egg" problem of NGV refueling infrastructure development. In *23rd World Gas Conference, Amsterdam*.

Goldberg, S., & Brown Jr., G. E. (2005). Equatioms and Models Describing Adsorption Processes in Soils. In *Chemical Processes in Soil*. United States Department of Agriculture.

Gottipati, R., Adiraju, B., & Mishra, S. (2012). Application of Granular Activated Carbon Developed from Agricultural Waste as a Natural Gas Storage Vehicle. *International Journal of Engineering and Technology*, *4*(4), 468–420. http://doi.org/10.7763/IJET.2012.V4.412

Hameed, B. H., & Foo, K. Y. (2010). Insights into Modelling of Adsorption Isotherm Systems. *Chemical Engineering Journal*, *156*(1), 2–10. http://doi.org/10.1016/j.cej.2009.09.013

Himeno, S., Komatsu, T., & Fujita, S. (2005). High-Pressure Adsorption Equilibria of Methane and Carbon Dioxide on Several Activated Carbons. *Journal of Chemical & Engineering Data*, *50*(2), 369–376. http://doi.org/10.1021/je049786x

Integrated Development Association (IDEA). (2004). *Energy for Sustainable Development Sri Lanka - A Brief Report with Focus on Renewable Energy & Poverty Reduction* (South Asia NGO Capacity Building for Poverty Reducing Sustainable Energy Solutions Project).

J. Alcañiz-Monge, M. A. De La Casa-Lillo, Cazorla-Amorós, D., & Linares-Solano, A. (1997). Methane Storage in Activated Carbon Fibres. *Carbon*, *35*(2), 291–297. http://doi.org/10.1016/S0008-6223 (96)00156-X

Jose P.B. Mota. (n.d.). Impact of gas composition on natural gas storage by adsorption - Mota - 1999 - AIChE Journal - Wiley Online Library. Retrieved January 23, 2016, from http://onlinelibrary.wiley.com/doi/10.1002/aic.690450509/abstract

Kaneko, K. (1994). Determination of pore size and pore size distribution: 1. Adsorbents and catalysts. *Journal of Membrane Science*, *96*(1–2), 59–89. http://doi.org/10.1016/0376-7388 (94)00126-X

Keller, J. U., & Staudt, R. (2005). *Gas adsorption equilibria experimental methods and adsorptive isotherms*. New York: Springer. Retrieved from http://public.eblib.com/choice/publicfullrecord.aspx?p=226050

Krich, K., Augenstein, A., Batmale, J., Benemann, J., Rutledge, B., & Salour, D. (2005). Upgrading dairy biogas to biomethane and other fuels. *Biomethane from Dairy Waste-A Sourcebook for the Production and Use of Renewable Natural Gas in California. California: Clear Concepts*, 47–69.

M. A. D. I. C. Kularatna. (2010, December). *Development of a Pilot Scale Biogas Plant to utilize Bio-methane as aTransportation fuel* (Thesis). University of Moratuwa.

Mahboub, M. J. D., Ahmadpour, A., Rashidi, H., & Jahanshahi, N. (2012). Investigating parameters on the preparation of mesoporous activated carbons by the combination of chemical and physical activations using the Taguchi method. *Adsorption*, *18*(3-4), 297–305. http://doi.org/10.1007/s10450-012-9401-7

Marsh, H., & Reinoso, F. R. (2006). *Activated Carbon*. Elsevier Science & Technology Books.

Mota, J. P. B. (1999). Impact of gas composition on natural gas storage by adsorption. *AIChE Journal*, *45*(5), 986–996. http://doi.org/10.1002/aic.690450509

Mota, J. P. B., Marta S. S. Lopes, Nunes, P. M. C., & Esteves, I. A. A. C. (2008). Adsorption of natural gas and biogas components on activated carbon. *Separation and Purification Technology*, *62*(2), 281–296. http://doi.org/10.1016/j.seppur.2008.01.027

Perrin, A., Celzard, A., Marêché, J. F., & Furdin, G. (2003). Methane Storage within Dry and Wet Active Carbons: A Comparative Study. *Energy & Fuels*, *17*(5), 1283–1291. http://doi.org/10.1021/ef030067i

Rios, R. B., Silva, F. W. M., Torres, A. E. B., Azevedo, D. C. S., & Jr, C. L. C. (2009). Adsorption of methane in activated carbons obtained from coconut shells using H3PO4 chemical activation. *Adsorption*, *15*(3), 271–277. http://doi.org/10.1007/s10450-009-9174-9

Rios, R. B., Stragliotto, F. M., Peixoto, H. R., Torres, A. E. B., Bastos-Neto, M., Azevedo, D. C. S., & Cavalcante Jr, C. L. (2013). Studies on the adsorption behavior of CO2-CH4 mixtures using activated carbon. *Brazilian Journal of Chemical Engineering*, *30*(4), 939–951. http://doi.org/10.1590/S0104-66322013000400024

Sapag, K., de Oliveira, J. C. A., López, R., Moreno-Piraján, J. C., Giraldo, L., Zgrablich, G., & Blanco, A. A. G. (2010). A study of the pore size distribution for activated carbon monoliths and their relationship with the storage of methane and hydrogen. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *357*(1–3), 74–83. http://doi.org/10.1016/j.colsurfa.2010.01.006

SciVal - Welcome to SciVal. (n.d.). Retrieved January 31, 2016, from https://www.scival.com/customer/authenticate/loginfull

Siangsai, A., Kumpoomee, N., Rangsunvigit, P., Kitiyanan, B., & Kulprathipanja, S. (2014). Comparative Study of Methane Adsorption on Activated Carbon and Metal Organic Frameworks. In *CHEMICAL ENGINEERING TRANSACTIONS* (Vol. 39, pp. 523–528). The Italian Association of Chemical Engineering. http://doi.org/10.3303/CET1439088

Solar, C., Blanco, A. G., Vallone, A., & Sapag, K. (2010). Adsorption of Methane in Porous Materials as the Basis for the Storage of Natural Gas. http://doi.org/10.13140/2.1.4587.6160

Sorption. (2007). In *Coalbed Methane: Principles and Practices* (pp. 143–190). Halliburton.

:: Sri Lanka Sustainable Energy Authority : (n.d.). Retrieved January 23, 2016, from http://www.energy.gov.lk/sub_pgs/energy_renewable_intro_policy.html

Stadie, N. P. (2013). *Synthesis and thermodynamic studies of physisorptive energy storage materials* (PhD). California Institute of Technology. Retrieved from http://resolver.caltech.edu/CaltechTHESIS:09092012-010239493

Sun, J., Jarvi, T. D., Conopask, L. F., Satyapal, S., Rood, M. J., & Rostam-Abadi, M. (2001). Direct Measurements of Volumetric Gas Storage Capacity and Some New Insight into Adsorbed Natural Gas Storage. *Energy & Fuels*, *15*(5), 1241–1246. http://doi.org/10.1021/ef010067n

Upgrading Biogas to Biomethane. (n.d.). Sustainable Energy Authority of Ireland.

Vargas, D. P., Giraldo, L., & Moreno-Piraján, J. C. (2012). CO2 Adsorption on Activated Carbon Honeycomb-Monoliths: A Comparison of Langmuir and Tóth Models. *International Journal of Molecular Sciences*, *13*(7), 8388–8397. http://doi.org/10.3390/ijms13078388

Walton, K. S., & LeVan, M. D. (2006). Natural gas storage cycles: Influence of non isothermal effects and heavy alkanes. *Adsorption*, *12*(3), 227–235. http://doi.org/10.1007/s10450-006-0142-3

Waltson, K. S., Cavalcante Jr, C. L., & LeVan, M. D. (2006). Adsorption of light alkanes on coconut nanoporous activated carbon. *Brazilian Journal of Chemical Engineering - BRAZ J CHEM ENG*, *23*(4). http://doi.org/10.1590/S0104-66322006000400013

Y. Pathiraja, S. Kalinga, & Y. N. Gunawardena. (2013). *REVIEW OF DEFICIENCIES IN AVAILABLE BIOMASS UTILIZATION TECHNOLOGIES IN SRI LANKA*. University of Moratuwa.

Zhang, T., Walawender, W. P., & Fan, L. T. (2010). Grain-based activated carbons for natural gas storage. *Bioresource Technology*, *101*(6), 1983–1991. http://doi.org/10.1016/j.biortech.2009.10.046

Zheng, Q. R., Zhu, Z. W., & Wang, X. H. (2015). Experimental studies of storage by adsorption of domestically used natural gas on activated carbon. *Applied*

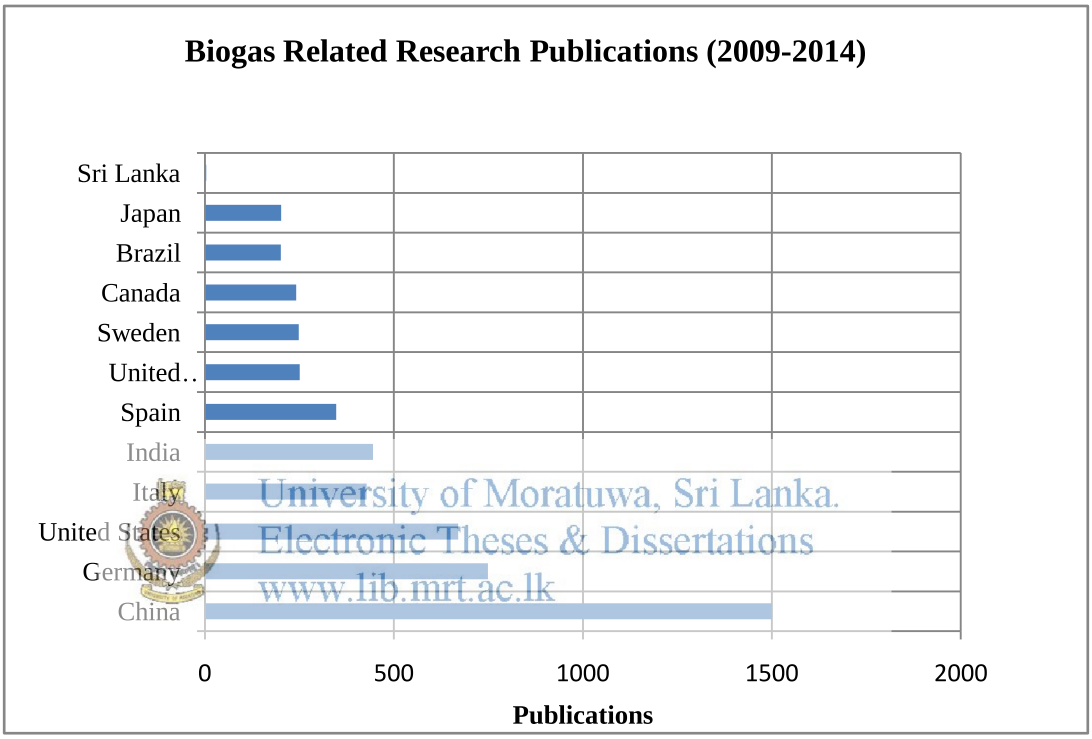
Thermal Engineering, *77*.
http://doi.org/10.1016/j.applthermaleng.2014.12.022

APPENDICES

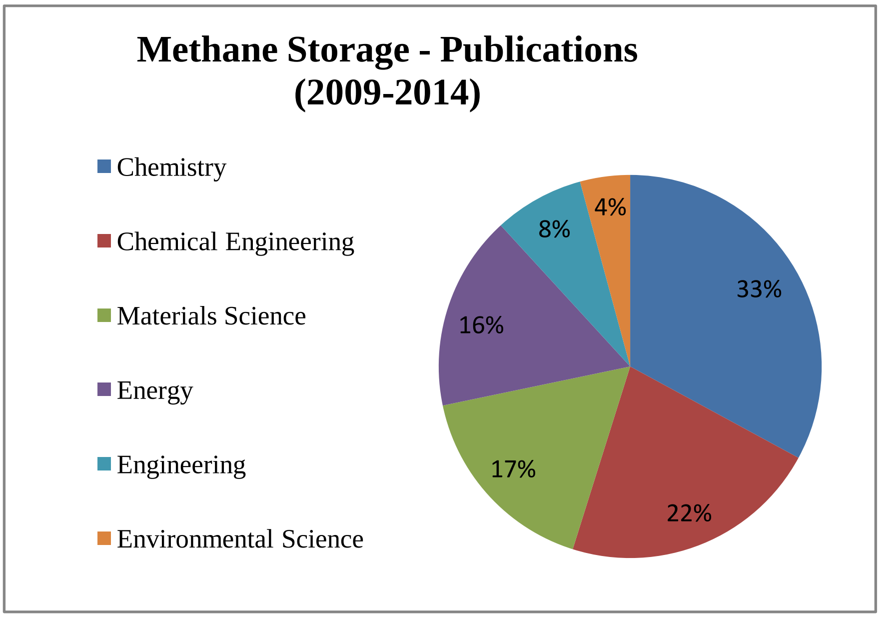
Appendix A

Scival Analysis on Bio-methane Storage on Activated Carbon

Country wise interests on biogas related research from 2009 to 2014 were analysed by using “biogas” as the keyword. Total 7804 publications were found, Sri Lanka only represents 3 among those. Country wise details are presented below.



Research interest on upgrading methane storage was analysed by using “methane storage” as the key word. Total 121 publications were found during the time period from 2009 to 2014 and categorized according to journal categories in a pie chart below.



Research interest on upgrading methane storage by activated carbon was analysed by using “methane storage” and “adsorption” and “activated carbon” as key words. Total 74 publications were found during the time period from 2009 to 2014 and categorized according to journal categories in a pie chart below

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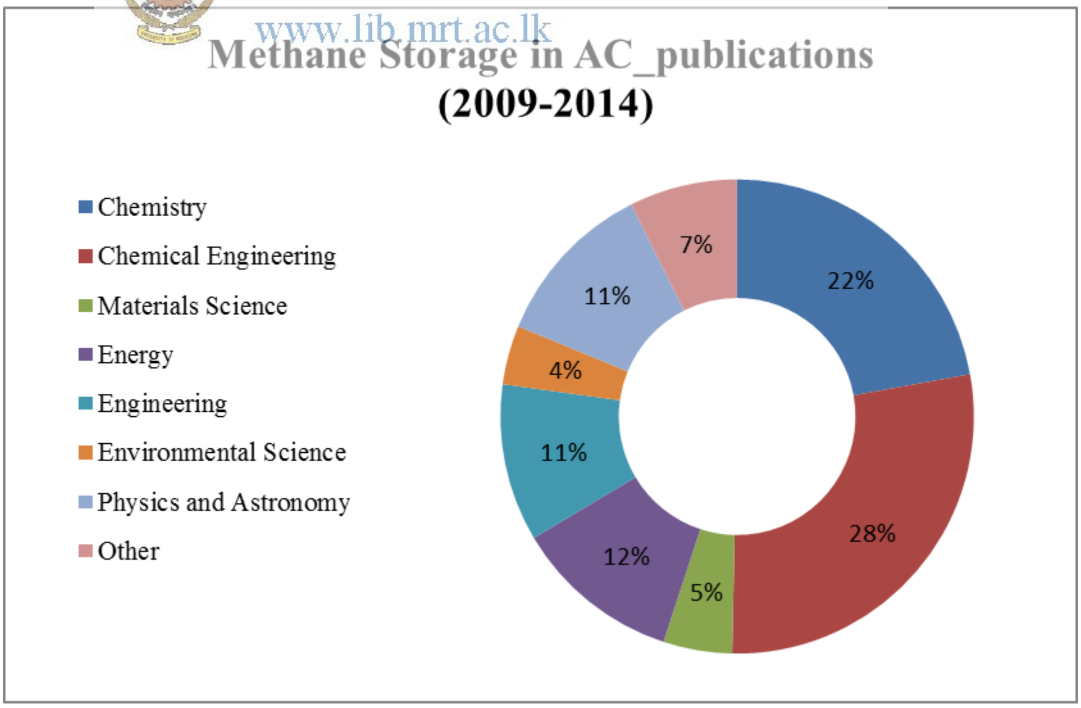

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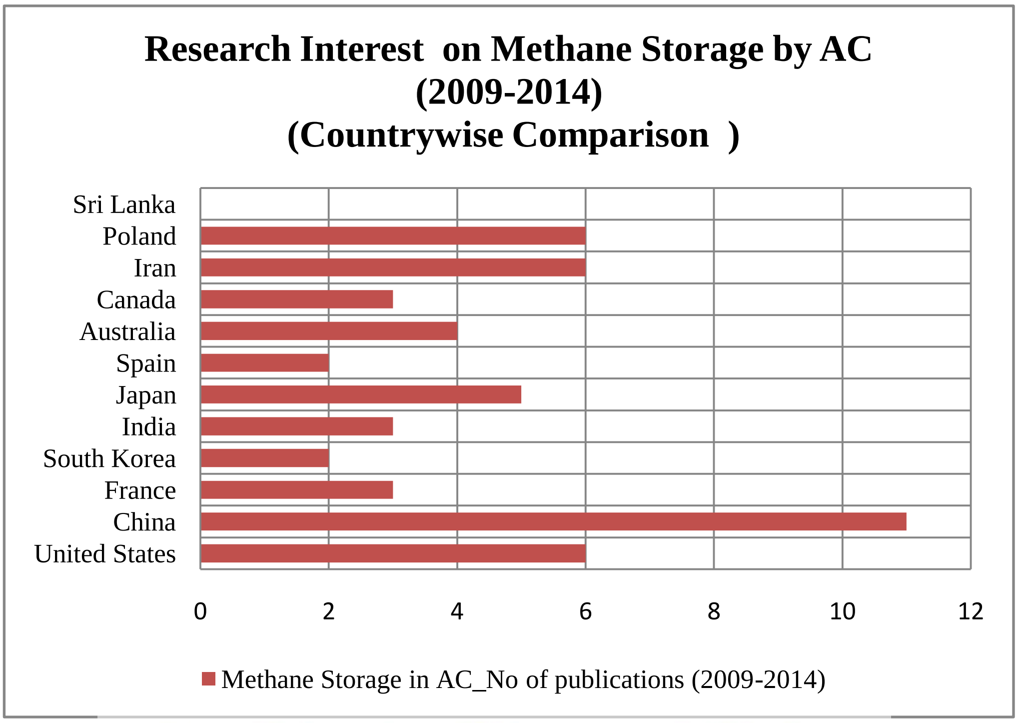
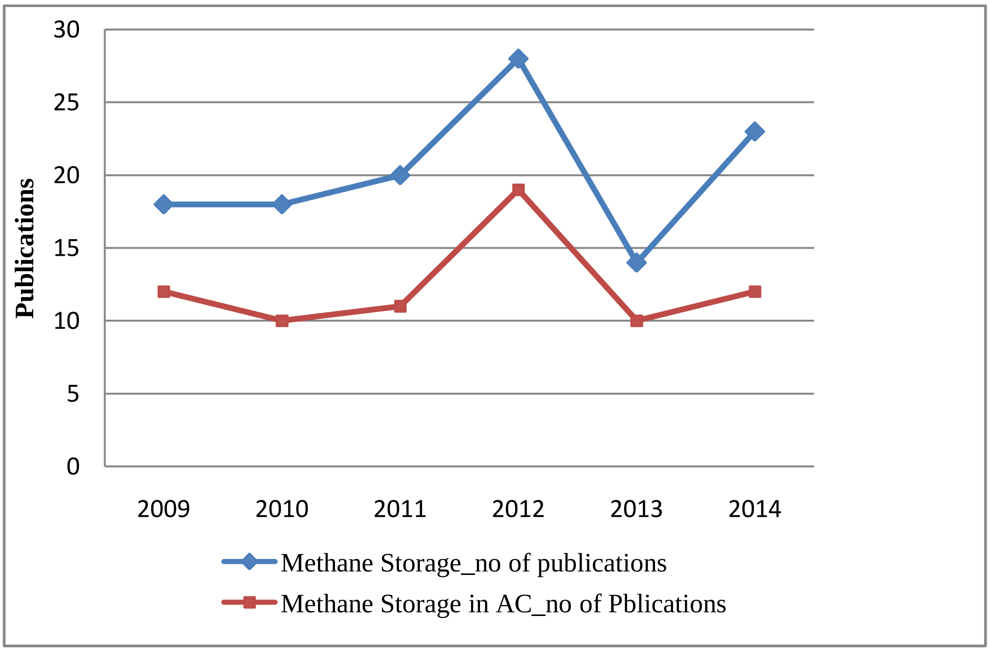
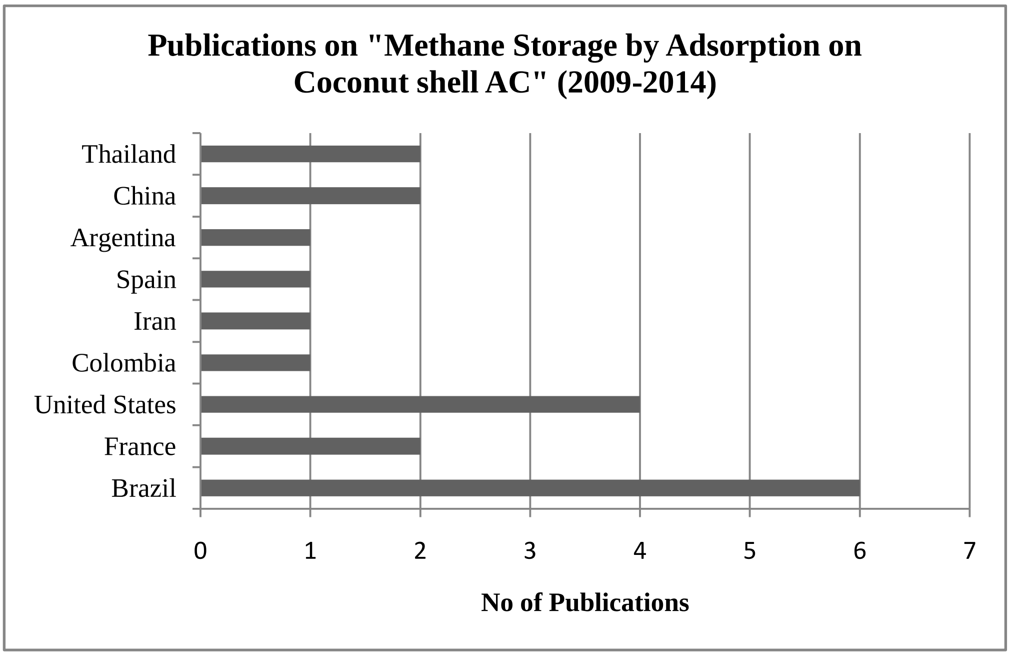
The below chart shows the country wise research interest on “methane storage by activated carbon” during 2009-2014



The yearly comparison of “methane storage” research area with “methane storage by activated carbon” is presented below. Most of the other methane storage publications are based on Metal Organic Frameworks (MOF) as the adsorbent.





The above chart shows the publication found from 2003 to 2014 period on methane adsorption on coconut shell activated carbon. All 15 publications were found are categorized according to the published country.

Appendix B

Activated Carbon Characterization Details found in Previous Publications

Raw Material	Activation Method	BET Surface Area (m^2/g)	Micropore Volume (cc/g)	Total Pore Volume (cc/g)	Apparent Density (g/cc)	Reference
Aeglemarmelos fruit shell	H_3PO_4	NG	0.56	0.58	NG	(Gottipati et al., 2012)
Coconut Shell	Steam, Burn off 58	1000	0.405	0.454	0.4	(Perrin et al., 2003)
	Steam, Burn off 86	1587	0.57	0.658	0.34	
	Steam, Burn off 120	2031	0.814	0.955	0.29	
Pinewood	H_3PO_4	1967	0.65	1.37	0.16	(Perrin et al., 2003)[17]
Coconut Shell	$ZnCl_2$	NG	0.268	NG	0.8	(Sapag et al., 2010)
	$ZnCl_2$ + CO_2, Burn off 20	NG	0.276	NG	0.65	
	$ZnCl_2$ + CO_2, Burn off 28	NG	0.34	NG	0.6	
NG	Commercial AC	899	0.48	0.5	0.48	(Siangsai et al., 2014)
	Commercial AC + KOH	935	0.5	0.52	0.48	
	Commercial AC + H_2SO_4	975	0.52	0.55	0.48	

Raw Material	Activation Method	BET Surface Area (m^2/g)	Micropore Volume (cc/g)	Total Pore Volume (cc/g)	Apparent Density (g/cc)	Reference
Coconut Shell	H_3PO_4 29%	520	0.3	0.34	0.32	(Rafael B. Rios et al., 2009)
	H_3PO_4 29%, H_2SO_4 washed	727	0.38	0.42	NG	
	H_3PO_4 36%	783	0.43	0.49	NG	
	H_3PO_4 36%, H_2SO_4 washed	844	0.5	0.55	0.45	
	H_3PO_4 44%	536	0.32	0.37	NG	
	H_3PO_4 44%, H_2SO_4 washed	767	0.44	0.51	0.33	
	H_3PO_4 53%	779	0.44	0.5	0.35	
	H_3PO_4 53%, H_2SO_4 washed	693	0.4	0.51	0.28	
	H_3PO_4 53%, H_2SO_4 washed+ carbonization	1441	0.73	0.86	0.26	
NG	Commercial	828	0.44	0.55	0.32	
	Commercial	1906	0.98	0.124	0.25	
Olive lexes	$ZnCl_2$	1291	0.54	0.91	0.38	(Solar et al., 2010)
	Steam	913	0.37	0.45	0.49	
	Steam	1015	0.42	0.47	0.5	

Raw Material	**Activation Method**	**BET Surface Area (m^2/g)**	**Micropore Volume (cc/g)**	**Total Pore Volume (cc/g)**	**Apparent Density (g/cc)**	**Reference**
Olive wood	$ZnCl_2$	2205	0.88	0.136	0.3	(Solar et al., 2010)
	Steam	1163	0.48	0.68	0.18	
	Steam	1117	0.46	0.75	0.21	
Graph Lex	$ZnCl_2$	1470	0.62	0.93	0.2	
Coconut Shell	$ZnCl_2 + CO_2$	2114	1.142	1.304	NG	(Bastos-Neto et al., 2005)
NG	Commercial	1967	0.945	0.957	NG	
Coconut Shell	$ZnCl_2$	1266	0.676	0.731	NG	(Cavalcante et al., 2007)
	$ZnCl_2$	1091	0.549	0.681	NG	
	$ZnCl_2 + CO_2$	1699	0.877	1.003	NG	
	$ZnCl_2 + CO_2$	2114	1.142	1.307	NG	
NG	Commercial AC (8 X 16)	1235	0.6	0.629	0.47	(Ercan et al., 2012)
	Commercial AC (30 X 70)	1589	0.706	0.747	0.39	
	Commercial AC (2 X 60)	1426	0.56	0.599	0.49	
	Commercial AC (12 X 40)	999	0.456	0.5	0.54	

Appendix C

Methane Adsorption Capacity on Activated Carbon found in Previous Publication

Raw Material	Activation Method	AC type	Methane Adsorption (V/V)	Pressure (MPa)	Temperature (K)	Reference
Coconut Shell	Steam, Burn off 58	PAC	107	8	275	(Perrin et al., 2003)
	Steam, Burn off 86		158	8	275	
	Steam, Burn off 120		121	8	275	
Pinewood	H_3PO_4	PAC	164	8	275	
Coconut Shell	$ZnCl_2$	Disc	30	3.5	298	(Solar et al., 2010)
	$ZnCl_2$ + CO_2, Burn off 20		42	3.5	298	
	$ZnCl_2$ + CO_2, Burn off 28		51	3.5	298	
Coconut Shell	$ZnCl_2$ + CO_2	NG	241	8	275	(Mahboub et al., 2012)
NG	Commercial AC	NG	44.1	3.5	303	(Siangsai et al., 2014)
	Commercial AC + KOH		52.1	3.5	303	
	Commercial AC + H_2SO_4		53	3.5	303	

Raw Material	Activation Method	AC type	Methane Adsorption (V/V)	Pressure (MPa)	Temperature (K)	Reference
Coconut Shell	H_3PO_4 29%	GAC	62	3.5	303	(Rafael B. Rios et al., 2009)
	H_3PO_4 36%, H_2SO_4 washed		95	3.5	303	
	H_3PO_4 44%, H_2SO_4 washed		67	3.5	303	
	H_3PO_4 53%		73	3.5	303	
	H_3PO_4 53%, H_2SO_4 washed		59	3.5	303	
	H_3PO_4 53%, H_2SO_4 washed+ carbonized		82	3.5	303	
NG	Commercial		59	3.5	303	
NG	Commercial		83	3.5	303	
Olive lexes	$ZnCl_2$	PAC	52	3.5	298	(Solar et al., 2010)
	Steam		28	3.5	298	
	Steam		57	3.5	298	
Olive wood	$ZnCl_2$		60	3.5	298	
	Steam		59	3.5	298	
	Steam		24	3.5	298	
Graph Lex	$ZnCl_2$		23	3.5	298	
Coconut Shell	$ZnCl_2$ + CO_2	PAC	80	4	298	(Cavalcante et al., 2007)

Appendix D

HAYCARB Characterization Report of Granular Activated Carbon

Appendix E

HAYCARB Characterization Report of Activated Carbon Pellets

Appendix F

Test Report of Biogas Chromatography Analysis

Appendix G

Calibration Certificate of Weighing Scale