

# Bio-methane Adsorption by Activated Carbon

## Understanding the Potential via Characterization of Sri Lankan Activated Carbon

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**Abstract**—There is 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 of higher storage capacity. Compressed bio-methane systems have been currently commercialized in Europe 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 & activated carbon (AC) has shown promise as a methane adsorbent. This study is based on identifying the potential absorptivity of bio-methane into commercially available AC in Sri Lanka. The paper presents the pathway envisage in this task. Two types of commercial AC samples as granular & pelletize forms have been used from supplier HAYCARB for the analysis. In this paper, characterization data from the principals is used to investigate the methane uptake potential into commercial AC. Further, the study has been continued in evaluating several developed correlations in literature on linear behaviour of micropore volume of AC to methane uptake & concluded that the linear parameters of micropore volume to methane uptake would vary according to AC properties. Thus a correlation for local AC is important to be developed. Hence, an experimental setup is developed to carry out detailed studies on bio-methane adsorption on commercial AC available in Sri Lanka.

**Keywords**—Biogas; Bio-methane; Activated Carbon; Adsorption; Characterization

### I. INTRODUCTION

Biogas is a waste to energy concept which has shown considerable advantage over conventional fuel from both environmental & economical point of view. Europe Union (EU) has stated that this as a best well-to-wheel fuel. When biogas is stripped off its carbon dioxide content, bio-methane is obtained which is equivalent to natural gas. Methane has higher H/C ratio and consequently a higher octane number [1]. However the greatest disadvantage of methane is its higher storage capacity requirement under normal atmospheric conditions. Thus, its usage as a fuel has been limited for most of applications when compared with other conventional transportation fuels.

Compressed biomethane systems have been commercialized as a solution to increase its low energy density but high pressures of methane (up to 25MPa) are needed as a vehicular fuel application which requires costly multi stage compression [1]. The cost of storage cylinders and high pressure facilities limits the practical use of biomethane as a compressed gas.

Alternatively, Adsorbed methane has shown a good potential towards methane storage under low pressure conditions (3.5-4MPa) [1]. Table1 illustrates that the density of Adsorbed Natural Gas (ANG) at 3.5MPa, 298K is 200 times of the density of methane at Standard Temperature & Pressure (STP) conditions and comparatively similar to the compressed natural gas (CNG) at 20MPa ,298K [1].

Selection of a proper adsorbent is the most significant step in methane storage via adsorption. The most crucial parameters of the adsorbent are high adsorption capacity, high packing density, high adsorption/desorption rates 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 [2]. Activated Carbon (AC) has been shown positive results towards above points with highest methane energy densities, thus higher storage capacities, which make AC promise for this application [1].

TABLE I. COMPARISON ON DIFFERENT METHANE STORAGE METHODS [1]

	Temperature	Pressure	Density	Relative Density
	<i>K</i>	<i>MPa</i>	<i>g/cc</i>	
LNG <sup>a</sup>	113	0.1	0.4	600
CNG <sup>b</sup>	298	20	0.15	230
CNG	298	3.5	0.023	36
ANG <sup>c</sup>	298	3.5	0.13	200
Gas	298	0.1	0.00065	1

<sup>a</sup>Liquefied Natural Gas (LNG), <sup>b</sup>Compressed Natural Gas (CNG), <sup>c</sup>Adsorbed Natural Gas (ANG)

Characteristics of the porous structure of activated carbon are most important factor in the adsorption process. Nature of the parent material, preparation process, activation conditions of the adsorbent are directly affected factors to the porous structure of the adsorbent [1],[3]. According to the literature, it has been identified that the adsorbent needs to be higher in packing density, higher in micropore volume with suitable micropore size distribution to achieve proper methane uptake [1]

Microporosity is the only range of porosity which is favourable for methane storage thus; AC should be essentially microporous with less mesoporosity & absence macroporosity[3]. Microporous structure of the sample leads to high packing density hence high volumetric capacities [2]. Microporosity analysis of AC sample will provide potential methane adsorption ability of the adsorbent. Hence characterization of porous texture of the adsorbent is important. Basically the characterization of the adsorbent is carried out by physical adsorption of gases as  $N_2$  at 77K &  $CO_2$  at 273K which supplies Micropore (size smaller than 2nm) & narrow micropore (size smaller than 0.7nm) details respectively.

Several theories have been developed to evaluate the observations of gas adsorption data. Dubinin–Radushkevich (DR) equation is used to calculate micropore details of porous materials [1] and Barret-Joyner-Halenda (BJH) Kelvin equation is used to calculate mesopore details of the porous material [4]. The DR equation for  $N_2$  adsorption calculates the volume of micropores (size smaller than 2nm) while DR value of  $CO_2$  calculates the volume of narrow micropores (size smaller than 0.7nm) [2]. The supermicropore volume (size in between 0.7 and 2nm) of the sample can be calculated by the difference between micropore volume to narrow micropore volume [1][2].

As per the published data on this research area, the optimum slit pore width for methane adsorption has been identified as 1.14nm from Monte Carlo Simulations [5] while the optimum pore size for methane desorption at ambient pressure is identified as 0.8nm [1]. Further it has been postulated that methane molecule can penetrate into adsorbent pores with diameter ranging from 1.0 to 1.5nm by considering “effective micropore” concept [6].

Thus, it is concluded that higher methane storage can be observed when increasing supermicroporosity of the adsorbent as the optimum pore sizes for methane adsorption & desorption are laid within the supermicropore range [2]. Similarly it is important to analyze micropore size distribution data of the adsorbent during the characterization process by considering suggested optimum pore sizes to identify methane adsorption potential of the adsorbent. It has been observed that the activated carbon samples which are having similar micropore volume may uptake different amount of methane under same operational conditions[1]. This is due to difference in its micropore size distribution [1]. The narrow micropore size distribution with peak value laid within the optimum range would shows higher methane storage potential.

Since biomethane is becoming more popular as environmental & economical advantageous alternative energy source in Sri Lanka, studying on upgrading of biomethane storage is beneficial.

This study focuses on identification of methane adsorption potential on commercial Sri Lankan AC by characterizing  $N_2$  adsorption data. Current production of AC of the country is targeted on applications like gas & air purification, water treatment, gold extraction, food & beverage industry etc. In this study, commercial AC supplied by HAYCARB PLC, the global leader in manufacturer of AC from a renewable source (coconut shell) in Sri Lanka, is analyzed to identify the methane adsorption potential with biogas storage in view.

## II. METHODOLOGY

Two types of commercial AC samples as granular & pellet forms, supplied by HAYCARB PLC have been used for this study. The samples were prepared by steam activation method which is the most common technique followed in Sri Lanka by the manufacturers. The other technique is chemical activation through the use of reactive chemicals or a combination.

The porous structures of the samples are characterized using the  $N_2$  adsorption data using Quantachrome Autosorb iQ-1 apparatus at 77K. 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 [6]. Average pore diameter was calculated using BET surface area ( $S_{BET}$ ) & total pore volume data, assuming cylindrical pore geometry [6].

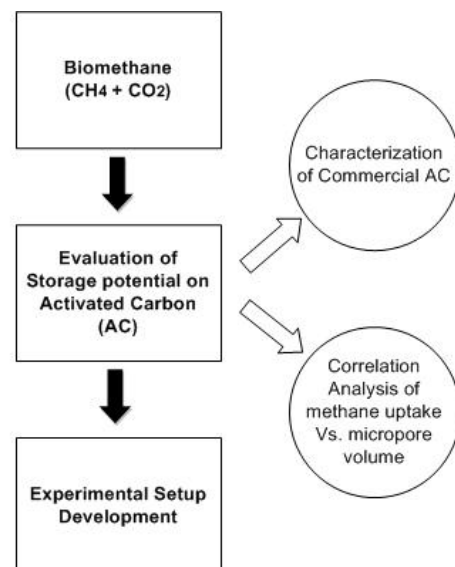


Fig. 1. Study framework.

TABLE II. GAS ADSORPTION (N<sub>2</sub> AT 77K) RESULTS

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>BJH</sub> (m <sup>2</sup> /g)	Total Pore Volume(cc/g)	V <sub>DR(N<sub>2</sub>)</sub> (cc/g)	Dry Bulk Density (g/cc)	Avg. Pore Diameter(nm)
Pellet	1155	28.27	0.5248	0.427	0.477	1.817
Granular	1232	30.63	0.5314	0.4567	0.56	1.725

The PSD was determined using Density Functional Theory (DFT) method [6]. Dry bulk densities of the samples were determined as per American Society for Testing & Materials (ASTM) standard test method D2854-09. The data analysis has been carried out considering porous structure requirements of AC for methane storage as stated in literature.

Several correlations [1], [2], [7] was developed in literature to predict the methane uptake potential by considering porous structure properties of the adsorbent. As the second step, applying suggested correlations into AC samples used in this study is analyzed. Fig.1 shows the key analysis framework planned for the overall study

### III. RESULTS & DISCUSSION

The characterization data of commercial AC, supplied by HAYCARB PLC were analyzed in this study. Importantly, these AC samples have been developed to fulfill the current application requirements in AC industry as manufacturer's criterion at present is not for methane storage purposes. The experimental step up is developed to carry out methane adsorption studies as a continuation of this work. The experimental results may subsequently indicate necessary process changes for current AC manufacturing process to optimize biogas storage.

#### A. Texture of Commercial AC

Porosity of commercial activated carbon samples are analyzed by physical adsorption data of N<sub>2</sub> at 77K (see Table 2). The obtained isotherms are presented in Fig.2. Granular sample shows much higher adsorbitivity towards N<sub>2</sub> than pelletized sample. The shape of both isotherms illustrate type I isotherm, characteristic of micropore material & type IV hysteresis loop; that is non-overlapping of adsorption and desorption branches, explains the presence of mesopores in the samples [3], [4].

TABLE III. RESULTS ANALYSIS

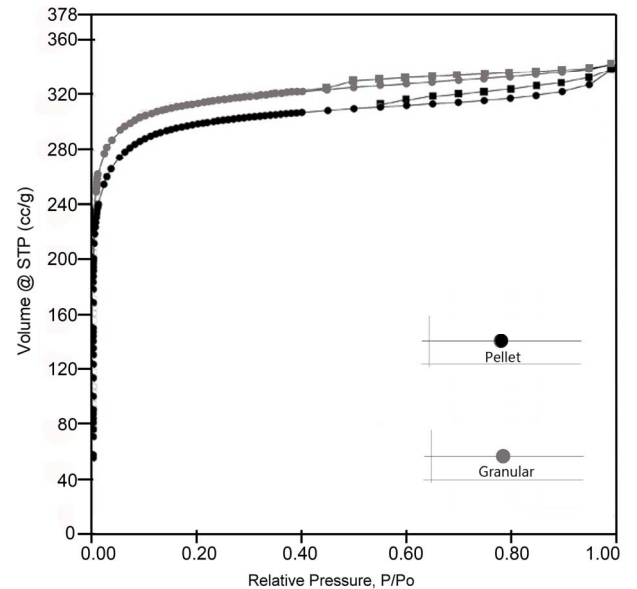
Sample	S <sub>BJH</sub> <sup>d</sup> /S <sub>BET</sub> <sup>e</sup>	Micropore ratio
Pellet	0.024	0.814
Granular	0.025	0.859

<sup>d</sup>Barret-Joyner-Halenda Surface Area (S<sub>BJH</sub>)<sup>e</sup>Brunauer-Emmett-Teller Surface Area (S<sub>BET</sub>)

The ratio between BET surface to BJH surface gives the mesoporosity of the sample while the ratio between total pore volume to DR(N<sub>2</sub>) micropore volume gives the microporosity of the sample[4], [6]. As per analyzed data presented in Table 3, both granular & pelletized AC samples shows low mesoporosity& high microporosity with similar mesoporosity & microporosity values.

Bulk Density of Granular form is bit higher than pelletize form (See Table 2). Higher bulk density would leads to higher volumetric energy densities hence higher volume of methane per volume of storage vessel (v/v) value.

PSD details of granular & pelletized forms of AC samples obtained from N<sub>2</sub> gas adsorption are presented in Fig.3. The figure confirms that the samples are mostly microporous & little mesoporous. PSD's of both are narrow, but granular sample is shown much wider distribution than pelletized AC sample. The peak is obtained around 1.1-1.3 nm range for both samples which indicates better methane adsorption potential as per literature [5], [6].

Fig. 2. N<sub>2</sub> adsorption isotherm.

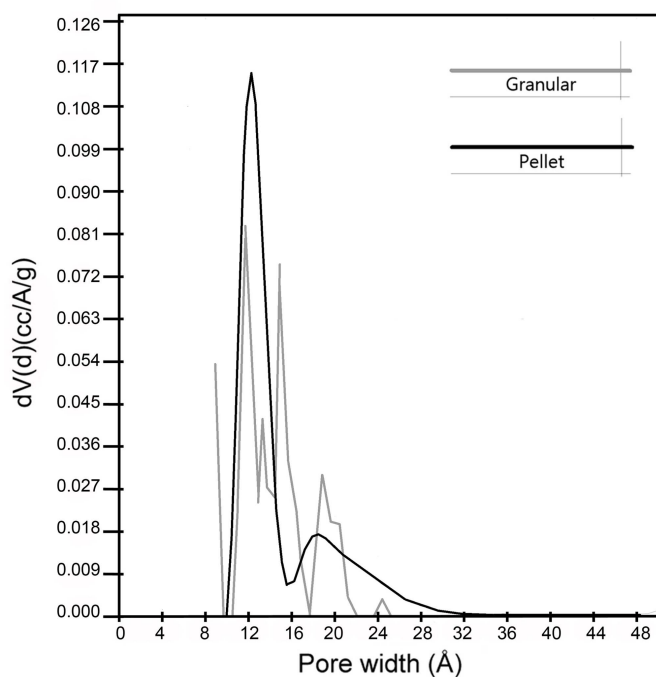


Fig. 3. Pore size distribution.

#### B. Correlation between methane adsorption & porous texture of AC

Identification of relation between methane uptakes to micropore volume of AC is important as it can be used in estimating methane adsorption potential of a provided AC sample with known micropore volume. In literature, several correlations have been proposed for methane adsorption at 298K with sample porosity considering both narrow & super microporosity which were assessed from CO<sub>2</sub> adsorption at 273K & N<sub>2</sub> adsorption at 77K data. The correlations were developed by plotting the trend line to experimentally obtained methane uptake results for developed sample series in each study. The physical form of AC sample, raw material, production process was differing from one study to the other (See Table 4) and sample series of each study has been developed by slightly varying the processing conditions & activating agents. However each correlation shows linear behavior between methane uptakes to micropore volume.

The correlation developed by [2] is complying with  $y = mx$  equation type. In this study, line was forced to pass through the origin by based on reasonable statement that a sample without any porosity will not exhibit any methane adsorption. The correlation developed by [1] is shown linear behavior complying with  $y = mx + c$  whiles the results of [7] are complying with  $y = mx - c$  equation type.

Thus, the presented correlations relevant to methane uptake Vs micropore volume have shown to be linear ( $y = mx \pm c$ ). The gradient ( $m$ ) of the equation can be expressed as methane uptake per unit micropore volume hence, it should be positive in value. However a large variation in gradient of [7] is visible compared to [1] and [2]. This is due to variable units used in these studies. The unit of the gradient in [7] is expressed in volumetric methane adsorption capacity per micropore volume on unit volume basis while the gradient in [1] and [2] is expressed as methane uptake in moles per micropore volume basis. The unit conversion from volume basis to mole basis was not possible as some properties (methane adsorption, bulk density, etc.) of each sample were not given in [7].

The positive gradient of the correlation explains that the development of microporosity would lead to higher methane uptake. The correlation in each paper was developed mostly using one single parent material for sample series by slightly varying the activation compounds, process or parameters of the production method. This leads methane uptake with micropore volume into a gradual increment. However the micropore volume indicates the range of pore size (size lower than 2nm) while there is optimum pore sizes within the microporous range which suits best for the methane storage applications [1], [5], [6]. Hence the difference in gradient from one correlation to the other, express the variation in micropore size distribution of each series of activated carbon samples. And it is reasonable to state that the highest methane uptake per unit micropore volume can be obtained by the samples which contain optimum micropore size distribution for methane uptake.

TABLE IV. CORRELATION DEVELOPMENTS

Type of AC	Raw material	Activation method	Correlation	Reference
ACF <sup>f</sup>	Petroleum-pitch CF	Physical (CO <sub>2</sub> /Steam)	$y=9.183x$	[2]
PAC <sup>g</sup>	Anthracite / Bituminous coal	Chemical	$y=6.407x+3.418$	[1]
GAC <sup>h</sup>	Bituminous coal	Physical & Chemical	$y=1294.5^i x-6.67^i$	[7]

<sup>f</sup>Fiber (ACF), <sup>g</sup>Powder (PAC), <sup>h</sup>Granular (GAC), <sup>i</sup>Decided from figure 9 in [7]; the units were in v/v form which is different from [1] and [2]

The intercept ( $c$ ) of equation can be expressed as initial methane uptake at zero micropore volume. Generally, this should be zero. However it has been declared positive & negative values for intercept in presented correlations. For the negative interception, it can be stated that there are micropore diameters which are not accessible to methane. The correlation developed by [1] has been presented positive intercept for powdered activated carbon samples. This positive intercept can be described as the methane storage in mesopores, macropores & inter particle space under bulk storage conditions which couldn't be assessed by Helium inert gas method. Thus, microporosity development & pore size distribution can be stated as the reason behind the variation of intercept & gradient from one correlation to the other which has occurred due to use of different parent material, activation compounds & procedures and different physical forms of samples in each study.

The commercial AC samples analysed in this study have been produced by using a different raw materials & preparation methods which are differ from the samples used in discussed correlations. Hence assessing of methane potential of these commercial AC samples by using any of proposed correlation wouldn't be much effective instead developing of a new correlation with suitable gradient & intercept is required.

An experimental set up has been developed to test on methane uptake capacity of commercial AC samples of all types (Fig.4). As a continuation of this work, development of a proper correlation which adheres to production method & raw material of Sri Lankan AC can be done.

#### IV. CONCLUSIONS

This study is based on analysis of biomethane storage potential in commercially available activated carbon in Sri Lanka. The bio-methane adsorption potential on AC is analyzed by the characterization data from  $N_2$  adsorption at 77K. In literature, it has been identified that the higher microporosity, higher bulk density and narrow pore size distribution are the key factors for better methane adsorption process. Both analyzed granular & pelletize AC samples show considerable microporosity & little mesoporosity, in similar manner. Thus, Granular type shows better methane potential from its higher bulk density while pelletized from shows better methane potential from its narrow pore size distribution details.

The correlations have been developed by early researchers in order to identify the linear behavior of methane uptake to micropore volume in AC. The variation in gradient & intercept of the linear behavior among correlations are observed due to their difference in parent material, production process, physical form & final packing density in used AC samples. The experimental set up has been developed to carry out practical studies as a continuation of this work.

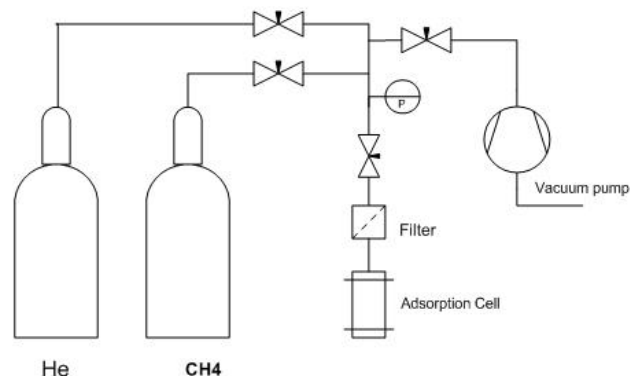


Fig. 4. Schematic diagram of experimental setup.

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