Application of Granular Activated Carbon Developed from Agricultural Waste as a Natural Gas Storage Vehicle

Ramakrishna Gottipati, Baradwaj Adiraju, and Susmita Mishra

***Abstract*—The novelty of the present work includes the preparation of the granular activated carbon (GAC) from the agricultural waste and its application in storage of methane gas. GAC, prepared from Aegle marmelos fruit shell by chemical activation (H3PO4) was characterized by N2 adsorption-desorption isotherms. The shape of isotherm and pore size distribution (PSD) of prepared AC at optimum conditions showed that the adsorbent is rich in micropores (< 20 oA) with high surface area (1657 m2/g). Methane storage capacity of the prepared GAC was tested at different temperatures (293 and 303 K) and pressures (up to 800 psia) and the effects of porosity and temperature on adsorption capacity were determined.**

***Index Terms*—Activated carbon; natural gas; aegle marmelos; pore size distribution; microporosity.**

I. Introduction

With the importance of alternative fuels in recent years, search for new methods for natural gas (contains 95 % methane) storage has been intensified because of its inherent clean burning characteristics. There are three technologies for natural gas storage: compressed natural gas (CNG), liquefied natural gas (LNG), and adsorbed natural gas (ANG). In the most popular storage method, CNG, gas is compressed to about 230 unit volumes to one unit volume of storage container. Therefore, CNG requires the use of expensive and heavy, high pressure compression technology and hence the cost for unit gas transportation increased tremendously [1], [2]. LNG is usually stored at –161oC as boiling liquid in cryogenic tank. This application requires specially designed storage tanks and refuelling procedures [3], [4]. An alternative to these storage methods is an adsorbed natural gas (ANG) which presents a promising future for the natural gas storage. This application involves storage of natural gas in porous materials at low pressures, and with high energy density. Among various porous materials, activated carbon (AC) was considered one of the best for methane uptake [5], [6].

The natural gas storage capacity of AC is usually evaluated in terms of its volumetric methane storage capacity (Vm/Vs), where Vm is the volume of stored methane at standard temperature and pressure, and Vs is the volume of the storage container. The volume of gas uptake by AC mainly depends on (i) elevated microporosity, and (ii) narrow pore size distribution (PSD). Elevated microporosity is responsible for the storage of small molecules like methane [7], [8] and narrow PSD optimizes the density of adsorbed phase [9]. Generally, the porous characteristics of AC depend upon the raw materials, activation process, and activation agents. ACs can be produced through two methods: physical and chemical activations. The porous structures can be created in the activation process by removing the disordered carbons, and by exposing the crystallites to activating agents [3]. Numerous studies have been carried out with different precursor materials and activation techniques to obtain ACs with high adsorption capacities [3], [10].

The objective of this study is to develop microporous AC from agricultural waste material by chemical activation with better methane storage capacity. The goal was to produce low-cost adsorbent that meets the targets established for low pressure natural gas storage materials.

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II. Materials and Methods

A. Materials

The agricultural waste used for the preparation of activated carbon, *Aegle marmelos* fruit shells, was collected from the university premises of N.I.T., Rourkela, India. Prior to impregnation, raw material was air dried, grinded and sieved to get uniform particle size of 1–2 mm. All the chemicals used were procured from Merck.

B. Experimental Methods

Preparation and characterization of AC. Raw material of 80 g was impregnated in 300 ml of different concentrations of diluted phosphoric acid for 12 h. The resulted material was dried at 100 ^{o}C for 12 h and then carbonized under inert atmosphere (N_2 – 100 ml/min) at different temperatures. Obtained samples were rinsed with warm distilled water to remove excess acid and then dried in over for 12 h.

Prepared ACs was characterized by N_2 adsorption-desorption isotherms by using Autosorb-1 (Quantachrome). Surface area of all the samples was calculated by applying Langmuir equation and the PSD was obtained by density functional theory (DFT). Total pore volume (V_t) and micropore volume (V_{mi}) were calculated from the amount of N_2 adsorbed at relative pressures of 0.95 and 0.1, respectively.

C. Evaluation of Adsorbent for Methane Storage

Adsorption of methane on prepared AC was conducted on the self-designed volumetric apparatus, shown in Fig. 1. Adsorption isotherms of methane at different temperatures i.e. 293 and 303 K were obtained with varying pressure (up

to 700 psia). The initial sample was degassed at room temperature for 2 h. The equilibrium pressures were measured by pressure transducers. The number of moles of gas sorbed (n_a) was estimated as the difference between the total amount of gas introduced into the void volume of sample cell (SC) (n_T) and the amount of free gas occupying the void volume (n_f).

$$n_a = n_T - n_f \quad (1)$$

The total number of moles of gas introduced into the sample cell at a single pressure point and constant temperature were estimated as

$$n_T = \left(\frac{V}{RT} X \left(\frac{P_{S1}}{Z_1} - \frac{P_{S2}}{Z_2} \right) \right)_{FV} \quad (2)$$

where, V is the volume of sample cell, T is the absolute pressure, R is the gas constant, P_{S1} and P_{S2} are the pressures of sample and reference cells, respectively, Z_1 and Z_2 are the compressibility factors calculated by using NIST mixture property database version 9.09 software.

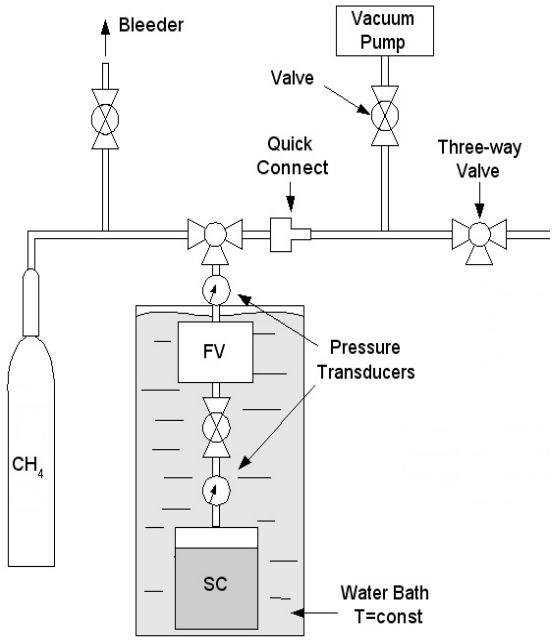

Fig. 1. Schematic of the volumetric methane adsorption apparatus

III. Results And Discussion

A. Porous Characteristics of AC Prepared at Optimum Conditions

Effect of different process parameters such as acid concentration (0–50 %), carbonization temperature (400–700 °C), and holding time at final temperature (0–240 min) on porous characteristics was analyzed and the optimum conditions found were 30 %, 400 °C and 60 min, respectively.

The adsorption-desorption isotherm of activated carbon prepared at optimum conditions shown in Fig. 2 resembles type – I isotherm (highly microporous) [11]. The Langmuir surface area, total pore volume and micropore volume obtained are 1657 m^2/g, 0.58 cc/g and 0.56 cc/g, respectively. The PSD estimated by DFT presented in Fig. 3, clearly shows that the major part of the porosity lies in the micropore range (< 20 °A).

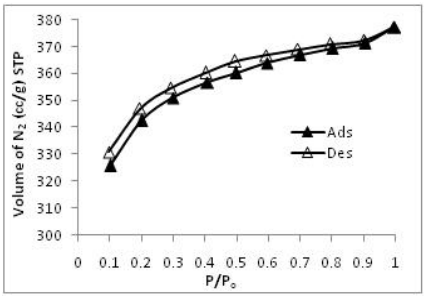

Fig. 2. Adsorption-desorption isotherms of prepared AC

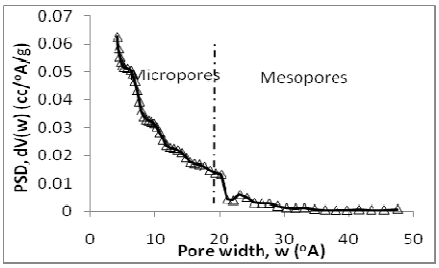

Fig. 3. PSD of the AC determined by DFT

B. Methane Adsorption Isotherms

Methane adsorption performance of prepared AC at temperatures of 293 K and 303 K were shown in Figs. 4 and 5, respectively. The adsorption isotherms obtained are of type – I, which represents microporous solids. The adsorption increases rapidly with increasing pressure in the low pressure range, indicating the strong interaction of CH_4 with AC and also due to the micropore filling. With increase of temperature the adsorption amount decreased at the same pressure due to the exothermic nature of adsorption. Hence, the adsorption of CH_4 at low temperature was more favorable.

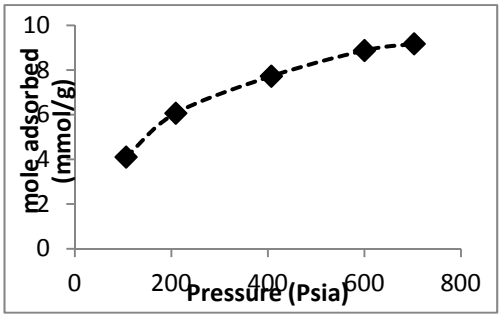

Fig. 4. Methane adsorption isotherm of AC at 293 K

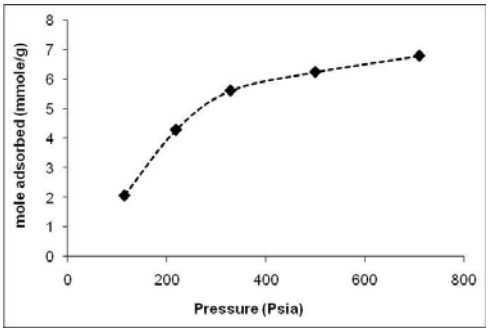

Fig. 5. Methane adsorption isotherm of AC at 303 K.

IV. Conclusion

The aim of this study was to prepare AC from the economically viable agricultural waste and to test it for natural gas storage capacity. High surface area (1657 m^2/g) AC was successfully prepared from *Aegle marmelos* fruit shell by H_3PO_4 activation and effectively applied for natural gas storage applications. The maximum adsorption capacity of the prepared AC obtained at 293 and 303 K were 9.17 and 6.79 mmol/g, respectively at 700 psia.

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