

Natural gas adsorption on biomass derived activated carbons: A mini review

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Abstract. Activated carbon materials are good candidates for natural gas storage due excellent textural properties that are easy to enhance and modify. Natural gas is much cleaner fuel than coal and other petroleum derivatives. Storage of natural gas on porous sorbents at lower pressure is safer and cheaper compared to compressed and liquefied natural gas. This article reviews some works conducted on natural gas storage on biomass based activated carbon materials. Methane storage capacities and deliveries of the various sorbents were given. The effect of factors such as surface area, pore characteristic, heat of adsorption, packing density on the natural gas storage capacity on the activated carbons are discussed. Challenges, improvements and future directions of natural gas storage on porous carbonaceous materials are highlighted.

1. Introduction

Natural gas is cheap, clean [1], safe and abundant energy source [2]. Due to these advantages, its storage, transportation and utilization have attracted global attention [3]. Natural gas (NG) is composed mainly of 85–95 mol% methane (CH₄), the remainder being carbon dioxide (CO₂), nitrogen (N₂) and small amounts of higher heavy gaseous hydrocarbons [1]. Natural gas from crude wells is known as associated gas, while those from gas wells or condensate is referred to as non-associated gas. NG from pores of coal is known as coalbed gas [2]. Until recently, Natural gas is stored as compressed natural gas (CNG) or liquefied natural gas (LNG). In (CNG), natural gas is stored as a compressed supercritical fluid at room temperature and at maximum pressure of about 200–250 bar [1]. Therefore, CNG requires expensive vessels and multi-stage compression [4]. Not only that, in terms of equal fuel-tank volume, the energy density of natural gas at pressure of 20 MPa, is only 29% that of gasoline [3]. NG is transported overseas as liquefied natural gas (LNG) in ships, LNG requires expensive cryogenic process [4]. It is usually stored as a boiling liquid at about (161^oC) in a cryogenic tank at a pressure of about 14.7 psia. LNG has volumetric energy density for about 72% of that of gasoline [5].

Due to high costs, safety and operational restrictions of CNG and LNG researchers are finding alternatives [1]. ANG (Adsorbed natural gas) is viewed as alternative technology to CNG and LNG. In ANG, the gas is stored on porous material packed into a vessel at much lower pressure [3]. In ANG the storage pressure is usually in

the range of 35–40 bar. Therefore, there is improved safety and low compression costs in ANG [1].

Among solid adsorbents, activated carbons have been used and evaluated for methane adsorption. They are good candidates for natural gas storage due to large surface area, large pore volume and low density. Activated carbons with diversified microporous structures constitute an important category of potential adsorbents for natural gas storage [6]. Properties of activated carbon required for natural gas adsorption include: high adsorption capacity, high packing density, high adsorption desorption rate, ratio of amount desorbed at 0.1 Mpa and the amount adsorbed at 4 Mpa should be close to one [7], less susceptible to temperature changes during adsorption and desorption, extremely hydrophobic and it should be inexpensive for the final user. [10]

For ANG to be commercially viable, the ANG technology requires a methane storage target of 180 v/v at an ambient temperature, with the energy density of ANG comparable to that of current CNG technology [9]. Recently, the United States Department of Energy (DOE) reviewed the volumetric objective for adsorbed natural gas from the old value of 180 cm³ (STP: 273.15 K, 1 atm)/ cm³ to a much ambitious value of 263 cm³ (STP: 273.15 K, 1 atm)/cm³ [10]. This paper reviewed the existing literature on natural gas/methane adsorption on biomass based porous carbons. Both single and gas mixture adsorption is discussed, challenges of ANG technology and improvements in the system are given.

2. Important ANG Adsorbent Parameters

For activated carbon to be considered as a good ANG material, certain parameters/properties such as adsorption capacity, deliverable gas, heat of adsorption, surface area, porosity and packing density needs to be assessed.

2.1. Deliverable Gas and Adsorption Capacity

Deliverable gas is the volume of gas delivered per volume of the storage container. It denotes the amount of gas released when pressure is reduced from high pressure mostly around 34 bars to atmospheric pressure. The storage capacity is usually greater than the delivered gas by about 15-30% [11]. The US Department of Energy (DOE) set target of absolute methane-adsorption capacity of 180 v/v (standard temperature and pressure equivalent volume of methane per volume of the adsorbent material) at 35 bars, under ambient temperature. CH₄ storage target was reviewed in 2012 to 230 v/v [12]. Methane adsorption on olive stones grain activated carbon chemically activated by ZnCl₂ led followed by physical activation with CO₂ gives 110V/V at 298K under 3.4MPa. Most of the studies conducted reported volumetric CH₄ capacities for activated carbons in the range of 100–170 v/v; therefore there is still need for improvement [12].

2.2. Heat of Adsorption

Adsorption of natural gas during charging into an adsorbent filled container is exothermic, while desorption is endothermic [13]. Increase in temperature brings about decrease in adsorption capacity of the sorbent. Therefore, fewer amounts CH₄ is stored during adsorption due to increase in temperature and more CH₄ is retained during desorption due to decrease in temperature [12]. Temperature changes in the ANG system can be managed by incorporating heat exchanger in the storage vessel, changes in the tank geometry, modification of the sorbent material and changes in nature and direction of flow. Higher thermal conductivities and heat capacity is required for the sorbent. Material with high heat capacity is less susceptible to temperature changes during charging and discharging of natural gas [12].

A study was carried out to determine the thermal effect of the adsorption heat on the discharge performance of an adsorbed natural gas (ANG) storage system [14]. It was found out that central region of the adsorbent bed suffers from the severest temperature fluctuation in a short period of discharge state; introduction of the hot water greatly reduce temperature fluctuation of the adsorbent bed, shorten the discharge process by 60% compared to that without supplemental heat [14].

2.3. Surface area and pore characteristics

Adsorbent for natural gas application is desired to have large surface area, predominantly microporous with low mesoporosity. Large surface area allows more contact between gas adsorbate and the solid adsorbent which translate to more adsorption. Low mesoporosity is required as feeder pores to provide easy access for the gas

molecules to/from the adsorbent micropores [5]. Micropores are pores that are less than 2 nm, while mesopores are pores between 2 to 50 nm [15]. Surface area of activated carbon used for natural gas adsorption was in the range of few hundreds to 3000 m²/g [5].

Biloe' [16] used Dubinin–Astakhov equation to determine the influence of the microporous characteristics of activated carbon on the performances of both charge and discharge of an ANG system. It was found out that for the charge stage, the activated carbon must be conductive with an average micropore width of 1.5 nm, and for the discharge, it should be permeable and sufficiently conductive with an average micropore width of 2.5 nm.

2.4. Packing Density

Packing density is defined as the mass of settled material per unit volume of storage space. A carbon sorbent material with high surface area and low parking density would still have low adsorption capacity [13]. Therefore, in addition to high surface area, high packing density is required for sorbent materials to be used as an ANG material. More porosity development in a carbonaceous sorbent lowers its packing density [17]. An adsorbents may have high uptake on a mass basis, but with the low packing density much of the potential advantage is lost and the volumetric energy densities will still be low [13]

For economic viability of ANG, it's good to have high energy density besides the high micropore volume on volumetric basis. In order to achieve that, the sorbent must have high packing density. Packing density of slit pores AC is higher than due to the additional space given for freedom of molecules between to parallel sides of slit pores [18]. [7] reported packing density of about 0.7 g/ml for activated carbon with BET surface area close to 2400 m²/g.

2.5. Other properties

ACs for use as ANG materials are required to be hydrophobic, which prevents competition between water and adsorbate molecule. The adsorbent should be hard, not easily broken or powdered [5].

3. Adsorption of Methane on AC

Methane uptake is usually reported as adsorbed volume at standard pressure and temperature (cm³ (STP) per volume of sample (cm³ (STP) cm⁻³), gravimetrically (cm³ (STP) g⁻¹), specific amount reported in mmol g⁻¹, or as sample- specific weight percent (wt.%) [19].

There are several studies conducted on use of activated carbon for methane adsorption. Activated carbon samples were prepared from Brazilian coconut shells modified by H₃PO₄ for methane adsorption [20]. The experiments were conducted at pressures between at 303 K. highest methane storage capacity was found to be 95 v/v at 303 K and 35 bar on the activated carbon samples. [21] prepared activated carbon (CAQF-30) from coconut shells by chemical activation with zinc chloride

followed by physical activation. The performance of the prepared AC was compared with commercial AC (SRD-21) for adsorption of methane. The prepared activated carbon showed approximately 0.14 g/g CH₄ adsorption capacity, while the commercial sample showed 0.17 g/g CH₄ adsorption capacity.

Activated carbon from rice husk (AC-RH) was synthesized and its methane adsorption capacity was determined [22]. The experiment was conducted at constant temperature and pressure up to 2.5 Mpa. The AC-RH demonstrated 2350 m²/g BET surface area and 0.95 pore volumes. The sorbent had 9.3 mmol/g adsorption capacities at 303.15 K under 2.5 Mpa. Activated carbons (ACs) were prepared by carbonization, impregnation with KOH and activation of sugarcane molasses [23]. The AC that had high surface area of 2202 m²/g was evaluated for methane adsorption. Highest methane adsorption capacity of 197.23 mg/g (12.33 mmol g⁻¹) at 50 bars and 20 °C was recorded.

In another study, theoretical and experimental study was carried out to determine the amount of adsorption and desorption of methane on MERC commercial granular activated carbon [24]. The experiments were carried using volumetric method for pressure up to 500 psia at constant temperature of 25°C. The adsorption and desorption capacity of the MERC activated carbon reached 0.127 g/g and 0.091 g/g. It was found out that BET surface area, micropore volume, packing density, and pore size distribution have significant effect on the amount of methane adsorbed [24]. Delevar et al. (2010) investigated the capacity of granular activated carbon (GAC) for the storage of methane. The methane adsorption was determined at different pressures (0-50 bar) and temperatures (285.15 - 328.15 K). The CH₄ adsorption capacity on the activated carbon samples was around 8 mmol/g at 298K, 40 bar. It was also revealed increasing the pressure and decreasing the temperature increases the amount of adsorption.

4. Adsorption of CH₄ and CO₂ Mixture

Some sources of natural gas are associated with CO₂, which is considered as an impurity. Presence of CO₂ reduces the energy content and heating value of natural gas, in the presence of water it corrupt transportation and storage system [25,26]. There is also need to remove CO₂ from the mixture in order to meet pipe line specification or to produce liquefied natural gas [26]. Adsorption on porous carbons is one of the techniques used to separate the CH₄/CO₂ gas mixture.

[27] used virgin palm shell activated carbon and PEI (polyethyleneimine) carbon molecular basket for methane and CO₂ adsorption. Virgin palm shell AC shows 3.03 and 10.79 (cm³/gSTP) CH₄ and CO₂ adsorption capacity with 3.56 as CO₂/CH₄ ideal selectivity. PEI (polyethyleneimine) carbon molecular basket demonstrated 15.68 and 51.11(cm³/gSTP) CH₄ and CO₂ adsorption capacity with 3.26 as CO₂/CH₄ ideal selectivity.

High-pressure adsorption of CO₂ and CH₄ in activated carbon was evaluated on Maxorb AC [26]. The

researchers found out that CO₂ is more adsorbed than CH₄ in all the conditions tested. Maximum amount adsorbed (q_{max}) from Sips isotherm for CO₂ and CH₄ reached up to 31.97 and 15.02 mol/kg. There is deviation of up to 20% between results obtained from static and dynamic adsorption. In a similar study, Coconut activated carbons were prepared and used for CO₂ and CH₄ adsorption [28]. CO₂ adsorption capacity of 2.55 mmol/g at 200 kPa, CH₄ adsorption capacity of 1.93 mmol/g were recorded at 200 kPa.

In a similar study, methane adsorption was investigated on activated carbon obtained from coffee husks [29] at 298.15 K and 303.15 K and pressures up to 30.00 atm. maximum volumetric methane uptake by the synthesised carbon monoliths was observed to be 130 V/V at 298.15 K and 30.00 atm. It was observed that there was increase in amount adsorbed due to increasing surface area, total pore volume and micropore volume.

[30] studied adsorption equilibrium of carbon dioxide, methane and nitrogen on microwave activated carbon (MAC). The capacities of pure gas CO₂, CH₄ and N₂ were reported to be 2.13, 0.98 and 0.33 mmol g⁻¹ at 298 K and the partial pressure of 100 kPa. [31] studied adsorption of methane and carbon dioxide on two microwave-activated carbon samples at different temperatures from 298 and 323 K. The results showed that the activated carbon modified by potassium carbonate sample has the higher equilibrium selectivity for CO₂ over CH₄. The adsorption capacities of CO₂ for unmodified and K₂CO₃ modified AC was 1.31 mmol/g and 1.63 mmol/g at 298 K and the pressure of 50 KPa, respectively. The ideal selectivity of CO₂/CH₄ is 2.66 and 7.42 for MAC and MAC/K₂CO₃ respectively.

5. Challenges and Improvements in ANG Technology

The first issue is that, according to the thermodynamic laws, during the process of adsorption, the temperature of the ANG system is increased, there by limiting the amount of natural gas uptakes. During desorption the temperature of the system diminishes which causes retention of some of the gas to be delivered [32]. Therefore, management of thermal effects as a result of adsorption heat on both charge and discharge processes of the ANG are still a bottleneck for developing the vehicular ANG storage technology [14]. MoreGasTech, a French company develop an efficient thermo-managing control system for cooling during adsorption or heating the adsorbent during discharge [32]. Another sorbent challenge is presence of impurities in the methane gas [19]. They compete favourably with CH₄ for pores and active sites. But issues related with impurity such as H₂O could be avoided by having a hydrophobic surface.

The volumetric storage of ANG still needs to be improved in order to favourably compete with other NG storage method. Increasing the packing density will help in this regard. Compacting the sorbents increases the density which in turn increases the adsorption capacity per unit volume. Another is problem is the difficulty in

direct packing of the adsorbent carbon into the storage vessel. Briquetting, or immobilizing, the carbon was considered as an alternative. But the binder blocks some of the pores there by reducing storage due to inaccessibility to the micropores [32]. Configuration, design and nature of the carbonaceous sorbent also enhance the storage capacity. New adsorbents such as monolithic carbons and compressed active carbon fibers used in non-cylindrical vessels have made possible to store the same capacity of gas as CNG tank [33].

6. Conclusions

Biomass materials which are precursors for producing activated carbon material are cheap and readily available. Utilization of biomass as an ANG material brings about cost effectiveness and improved profitability in ANG related industries, with concomitant waste minimization. Choice of proper synthesis and modification conditions leads to sorbent with the desired properties for natural gas adsorption. Emphasis should be on having a material that is microporous with little mesopore; a material with high packing density, high adsorption and desorption capacity, low isosteric heat of adsorption, good mechanical strength, tolerant to impurities and cheaper. Biomass based AC have great potential as adsorbents for natural gas storage. But still there need to improve the volumetric capacity to the driving range to levels closer to that of gasoline vehicles.

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