Applied Thermal Engineering 98 (2016) 778–785

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research Paper

Development of composite adsorbents and storage vessels for domestically used adsorbed natural gas

Q.R. Zheng *, Z.W. Zhu, Y.L. Feng, X.H. Wang

Provincial Key Laboratory of Naval Architecture & Ocean Engineering, Institute of Marine Engineering, Jimei University, Xiamen 361021, China

HIGHLIGHTS

- The composite adsorbent has a higher thermal conductivity.
- The Toth model is suitable for methane adsorption on carbon-based composite.
- Conformable design is appropriate to serve as domestic ANG vessel.
- The composite produces a better thermal conductivity than partition plates.

ARTICLE INFO

Article history:
Received 18 October 2015
Accepted 27 December 2015
Available online 7 January 2016

Keywords:
ANG
Conformable tank
Thermal effect
Composite adsorbent

ABSTRACT

Experiments were designed to develop an adsorbed natural gas (ANG) technique suitable for household environment. The composite adsorbent was synthesized based on four key factors in terms of the maximization of thermal conductivity. The Toth equation was used to analyze adsorption equilibrium of methane on the composite. Charge/discharge cycles of methane on a cylindrical tank and a conformable tank were assessed for evaluation of the structure of tank and the partition plates, the composition of adsorbent, and the dynamic behaviors of storage system. The results show that the maximum thermal conductivity of the composite occurs where the composite adsorbent was consisted of the equal amount of activated carbon and expanded graphite (ENG), heated at the temperature of 600 °C for the duration of 30 seconds, and consolidated under pressure 9 MPa. It also indicates that thermal effect on the conformable tank is much weaker in comparison to that of cylindrical tank. As a consequence, in the case where the composite adsorbent is used, the insertion of partition plates into a conformable ANG vessel does not significantly improve heat conductivity. It suggests that the use of the composite adsorbent in a conformable tank provides a promising method to store natural gas for domestic purposes.

1. Introduction

Because it requires a much lower storage pressure, ANG has been regarded as a promising alternative to compressed natural gas since 1980s [1–3]. Searching for high performance adsorbents and the structural optimization of an ANG storage vessel are ways to commercialize the ANG technique [4,5]. This paper explores the gap between what has been achieved and what is required for commercial purposes of ANG.

Commercially, an ANG system for domestic purposes should be compact in structure and light in weight. It should allow the amount of gas in need to be released without difficulty, and the storage vessel should be strong enough for safety purposes [6]. The development of micro-porous adsorbents of which the specific surface area is large and the packing density is high was extensively discussed in literatures [7–10]. In practice, the densification of the adsorbent is a key way to increase the packing density, and this can be achieved by using the binders to prepare monoliths or by compacting the pellets mechanically. The use of binder improves the strength and the thermal conductivity of the adsorbent, but it blocks the micro-porosity and reduces the gas flow through the adsorbent, which results in strong thermal effect on the storage vessel [8,11]. Carbon monoliths or carbon pellets fabricated by binderless methods showed higher storage densities of methane, but those samples were compacted under high pressures without taking measures for enhancing heat and mass transfer performance of the adsorbents [12,13]. Obviously, in viewpoint of practical application, it can be concluded that application of an addictive that can both be a thermal binder and mechanical binder is more easily performed and should be preferentially emphasized, and this has already been proved in our previous studies [14,15]. However, the solution of this technical problem also relies on such measures as enhancing the heat and mass transfer properties of the monolith adsorbent, and selecting a thermal binder with the structure to allow the gas flow.

* Corresponding author. Tel.: +86 592 6183533; fax: +86 592 6180332.
E-mail address: zhengqr@jmu.edu.cn (Q.R. Zheng).

http://dx.doi.org/10.1016/j.applthermaleng.2015.12.127
1359-4311/

Moreover, the storage pressure of ANG tank is targeted at 4 MPa, which limits the space available for the storage tank. An ANG storage system should function in a way to achieve the longest service time. Currently the cylindrical tank with spherical headers is commonly used for storage of natural gas mainly due to its uniform stress distribution. But with a spherical header, the external space of tank is not fully used. Its space usage is only 52.36%, which is well below 78.50% of the storage tank in conformable shapes with completely flat ends [4,16]. It was recognized in 1990s that increase in conformity of ANG tank improves the space usage, and DOE recently set out that the technical target for the conformity of tank must be greater than 90% [17]. However, the increase in conformity also causes the stronger thermal effect on the storage system because the greater amount of heat and mass is to be transferred within the limited space. Therefore optimization between increase in the conformity of storage tank, enhancement of the heat and mass transfer performance of the storage system, and reduction of the stress concentration in storage tank is required. Substantial studies of these issues have not been conducted yet, and researches carried out are separately on such aspects as of designing storage vessel, managing thermal effect and developing high performance adsorbent [4,18–20]. The targeted storage density of ANG systems was set at 12 MJ/kg, which is equivalent to 9.2 MJ/L for fuel volumetric density. Obviously, systematical studies are necessary to achieve these targets by means of finding an efficient adsorbent and a useful tank design.

A conformable design of an ANG vessel needs to be designed in such a way that it is suitable for domestic purposes, especially where the available space is limited. The measures for managing the thermal effect should be convenient for users to adjust the flow rate in need. In general, in an ANG storage vessel, the improvement in the apparent thermal conductivity of the storage system results in reduction in the thermal effect from adsorption and compression of the adsorbate molecules. The thermal conductivity of the storage system can be considerably improved by binding the adsorbent, which was composited with addictives of high thermal conductivities, and by shortening the transfer path of heat and mass. As discussed in the previous studies, the ENG in the composite adsorbents formed by activated carbon and ENG can serve as a thermal binder to improve heat transfer, and the adsorption of methane on the adsorbent mainly results from the contribution of the activated carbon [7,8,15]. In literatures, it was suggested that to obtain the most closely fit space, a conformable tank with different sections, which were separated by partition walls, can be used [21,22]. The partition walls also functions as the thermal bridge for transfer of heat out from the central region of the tank. It is therefore necessary to evaluate the efficiency of ENG and the partition wall as a way to enhance the heat transfer of the storage system.

To optimize the structure of the adsorbent and the storage vessel for domestic purposes, this paper focuses on three aspects. First, the analysis based on orthogonal array design (OAD) was used to evaluate the effect of each factor on the thermal conductivity in synthesizing ENG. Second, the thermal effects associated with the dynamic process of ANG were evaluated by analyzing adsorption equilibrium of methane on composite adsorbents. Third, the results from charge and discharge tests were used to evaluate the efficiencies of ENG, conformable design and the partition wall on mitigation of thermal effect.

2. Experimental

2.1. Materials

The activated carbon and the expandable natural graphite were synthesized to form a composite adsorbent. The expandable graphite was from Shanghai Yifan Graphite Ltd, and it was placed in a muffle burner with the temperature in the range from 600 °C to 1000 °C within the duration about 100 seconds. The Selected activated carbon SAC-02 in 80–100 mesh was supplied by Ningde Xinsen Activated Carbon Ltd.

Theoretically the adsorption performance and the thermal conductivity of the composite adsorbent are closely related to heating temperature (T) and heating duration (t) of ENG, the mass ratio of ENG to AC and consolidating pressure (p). The orthogonal experiment was designed in accordance to these four factors to find out the effectively optimized experimental conditions [23]. The compressibility of the expandable graphite was assessed with a hydraulic unit under the pressure of 1 MPa to 25 MPa. The expansion was examined by maintaining the heating duration for 100 seconds. The thermal conductivity (λ) was measured by using C-Therm Tci Thermal Conductivity Analyzer. It was observed that the change in shape of the sample under the pressure of 12 MPa and for the duration of 70 seconds was negligible. Therefore, a $L_{16}(4^5)$ OAD procedure was adapted in which each of the four factors was tested at four levels and the results were shown in Table 1, in which the mass ratio is determined by the input mass of ENG and activated carbon. Quantitative analysis of the contribution of each factor was used to determine its value at which the thermal conductivity of adsorbent reaches the maximum. The mean value and the range of the thermal conductivities were respectively calculated for each factor at the same level, and the results were listed in Table 2, in which I stands for the level and R stands for the range. For example, I(1,1) = 0.315 is the average thermal conductivities of the samples, which were heated at 600 °C, and I(1,2) = 0.302 is the mean value of the thermal conductivities of the samples, which were expanded for 10 seconds. The detailed discussions were presented in References 14 and 15. Based on the data from experiments, the relationships of the thermal conductivity to each factor were shown in Fig. 1.

As shown in Fig. 1, the thermal conductivity is higher where the heating temperature or the mass ratio of activated carbon to ENG is lower; the thermal conductivity reaches its highest where the sample was expanded for 30 seconds or the sample was consolidated under the pressure of 9 MPa. In other words, the composite adsorbent, which was prepared by mixing the same amount of ENG and

Table 1
Orthogonal experiments with 4 levels and 4 factors.

No.	T/°C	t/s	The mass ratio/ ENG: Activated carbon	p/MPa	λ /W/(m·°C)
1	600	10	1:1	3	0.451
2	600	30	1:2	6	0.435
3	600	50	1:3	9	0.205
4	600	70	1:4	12	0.167
5	700	10	1:2	9	0.386
6	700	30	1:1	12	0.545
7	700	50	1:4	3	0.112
8	700	70	1:3	6	0.153
9	800	10	1:3	12	0.227
10	800	30	1:4	9	0.133
11	800	50	1:1	6	0.410
12	800	70	1:2	3	0.240
13	900	10	1:4	6	0.146
14	900	30	1:3	3	0.150
15	900	50	1:2	12	0.224
16	900	70	1:1	9	0.572

Table 2
Results determined from data of orthogonal experiments.

Factors(j = 1–4)	Temperature	Heating time	The mass ratio	Consolidating pressure
I_j	0.315	0.302	0.494	0.238
II_j	0.299	0.316	0.321	0.286
III_j	0.253	0.238	0.184	0.324
IV_j	0.273	0.283	0.140	0.291
R_j	0.062	0.078	0.354	0.086