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Applications of organic phase change materials embedded in adsorbents for controlling heat produced by charging and discharging natural gas

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Abstract This paper studied the thermal effect resulting from the adsorption of natural gas on both charge and discharge on an absorbed storage system using a phase change material (PCM) as heat exchanger. A kind of organic PCM whose phase change heat is 153 J/g, measured by DSC,consisting of decanoic acid and lauric acid was prepared. The PCM was used to control the heat effect during the adsorption and desorption of natural gas. By adding the volume ratio of 6.10 % of the PCM into the adsorption tank, the temperature change can be reduced 21.8 °C during adsorption and can be increased 22.7 °C during desorption. Meanwhile, the delivered natural gas volume was increased 39.4 % with the use of the PCM compared to the case without PCM for a 0–3.5 MPa of pressure swing. Application of this kind of cheap PCM in the adsorption tank is an effective method to reduce the adverse effects of adsorption heat and thereby enhance storage capacity and delivery.

Keywords Organic phase change material · Natural gas · Adsorption heat

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1 Introduction

Nowadays, energy and environment are common issues for the whole world. As a vehicle fuel, natural gas is much cleaner, cheaper and abundant than petroleum. But the main drawback of natural gas is its low volumetric energy density (Matranga et al. 1992). In order to maximize the volume of natural gas capable of being stored at a given pressure within a given storage volume, an adsorbent medium for the natural gas is employed. The adsorbed natural gas (ANG) technique, which stores natural gas by adsorption in microporous carbonaceous adsorbents at medium pressure and room temperature, is being considered as an on-board storage technology for natural gas vehicles because of its low capital and operation costs in comparison to compressed natural gas (CNG) storage (Matranga et al. 1992). Much progress has been made in ANG technology in improving the quality of adsorbents to achieve the goal of commercial application for natural gas vehicles (Marsh and Yan 1984; Cal et al. 2000; Coskun and Tollefson 1980; Li et al. 2003; Li and Chen 2011). However, adsorption heat generation during charging and discharging natural gas significantly affects adsorptive efficiency. Specifically, the released heat will result in significantly reduced adsorption capacity during the adsorption process which is exothermic; while in the process of desorption which is endothermic, heat-absorption will lower the temperature, resulting in reduced desorption capacity and extended desorption time. There are few reports on how to solve the adsorption heat issue.

Phase change material (PCM) is an advanced environmental friendly energy storage material (He et al.1994; Nallusamy et al. 2007; Karaipekli and Sari 2009; Wang et al. 2012).

Chemical bonds are used to store and release heat. PCM is material that stores energy in the process of changing the aggregate state from solid to liquid. When PCM reaches the temperature at which they change phase (their melting point), they absorb large amounts of heat without getting hotter. When the ambient temperature in the space around the PCM material drops, the PCM solidifies, releasing its stored latent heat. In melting and solidification cycle, PCM absorbs and emits heat while maintaining a nearly constant temperature. They store 5–14 times more heat per unit volume than sensible storage materials such as water, masonry, or rock (Ghoniem and Klein 1989).

At present, paraffin waxes and fatty acids have been widely studied as PCMs for latent heat thermal energy storage applications(Yuan et al. 2014; Xu and Li 2013; Sari and Kaygusuz 2002; Rozanna et al. 2005). Myristic acid-Palmitic acid-Stearic acid/expanded graphite PCM was fabricated (Yang et al. 2014). Capric acid and palmitic acid eutectic mixture was used as PCM to prepare the phase change gypsum wallboard as novel phase change wallboard for latent heat thermal energy storage (Karaipekli and Sari 2010). A composite paraffin-based PCM was prepared by blending composite paraffin and calcined diatomite through the fusion adsorption method (Sun et al. 2013). PCM was used on an adsorbed carbon dioxide storage system (Toledo et al. 2013).

A PSA method using a composite adsorption bed comprising an adsorbent and PCM agglomerates was published (Monereau and Pullumbi 2013). The PCM agglomerates consisting of organic compounds and a binder. PCM agglomerates were mixed with the adsorbent particles. The shortcoming of this patent was contamination to the adsorbent, which not only reduced the adsorptive capacity of the adsorbent but also made it difficult to be reused.

Although a considerable number of studies on PCM can be found in the literature, few studies were devoted to study the thermal behavior of ANG storage during dynamic charge conditions and no one studied application of PCM in damping temperature fluctuations during the charging and discharging of ANG storages.

In this article an attempt is described to add cheap organic PCM in the natural gas tank which is filled with adsorbents to reduce the adverse effects of adsorptive heat. The advantage of this idea is to improve the utilization efficiency of natural gas without introducing additional energy.

2 Methods

Gas chromatography (GC-2020) was used to analyze the composition of natural gas (Table 1).

Table 1 Composition of natural gas (v) %

CH_4	C_2H_6	C_3H_8	CO_2	N_2	O_2	H_2S
86.98	4.30	4.96	0.01	2.56	0.71	0.48

Gas gravimetric adsorption capacity (m/m: mass of adsorbed gas/mass of adsorbent) was determined with a pressurized thermo-gravimetric analyzer (CHAN-100 USA) (Li et al. 2003). Gas volumetric adsorption capacity (v/v: volume of adsorbed gas/volume of adsorbent) was determined with an evaluation apparatus built by the author's laboratory for natural gas volumetric adsorption capacity (Li et al. 2003).

2.1 Preparation of adsorbents

Adsorbents were prepared from petroleum coke in author's lab. The main course includes pre-activated, activated in rotary kiln in N_2 atmosphere. The detailed process was presented in previous papers (Li et al. 2002, 2003). The specific heat of the adsorbent was measured with differential scanning calorimeter (DSC) TA5000-type USA.

2.2 Preparation of PCM

In order to choose a suitable PCM to control the adsorption heat for the ANG use, a variety of PCM including inorganic compounds, eutectics, paraffins and fatty acids were investigated. Inorganic compounds are known by the formula M_nH_2O and have been studied for many years. They have relatively high latent heat but their melting-solidification processes are irreversible because of segregation. Eutectics are mixture of two or three compounds which melt without segregation (Demirbas 2006). Paraffins are compounds that appear in form of waxes are at room temperature. Chemically they are hydrocarbons with alkane C_nH_{2n+2}. The melting point increases with the increase of C atoms. Their drawback is that they are poisonous and they are expensive. Fatty acids can be characterized with the formula $C_nH_{2n}O_2$. Their melting point is similar to those of paraffins and their price is lower than those of paraffins. They also have relatively high phase change heat. After a comprehensive study on these different kinds of PCM, considering their performances of melting point, latent heat, reversibility, toxicity, price and operability, mixed fatty acids were chosen as main substance for this study.

The preparation of PCM was as follows: according to the required ratio, all components were accurately weighed and ground into homogeneous fine powder in a mortar and

then loaded into a copper tube. The copper tube was sealed with a cap. Seven identical copper tubes were needed.

The materials used for PCM are decanoic acid and lauric acid. Decanoic acid: 98.5 %, melting point at 31 °C. Lauric acid: 99.8 %, melting point at 43–44 °C. The composition of mixture has important effect on PCM'S performance like latent heat, reversibility. We determined the weight proportion of decanoic acid and lauric acid was 3:7 by a large number of experiments.

TA5000-type differential scanning calorimeter (DSC) measurements were performed to measure the phase change latent heat and specific heat of the prepared PCM.

2.3 Natural gas charging and discharging experiment

2.3.1 PCM distribution in the adsorption tank

PCM distribution in the adsorption tank is shown in Fig. 1.

Because of copper (whose thermal conductivity is 401 W/(m K), only second to that of Ag) having good thermal conductivity, relatively low price and easy-to-processing properties, it is chosen to be the PCM container.

Size of absorption tank

Height: 400 mm; inside diameter 60 mm. Volume of tank: 1130 ml

360 g adsorbent was loaded in the tank (black dots in Fig. 1 stands for adsorbents).

Size of copper tube

Height: 350 mm; outside diameter: 6 mm. Volume of 7 tubes: 69.20 ml. Ratio of volume tube/tank: 6.1 %.

9 g PCM was loaded in each tube and the total PCM was 63 g.

After being filled with PCM and sealed, the copper tubes were distributed evenly inside of adsorbent in the adsorption tank. One was in the center other six were equidistant around the center and 20 mm away from the center.

Placement of thermocouple

From top to bottom, five thermocouples were placed along the vertical central axis of the tank to measure the temperature change. The distance between two thermocouples was 85.5 mm. They were labeled as:T1, T2, T3, T4, T5 in the following Figs. 6, 7 and Tables 3 and 4.

2.3.2 Experimental process

Temperature changes during the charging and discharging were determined by an evaluation apparatus built by the author's laboratory capacities (Fig. 2).

Natural gas in the high pressure cylinders was decompressed and firstly passed through a purification tank whose function was to pre-adsorb some minor components like H_2O and H_2S in natural gas and secondly passed through mass flow meter, before entering the adsorption tank which was described in Sect. 2.5.1, Fig. 1. The flow chart of CH_4 adsorption and desorption was shown in Fig. 2. The inlet valve 1 controlled the filling speed. When pressure was up to intended pressure, the inlet valve 1 was closed and the outlet valve 6 was opened to exhaust gas till atmospheric pressure. Desorption volume was measured by mass flow meter 7. Temperature changes during the adsorption–desorption process were measured by five thermocouples distributed along the axial direction in the adsorption tank 4.

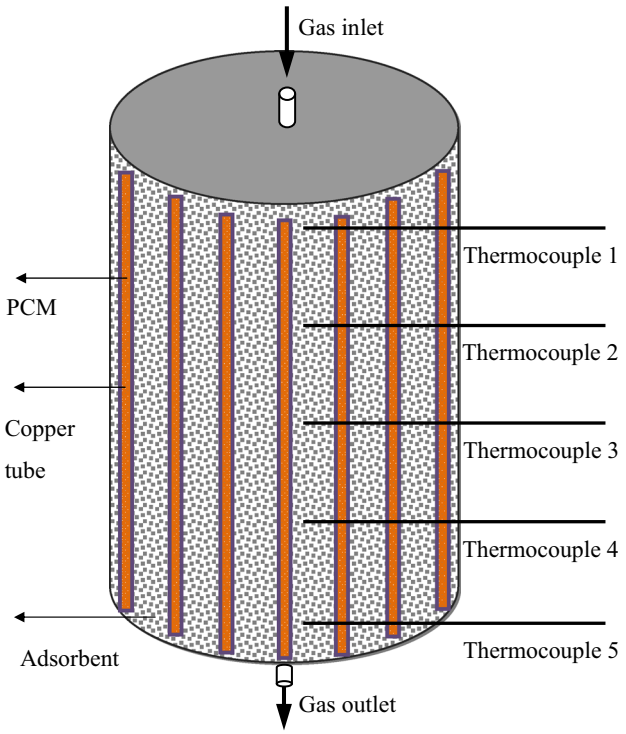
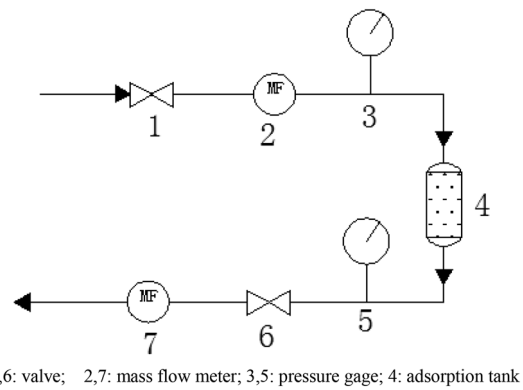


Fig. 1 Distribution of PCM in adsorption tank



1,6: valve; 2,7: mass flow meter; 3,5: pressure gage; 4: adsorption tank

Fig. 2 Flow chart of natural gas adsorption and desorption

3 Results and discussion

3.1 Isosteric heat of adsorption of methane

The gravimetric adsorption capacity of methane on adsorbent prepared in author' lab at 3.5 MPa, 25 °C was 0.136 (m/m) (Li et al. 2003).

Adsorption isotherms

Methane adsorption isotherms at different temperatures are presented in Fig. 3.

CH_4 capacity (v/v) increases with increasing pressure, but decreases with increasing temperature. Adsorption isotherm type belongs to type I which matches the type of Langmuir adsorption equation, we can use this equation to calculate the saturated adsorption capacity.

Langmuir equation:

$$\frac{P}{Q} = \frac{P}{Q_{\max}} + \frac{1}{Q_{\max} b}$$

P: pressure MPa, Q: CH_4 capacity(v/v), Q_{max}: CH_4 saturated capacity(v/v), b: adsorption equilibrium constant.

Take 25 °C as an example, (P/Q) was graphed as P to obtain a straight line, the reciprocal of slope of the line is $Q_{max,25\ °C}$. $Q_{max,25\ °C} = 251.5$(v/v)

Clausius–Clapeyron equation:

$$Q_d = \frac{RT_1T_2\ln(P_2/P_1)}{T_2 - T_1}$$

Q_d: isosteric heat of adsorption, R: gas constant, T: temperature, P: adsorption pressure.

Using data in Fig. 3 and Clausius–Clapeyron equation, Q_d can be obtained from one certain constant adsorption capacity corresponding to two temperatures and two pressures on two adsorption isotherms. Isosteric heat of adsorption of methane in different temperature ranges was calculated and presented in Table 2.

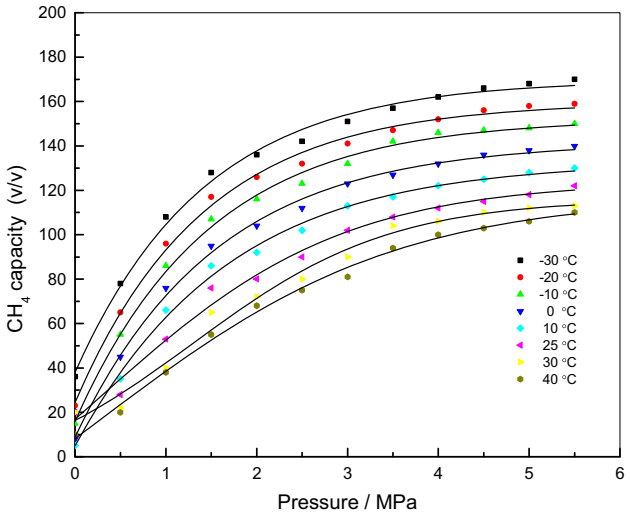


Fig. 3 Methane adsorption isotherms at different temperatures

The average isosteric heat of adsorption of methane was 13.3 kJ mol^{-1}, i.e., 831.3 J g^{-1} (Molecular weight of CH_4 = 16 g mol^{-1}).

3.2 Specific heat of adsorbent

Specific heat of adsorbent was measured with differential scanning calorimeter (DSC) TA5000-type USA. Relationship between Specific heat (C_p) and temperature (T) was presented in Fig. 4.

From the points in Fig. 4, we obtained a fitting equation between Cp and T as follows,

$$C_p = 28.14 - 0.06T - \left(7.47 \times 10^5\right)/T^2$$

Room temperature (T = 298 K) substituted into the formula, it can be obtained C_p = 1.85 J/(g K of the prepared adsorbent at room temperature.

3.3 DSC of prepared PCM

Figure 5 shows the DSC of the PCM.

Since PCM is a mixture of multiple ingredients, the phase transition temperature is not determined by a point. Its melting heat also shifts with respect to the pure phase change agents. As can be seen from the DSC diagram, the melting range is between 20 and 50 °C. The phase change heat of the PCM is 153 J/g.

3.4 Temperature change during the charging and discharging

With the apparatus in Fig. 2 and according to the procedure of 2.5.2 experimental process, the fast charging (5 min) experiment without PCM (Fig. 6) and slow discharging (60 min) experiment without PCM (Table 3) were firstly investigated. The fast charging (5 min) experiment with PCM (Fig. 7) and slow discharging (60 min) experiment with PCM (Table 4) were secondly investigated.

Compared with Figs. 6 and 7, temperature in Fig. 7 significantly reduced.

Compared with Tables 3 and 4, temperature changes in Table 4 are significantly reduced, T5 is most obvious (from 68.6 to −6.5 °C without PCM; from 53.1 to 16.2 °C with

Table 2 Isosteric heat of adsorption of methane in different temperature range

Temperature	Qd (kJ mol^{-1})
243–293 K	13.6
253–273 K	13.4
293–313 K	13.1
323–353 K	12.9

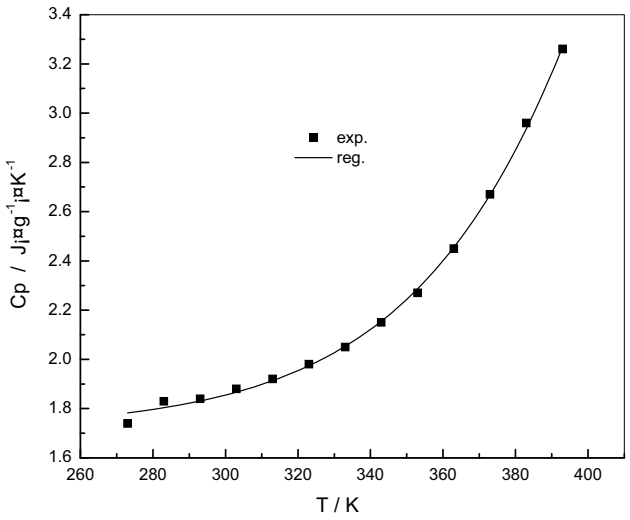


Fig. 4 Specific heat (C_p) and temperature (T) of the adsorbent

PCM). The amount of delivered natural gas was also greatly increased. Table 5 gave the results of temperature changes during charging and discharging in the case of with PCM and without PCM.

As can be seen from Table 5, with the utilization of PCM, the highest temperature during the adsorption is reduced from 85.6 to 63.8 °C; and the lowest temperature in the desorption is increased from −6.5 to 16.2 °C; it achieved approximately 28(99-71)L more natural gas desorbed than in the case without PCM from 0 to 3.5 MPa of adsorption pressure, the increased percentage is 39.4 %.

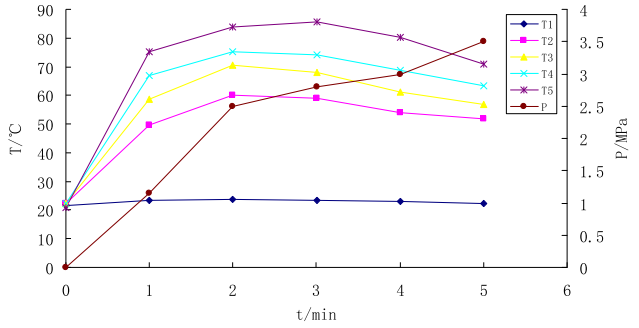


Fig. 6 Fast charging (5 min) without PCM

Energy balance calculations

Take charging course as example,

[Without PCM]

$Q_{\text{heat of adsorption}} = Q_{\text{sensible heat of adsorbent}}$

360 g × 0.136(g/g) × 831.3(J/g) = 360 g × 1.85 J/(g °C) × Δt_1

$\Delta t_1 = 61$ °C

The theoretical temperature was 86 °C (room temperature 25 + Δt_1 61);

The actual highest temperature was 85.6 °C in the experiment.

[With PCM]

$Q_{\text{heat of adsorption}} = Q_{\text{sensible heat of adsorbent}} + Q_{\text{latent heat of PCM}}$

360 g × 0.136(g/g) × 831.3(J/g) = 360 g × 1.85 J/(g °C) × Δt_2 + 63 g × 153 J/g $\Delta t_2 = 46.6$ °C

Fig. 5 DSC of PCM

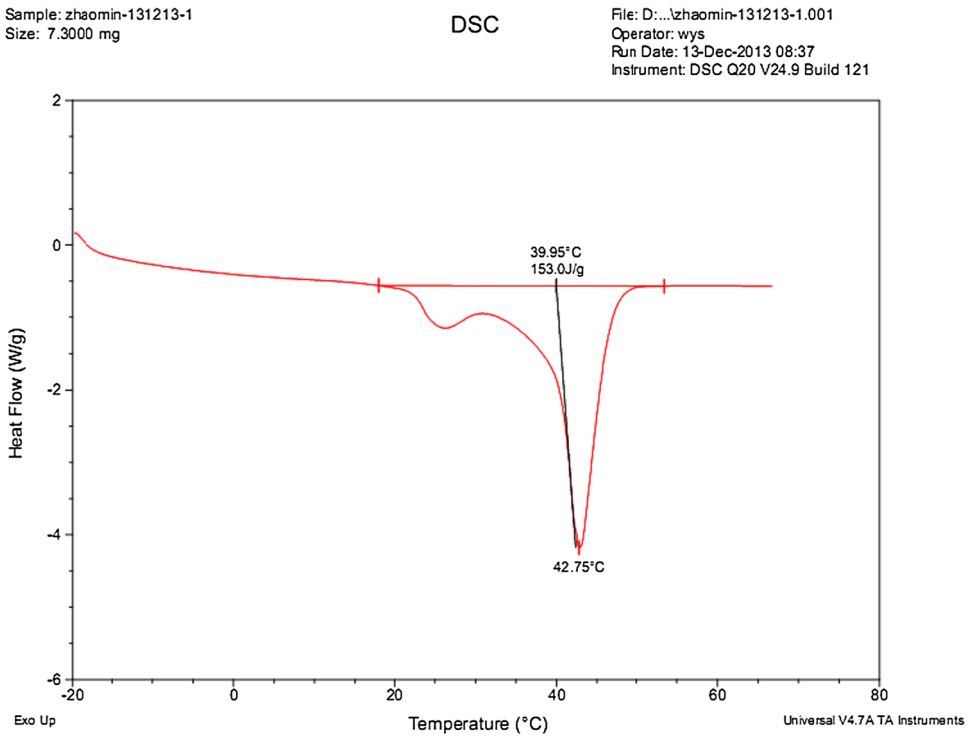


Table 3 Slow discharging (60 min) without PCM

t (min	0.5	5	10	15	20	25	60
P (MPa)	3.45	1.40	0.60	0.20	0.10	0.02	0
T(°C)							
T1	26.3	20.5	19.6	19.0	18.6	17.0	21.5
T2	55.2	40.3	23.7	16.1	11.2	3.71	22.2
T3	56.3	40.0	21.9	16.2	11.0	2.7	22.1
T4	56.1	39.7	22.0	13.3	9.2	1.0	22.0
T5	68.6	49.6	19.3	7.3	−1.5	−6.5	19.9
Flow (L)	0	21	42	53	59	64	71

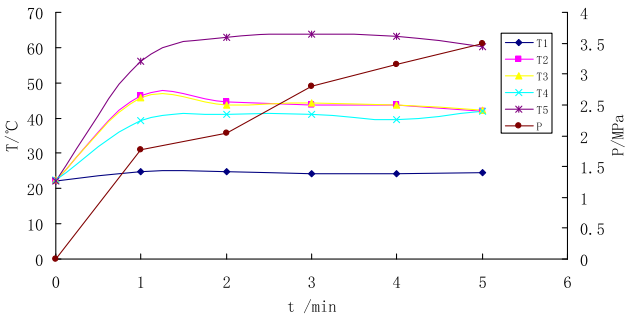


Fig. 7 Fast charging (5 min) with PCM

Table 4 Slow discharging (60 min) with PCM

t (min)	0.5	5	10	15	20	25	60
P (MPa)	3.40	2.55	0.95	0.26	0.15	0.05	0
T(°C)							
T1	24.2	23.0	23.2	23.0	23.1	23.0	23.0
T2	38.7	34.1	24.2	22.2	21.7	21.1	24.1
T3	38.8	34.0	24.6	23.3	22.5	21.0	23.3
T4	38.1	34.2	25.5	24.9	23.1	21.3	23.4
T5	53.1	41.7	23.7	18.0	16.9	16.2	21.9
Flow (L)	0	19	52	78	88	96	99

Table 5 Comparison of without PCM and with PCM

Item	Highest T (°C)	Lowest T	Delivered gas (L)
Without PCM	85.6	−6.5	71
With PCM	63.8	16.2	99
difference	21.8	22.7	28

The theoretical temperature was 71.6 °C(room temperature 25 + Δt_2 46.6);

The actual highest temperature was 63.8 °C in the experiment.

As can be seen from the above data, the PCM can significantly damp temperature changes during the process of adsorption and desorption, thereby significantly improve the released volume of natural gas. This indicates that adding PCM into the adsorption tank is an effective method to reduce the adverse effects of adsorption heat in the ANG technology.

4 Conclusions

The methane gravimetric adsorption capacity, volumetric adsorption capacity, saturated volumetric adsorption capacity, isosteric heat of adsorption are 0.136(m/m), 115(v/v), 251.5(v/v), 831.3 J g^{-1} respectively on the adsorbent produced in the study at 3.5 MPa, 25 °C. The component of the prepared PCM are decanoic acid and lauric acid, the melting range is between 20 and 50 °C and the phase change heat is 153 J/g measured by DSC.

By adding the volume ratio of 6.10 % of the PCM into the adsorption tank, the highest temperature can be reduced by 21.8 °C during the adsorption. The lowest temperature during the desorption can be increased by 22.7 °C. The amount of delivered natural gas can be increased by the volume ratio of 39.4 % than in the case without PCM from 0 to 3.5 MPa of adsorption pressure. This indicates that adding PCM into the adsorption tank is an effective method to dampen the adverse effects of adsorption heat, thereby enhancing the utilization efficiency of natural gas without introducing additional energy.

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