九州大学大学院総合理工学報告
第29巻　第2号　300-306頁　平成19年12月

Engineering Sciences Reports, Kyushu University
Vol. 29, No. 2, pp. 300-306, DEC. 2007

A New Apparatus for Measurement of Adsorption Isotherms and Heat: Activated Carbon and Methane Pair

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(Received July 9, 2007)

We have developed a new apparatus for the measurement of adsorption isotherms on the basis of desorption method between two equilibrium states, and the enthalpy of adsorption at constant adsorbate, pressure and temperature conditions. The adsorption isotherms of methane on highly porous activated carbon (Maxsorb-III) over a temperature ranging from 278 to 333K and pressures varying from 0.1 to 2.0 MPa have been measured experimentally by the newly developed apparatus. The experimentally measured isotherm data are fitted in Dubinin-Astakhov (DA), Langmuir and Tóth isotherm models, extrapolated up to 5 MPa and agreed well within the acceptable uncertainty limits. The results are also compared with the studies of similar specimens previously conducted by other researchers using different adsorption measurement methods and found to be fairly consistent.

Key words: *Desorption method, Adsorption isotherms, Isosteric heat of adsorption, Methane, Activated carbon*

1. Introduction

For the last few years, several countries are trying to promote natural gas to be a dominant fossil fuel in order to combat greenhouse gas emissions. Comparing with the other fossil fuels, natural gas has the advantage of being clean during burning and after burning no ash particles are left. It also plays a vital role for a clean environment because it has relatively lower emissions of sulphur, carbon and nitrogen. In transport sector, compressed natural gas (CNG) is familiar. But the problem with CNG is that high pressure is required which results in higher costs. Adsorbed natural gas (ANG) can overcome this problem because it can operate at low pressure and thus storage tank thickness can be reduced substantially which may lead to substantially lower cost. Methane is the main ingredient of natural gas. The physical adsorption characteristics of methane into any adsorbent are the deciding factor of the performance of the ANG. In this context, many researchers are working in adsorption of methane on microporous solids[1-11]. A perfect adsorbent that will maximize methane uptake per storage volume should have higher micropore volume and surface area. Activated carbons having surface area > 1000 m^2/g and micropore volume > 1.0 cc/g are the most suitable adsorbents among other adsorbents. In this experiment, Maxsorb III specimen is chosen to be a suitable adsorbent for methane as this has a Brunauer-Emmet-Teller (BET) surface area of around 3200 m^2/g and micropore volume of 1.7 cc/g.

In general, adsorption parameters are obtained through different measurement techniques such as volumetric methods[12-14], gravimetric methods[15-17] or magnetic suspension methods[5, 11] etc. In this study, we have introduced a new and quick experimental procedure for extracting adsorption parameters, which is named as desorption method. The operating principle of this method is different from the other general methods. Desorption method can evaluate the adsorption characteristics at a relatively lower cost and reduce errors in data reduction. By this method, one can also calculate the isosteric heat of adsorption by varying pressure and temperature at constant concentration.

2. Adsorption Measurement Methods

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A brief description of the general techniques of measuring adsorption parameters are presented in the following sub-sections.

2.1 Volumetric method

The volumetric or constant volume variable pressure (CVVP) apparatus is equipped with a gas supply chamber, an adsorption cell, a gas cylinder and a number of valves. To measure the pressure inside the supply chamber and adsorption cell capacitance manometers are used. Similarly resistance temperature detectors (RTD) are used to measure the temperature inside the two chambers. Prior to the experiment, it is needed to depressurize the whole setup to remove any pre-adsorbed or inert gases. In this method, the gas is charged first to the supply chamber and then to the adsorption cell. The adsorbent is kept inside in the adsorption cell. The function of the supply chamber is to measure the amount of gas which is charged from the cylinder before adsorption. Then the gas is adsorbed in the adsorbent cell. The amount of the gas adsorbed is obtained from the difference between the mass of adsorbed adsorbent and the mass of dry adsorbent. H.T. Chua et al.[12] used volumetric method and measured adsorption characteristics of water on RD type silica gel. The volumetric method is useful because it is simple, easy to operate and do not require sophisticated high tech equipment. But the demerits of this method are: it is an indirect method so the possibility for occurring an error is higher. Another problem is that it is time consuming and the isosteric heat of adsorption cannot be measured directly.

2.2 Thermo-gravimetric (TG) method

This method is based on the principle of the change of mass of adsorbent, as a function of time and is carried out with a resolution thermogravimetric analyzer which is equipped with a platinum pan and a temperature controller, and programmed automatically. Prior to the experiment, the setup is evacuated to eliminate any pre-adsorbed gases. The initial weight of the adsorbent is recorded. The gas is allowed to pass to the adsorbent cell. The difference between the final weight of the adsorbed adsorbent and the initial weight of the adsorbent gives the mass of uptake of gas. TG provides quantitative measurement of mass change in materials associated with transition and thermal degradation. Using TG method, D. Pan et al.[15] evaluated adsorption parameters of argon on activated carbon. One of the main merits of this method is that this is a direct method so there is a little possibility for occurring an error and also this method is very quick. The disadvantage of TGA method is that TG instrument is very expensive and the isosteric heat of adsorption cannot be measured directly. Error may also occur due to buoyancy effect which is needed to be corrected.

2.3 Magnetic suspension method

In magnetic suspension method, a crucible is suspended to a permanent magnet. Due to electromagnet, the permanent magnet is kept in suspension state. The electromagnet is hanged from the hook of an analytical balance. The position of the permanent magnet is fixed by a sensor core, sensor coil and a controller. Since the position of the permanent magnet is kept fixed, the force exerted to the analytical balance is equal to the weight of the crucible-adsorbent-adsorbed phase system. In the adsorption chamber, the crucible, the coupling system and the permanent magnet are located. During experiment, the gas is charged into the adsorption chamber. Using magnetic suspension method, M.G. Fre`re et al.[11] measured adsorption isotherms of N_2, CH_4 and C_3H_8 on activated carbon. The advantage of magnetic suspension balance method is that it is used for the measurement of adsorption characteristics of corrosive gases (NH_3, SO_2, NO_x etc.) on porous materials. It is a direct method so there is also a little possibility for occurring an error. The disadvantage of this method is that there is a chance for mechanical disturbance during the installation of the setup, which ultimately causes errors. The isosteric heat of adsorption cannot be measured directly by this method.

3. Experimental Sections

3.1 Materials

The Kansai Coke Company supplied the activated carbon (Maxsorb III specimen) which is labeled as MSC-30. The specifications of the adsorbent are shown in the Table 1.

3.2 Experimental setup

The schematic diagram and the photograph of the experimental setup are shown in Fig. 1 and Fig. 2, respectively. The Maxsorb-III specimen is packed in an adsorption cell which is of cylindrical shape. The physical dimensions

of the adsorption cell are listed in Table 2. The Maxsorb-III specimen has a mass of 65.66 g and net packing density of 0.31 g/cc. The nominal stainless steel of thickness (t) 0.635 mm and inner diameter (ID) of 4.35 mm is used to make the external plumbing, and the total volume of the internal plumbing is estimated to be 13.1 cc. All valves are of Swagelok SS 304 type. A salient feature of the unit is that the cell temperature can be measured directly by hanging the thermo well that consists of fine capillary from the top flange and nipping at the cell end. For temperature measurement, a thermocouple is put inside the well.

3.3 Instrumentation

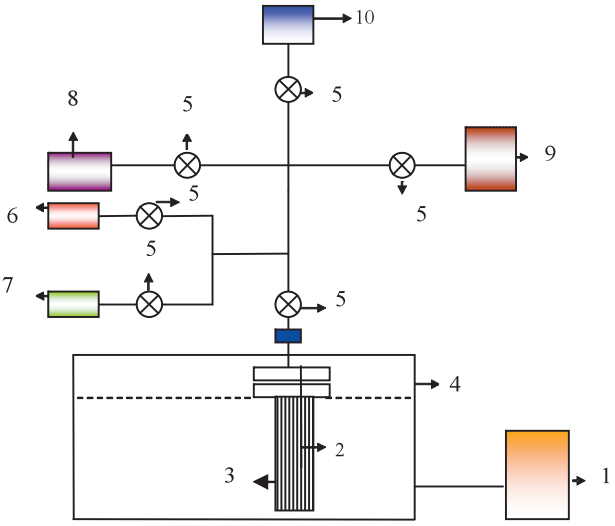
The instrumentation consists of a mass flow regulator, a pressure transducer, several K type thermocouples, a water circulating bath and a data acquisition system. The mass flow regulator (Kojima-Kofloc-5100) has a flow capacity of 10 SLPM (at 20˚C and 1 atm) and measurement uncertainty of ±1% of full scale (1.67 cc/s). The pressure transducer (Kyowa-PGS-50KA) has an uncertainty measurement of ±0.1% of full scale. A number of K type thermocouples are used to measure the temperatures of the cell, the ambient and the water bath where the entire cell is kept inside. Data are recorded using a data acquisition system (Keithtly 2700). To control water flow and temperature, a water circulating bath is used which has a stability of 0.1˚C.

Table 1 The Specifications of the assorted activated carbon

Property	Value
BET Surface area	3140 m^2/g
Micropore volume	1.7 cc/g
Mean particle diameter	72 μm
Ash content	< 0.1%
Moisture	< 0.8%
pH	4.1

Table 2 Physical dimensions of the adsorption cell

Property	Value
Cylinder ID	30 mm
Cylinder depth	300 mm
Cylinder volume	212 cc
Maximum pressure tolerance capacity	50 bar
Maximum temperature tolerance capacity	150˚ C



1: Water circulator, 2: Thermocouple well, 3: Adsorption cell, 4: Temperature controlled water bath, 5: Regulating valve, 6: Pressure transducer, 7: Vacuum gauge, 8: Vacuum pump, 9: Mass flow regulator, 10: Cylinder containing methane

Fig. 1 Schematic diagram of the experimental setup

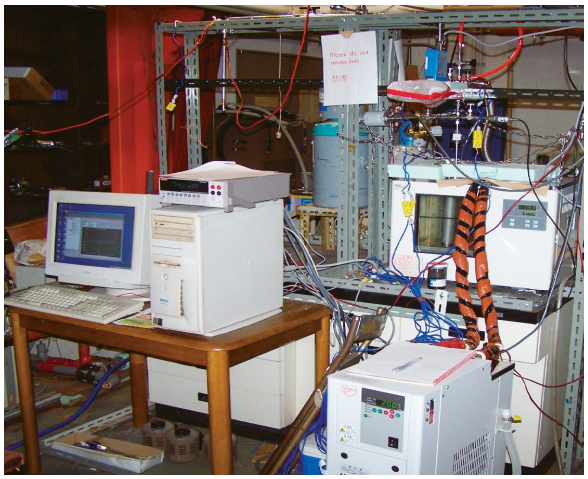


Fig.2 Photograph of the experimental setup

3.4 Experimental procedures

Prior to the experiment, evacuation is needed to remove any pre-adsorbed gases remaining in the system. For this reason, degassing is performed for 3 to 5 days using a vacuum pump until the pressure in the cell reaches at 25 Pa and at the same time the cell temperature is raised at 75˚C in the water bath. Methane was flushed in the cell and degassed at heated condition. Methane was charged again at 5˚C and then evacuated while the cell

temperature was raised from 5 to 75°C. This process of flushing and degassing were continued few times to ensure that the remaining gas is only methane.

Experiments are conducted in two ways. In the first way, methane is charged slowly in the cell at a temperature of 5-10°C. When equilibrium attains, the temperature of the cell is raised isosterically to the desired temperature. As a result, both pressure and temperature are increased and are collected to obtain isosteric heat of adsorption. When the cell achieves equilibrium at the desired temperature, the pressure at that point is referred as initial pressure (p_i) before desorption. Desorption is then started by opening the valve just above the cell and the valve near the mass flow regulator. As a result, pressure started falling. When the flow rate reaches at a value where errors are like to occur, both valves are closed. Therefore, the pressure inside the cell is raised. When pressure is stabilized, another bout of experiment is started. This is repeated several times to get as much gas out as possible. When flow is no longer measurable, the process is stopped. After desorption, the pressure of the cell is raised again and achieves equilibrium which is referred as final pressure (p_f). In the second way, methane is adsorbed in the cell at a given temperature and after reaching equilibrium desorption was started at that temperature.

3.5 Data reduction

The initial data of flow rate, the cell temperature and pressure are collected and they are time dependent. The flow data are directly reduced to standard liters desorbed by numerical integration of the flow record and converted to total mass desorbed using standard conditions specified by the flow meter manufacturer. This desorbed mass is required to be corrected for the void volume in the cell[18]. There are two types of void, one is for cell void and other for pipeline void. Void volume is calculated by assuming that adsorption occurs in the micropores of the assorted adsorbent:

$$V_{void} = V_{cell} - m_{ac} / \rho_s - m_{ac} V_{micropore} \tag{1}$$

Therefore the desorbed mass will be as follows:

$$M_{void-cell} = V_{void}[\rho_{cell-initial}(p_i, T_{des}) - \rho_{cell-final}(p_f, T_{des})] \tag{2}$$

$$M_{void-pipe} = V_{void}\left[\begin{array}{l}\rho_{pipe-initial}(p_i, (T_{des} + T_{amb})/2 \\ -\rho_{pipe-final}(p_f, (T_{des} + T_{amb})/2\end{array}\right] \tag{3}$$

The density data of methane are collected from NIST.

4. Theoretical Analysis

In this study, the experimental data are fitted with Langmuir, Tóth and Dubinin-Astakhov (DA) isotherm equations and the isotherm equations are shown by Eq. (4), Eq. (5) and Eq. (6), respectively[19]:

$$\frac{C}{C_o} = \frac{k_0 \exp\left(Q_{st}/RT\right) p}{1 + k_0 \exp\left(Q_{st}/RT\right) p} \tag{4}$$

$$\frac{C}{C_o} = \frac{p}{\left[\dfrac{k_0\sqrt{MT}}{\exp\left(Q_{st}/RT\right)} + p^t\right]^{1/t}} \tag{5}$$

$$W = W_o \exp\left[-\left\{\frac{RT}{E}\ln\left(p_s/p\right)\right\}^n\right] \tag{6}$$

where $W = Cv_a$, with va being the adsorbed phase volume. In the present study, v_a is investigated in three different ways. In the first way, no volume corrections, so the Eq.(6) becomes,

$$C = C_o \exp\left[-\left\{\frac{RT}{E}\ln\left(p_s/p\right)\right\}^n\right] \tag{7}$$

In the second way, v_a can be written as,

$$v_a = v_b \exp[\Omega(T - T_b)] \tag{8}$$

where Ω = 0.0025 which is taken from Himeno et al.[14], and in the third way, Ω =1/T. Since, Ω is supposed to represent isosteric expansion coefficient of the adsorbed volume, the above equations (Eq.4,5 and 6) can be expressed to the following for desorption at a given temperature between initial and final pressures (pi and pf):

$$\Delta C_{T_{des}} = C_o \left[\frac{k_0 \exp\left(Q_{st}/RT_{des}\right) p_i}{1 + k_0 \exp\left(Q_{st}/RT_{des}\right) p_i} - \frac{k_0 \exp\left(Q_{st}/RT_{des}\right) p_f}{1 + k_0 \exp\left(Q_{st}/RT_{des}\right) p_f} \right] \quad (9)$$

$$\Delta C_{T_{des}} = C_0 \left[\frac{p_i}{\left(\frac{k_0 \sqrt{MT_{des}}}{\exp\left(Q_{st}/RT_{des}\right)} + p_i^t \right)} - \frac{p_f}{\left(\frac{k_0 \sqrt{MT_{des}}}{\exp\left(Q_{st}/RT_{des}\right)} + p_f^t \right)} \right] \quad (10)$$

$$\Delta C_{Tes} = \frac{W_0}{v_a} \left[\left(\exp\left(-\left(\frac{RT_{des}}{E} \ln\left(p_s/p_i \right) \right)^n \right) - \exp\left(-\left(\frac{RT_{des}}{E} \ln\left(p_s/p_f \right) \right)^n \right) \right) \right] \quad (11)$$

The experiments are performed in the super critical range, so we have used a pseudo-relation to obtain the saturation pressure p_s at the desired desorption temperature [20],

$$p_s = (T/T_c)^2 \, p_c \quad (12)$$

5. Results and Discussion

Fig. 3 depicts the adsorption isotherms of methane on Maxsorb-III at three different temperatures (10, 45 and 75˚C), where pressure varies from 0 to 6000 kPa. The Dubinin-Astakhov (DA) isotherm model has been used to fit these data. It is found from Fig. 3 that our experimental data match well with the results of Himeno et al.[14]. In ref.[14] the volumetric method has been used to measure the isotherms. It is also seen from Fig. 3 that the maximum uptake of methane for DA model is about 0.22 kg/kg which is fairly consistent with the maximum uptake data of Himeno et al.[14]. The Langmuir (Eq. 4) and Tóth (Eq. 5) isotherm models also agree well with the present experimental data. The adsorption isotherms of methane on Maxsorb-III using Langmuir and Tóth models at three different temperatures (25, 45 and 75˚C) and pressures varying from 0 to 6000 kPa are shown in Fig. 4. It is noticeable from Fig. 4 that the maximum uptake of methane for Langmuir and Tóth models are about 0.208 and 0.207 kg/kg, respectively. The parameters of DA, Langmuir and Tóth models for methane + Maxsorb-III system are regressed from our experimental data and these are furnished in Table 3.

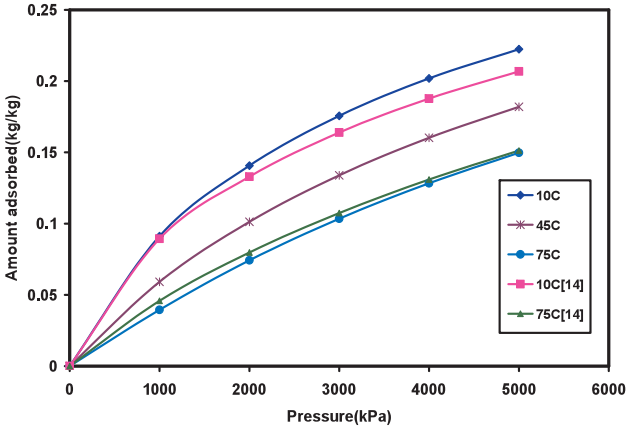


Fig. 3 Isotherm of methane on activated carbon using DA model

The effect of isosteric heat of adsorption on adsorbate (methane) uptake is shown in Fig. 5. It is found from Fig. 5 that using Langmuir and Tóth models, one can observe the straight line behavior of isosteric heat of adsorption for adsorbate (methane) uptake, which indicates the average value of isosteric heat of adsorption. The values of isosteric heat of adsorption for Langmuir and Tóth models are listed in Table 3. It is also observed from the Fig. 5 that the isosteric heat of adsorption decreases with increasing adsorbate (methane) when DA model is applied. The Maxsorb-III consists mainly of micropores with different width and methane adsorbs rapidly onto sites of high energy, and as adsorption progresses, molecules adsorb onto sites of decreasing energy. The methane molecules first penetrate into narrower pores of Maxorb-III, resulting in a stronger interaction between methane and Maxsorb-III. This implies a higher value of isosteric heat of adsorption at lower loading. After completely filling the smaller pores, methane molecules are gradually accommodated in larger pores, in which the adsorption affinity becomes weaker. Therefore a monotonic decrease in isosteric heat of

adsorption as a function of adsorbate (methane) uptake is observed in Fig. 5.

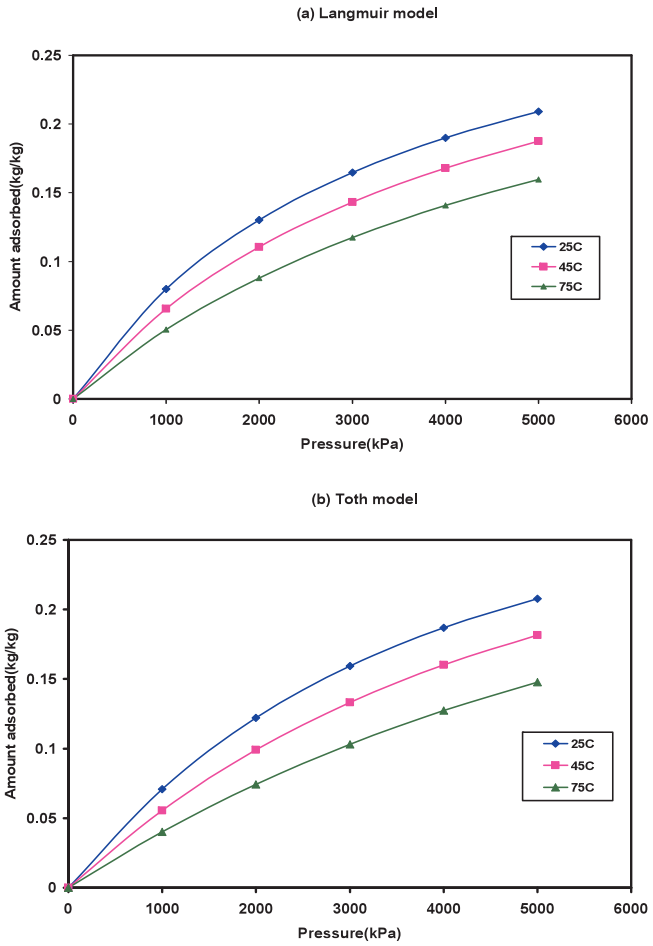


Fig. 4 Isotherm of methane on activated carbon; (a) Langmuir model; (b) Tóth model

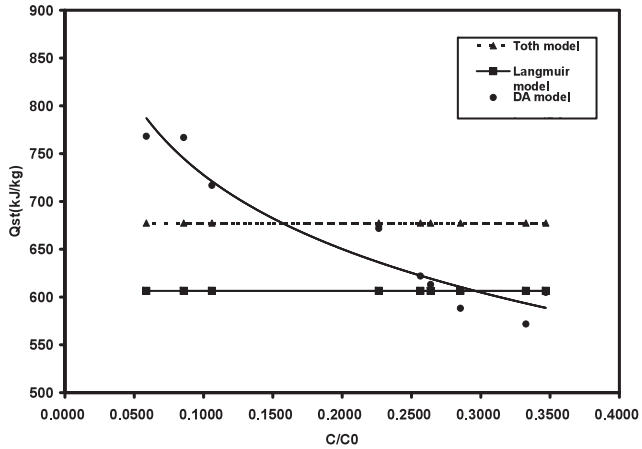


Fig. 5 Isosteric heat of adsorption varying with concenration

Table 3 Adsorption parameters for various isotherms

Parameters	Dubinin-Astakhov	Langmuir	Tóth
Limiting uptake	W_0 = 1.17 cm^3/g	C_0 = 0.35 kg/kg	C_0 = 0.33 kg/kg
Activation coefficient	E = 320 kJ/kg		
Heterogeneity constant	n = 1.42		
Pre-exponential coefficient		k_0 = 5.8×10^{-6}	k_0= 3×10^{-6}
Isosteric heat of adsorption		Q_{st} = 606 kJ/kg	Q_{st} = 677 kJ/kg
Tóth constant			t =1.25

6. Conclusions

A new experimental setup for measuring adsorption characteristics has been constructed. Using desorption method, we have experimentally measured adsorption isotherms and isosteric heat of adsorption of methane on activated carbon (Maxsorb–III specimen). Dubinin- Astakhov (DA), Langmuir and Tóth isotherm models are applied to fit the experimental data and the fitted values are found to be fairly consistent within the experimental errors. The present data of adsorption isotherms and isosteric heat of adsorption are useful in designing environmental friendly adsorption cooling and storage systems.

Nomenclature

V_{void}	void volume	m^3
V_{cell}	cell volume	m^3
m_{ac}	mass of activated carbon	kg
ρ_s	solid density	kg/m^3
$V_{micropore}$	micropore volume	m^3/kg
$m_{cell\text{-}void}$	mass of void cell	kg
$m_{pipe\text{-}void}$	mass of pipe void	kg

$\rho_{cell\text{-}initial}$	initial cell density	kg/m^3
$\rho_{cell\text{-}final}$	final cell density	kg/m^3
T_{des}	temperature at desorption	˚C
T_{amb}	ambient temperature	˚C
Q_{st}	isosteric heat of adsorption	kJ/kg
R	universal gas constant	kJ/kg-K
k_o	pre-exponential coefficient	
M	molecular weight	kg/kmol
T_c	critical temperature	˚C
t	Tóth constant	
E	activation coefficient	kJ/kg
p_c	critical pressure	kPa
p_s	saturation pressure	kPa

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