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**Research Article**

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# Study on pore characteristics of coal based on mercury injection liquid nitrogen method

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**Abstract** The problem of coal and gas is an important problem in the process of coal mine safety production in China, It is helpful to the extraction of coal seam gas and the prevention of coal and gas accidents by Carrying out research on the gas adsorption characteristics of coal. With the increase of mining depth, the metamorphic degree of coal increases. It is of great significance to study the pore structure characteristics of high rank coal for gas control in deep coal seam.

**Keywords** Supercritical $CH_4$; Gravimetric method; Absolute adsorption capacity; Pore characteristics; Adsorption model

## 1. Introduction

As a porous medium, coal has a strong adsorption capacity [1]. Methane (also known as gas), as the main component of coalbed methane, exists in the pores and fissures of the coal seam and surrounding rock in the free state, the adsorbed state and the absorbed state. Among the three states, methane mainly exists in the coal matrix in the adsorbed state On the surface of particles and micropores, the adsorbed methane occupies about 80% ~ 90% of coal [2-3]. Due to the unique existence of methane in the coal body and its combustion and explosion characteristics, coal and gas accidents have become an important factor restricting the production and development of coal resources in China. At the same time, methane is also a clean energy and a good chemical raw material, and has broad application prospects. At present, China's oil and natural gas resources are in short supply and CBM reserves are abundant. In 2018, China's CBM resources proved to be 304.63 billion cubic meters [4]. In-depth research on the mechanism of coal and gas adsorption characteristics is of great significance for the effective development and utilization of coalbed methane resources and prevention of coal and gas accidents in mines.

Since the 21st century, scholars at home and abroad have gained a new understanding of the model of coal adsorption methane. Collins et al. [5] proposed a comprehensive adsorption theory based on thermodynamics and comprehensive dynamics, thermodynamics and potential energy theory. When the adsorption equilibrium is reached, the surface of the adsorbent is a single layer of adsorption, and the outside of the surface of the adsorbent is a liquid-like phase, a filled gas phase, and a free phase in the environment. Xiao Shuyue [6] used a simplified local density model to study the adsorption of gas in nanoscale pores. From the perspective of mechanics, Zhu Jie [7] et al. Established a mechanical model of adsorption-desorption deformation to describe the characteristics of coal deformation during adsorption. Jiang Wei [8] described the comprehensive model of coal adsorption of methane through the theory of adsorption potential. Based on the theory of adsorption potential, Zhang Qun et al. [9] proposed a T-P comprehensive adsorption model for coal adsorption characteristics of methane. Yue Jiwei et al. [10] predicted the adsorption isotherm of coal through the T-P model and believed that the adsorption isotherm of coal had a good prediction effect through the T-P model.

## 2. Study on microscopic pore structure characteristics of coal samples

### 2.1 Selection of experimental coal samples and testing of basic parameters

On-site collection of three coal samples from Hebi No. 8 Coal Mine (HB), Jiaozuo Jiulishan Coal Mine (JLS), Anyang Longshan Coal Mine (LS), and a coal crusher was used to crush the above coal samples in the laboratory, and the screen size was 0.18-0.25mm, 3-6mm coal samples, placed in a drying oven to dry for 6 hours. According to GB / T212-2008 "Industrial Analysis Methods of Coal", the coal samples with particle size of 0.18-0.25mm were selected for industrial analysis. The industrial analysis results of coal are shown in Table 1.

**Table 1:** Industrial analysis results

| Coal sample number | $M_{ad}$/% | $A_{ad}$/% | $V_{ad}$/% | $F_{ad}$/% | Deterioration |
|---|---|---|---|---|---|
| HB | 1.17 | 15.64 | 15.33 | 67.86 | Lean coal |
| JLS | 1.20 | 14.31 | 6.43 | 78.06 | No. 3 anthracite |
| LS | 1.16 | 16.30 | 5.58 | 76.96 | No. 2 anthracite |

The metamorphism degree of coal samples is divided according to the standard of GB / T5751-2009 "China Coal Classification". From the industrial analysis results of coal in Table 1, it can be seen that the three coal samples are all highly metamorphic coal, of which Longshan coal sample It has the highest metamorphism and belongs to No. 2 anthracite. Jiulishan coal sample is less metamorphic than Longshan coal sample and higher than Hebi coal sample. Among the three coal samples, the Hebi coal sample has the lowest metamorphism and is a lean coal.

### 2.2 Study on the pore structure characteristics of coal samples

Coal is a porous medium composed of pores and fissures and coal molecular framework, with a developed pore structure [11]. The microscopic pore structure of coal is the main reason for the coal's adsorption of methane. Therefore, the study of microscopic pore structure is of great significance for the adsorption, desorption and diffusion of methane in coal.

There are many methods for classifying pores in coal. Common classification methods include classification according to the cause of pores, pore size, and pore structure. In this section, pores in coal are mainly classified according to the size of the pores. According to the pore size classification, the pores in coal can be divided into micropores, transition pores (small pores), mesopores, and macropores. Among them, micropores and small pores have a large specific surface area, which determines the adsorption capacity of coal, and methane migrates in it through diffusion; mesopores, macropores, and visible pores and cracks determine the permeability of coal. A slow infiltration movement occurs in the pores, and the methane seepage capacity in the large pores is stronger than that in the middle pores, mainly due to severe laminar and turbulent flow [12]. Researchers at home and abroad have differences in the size of the pores due to the different research purposes and experimental methods. The common pore structure division methods are shown in Table 2 [13].

**Table 2:** Pore size classification of coal (unit: nm)

| Researcher | Propose time | Micro pores | Small pores | Middle pores | Big pores |
|---|---|---|---|---|---|
| Hodot | 1961 | <10 | 10～100 | 10～100 | >1000 |
| Gan | 1972 | <12 | —— | 1.2～30 | >30 |
| IUPAC | 1978 | <2 | 2～50 | —— | >50 |
| Grish | 1987 | <2 | —— | 2～50 | >50 |
| WANG | 1992 | <1000 | —— | 1000～10000 | >10000 |
| QIN Y | 1994 | <15 | 10～50 | 50～450 | >450 |
| ZHAO Z | 2000 | <7.5 | 7.5～200 | 200～2000 | >2000 |
| Yiwen | 2005 | <15 | 15～100 | —— | >5000 |

For the division of pore size, this article mainly adopts the Hodot classification method used more in the coal industry, namely:

Micropores: Pore diameter below 10nm, constituting coal adsorption volume;

Small pores: also called mesopores, the pore size is between 10 and 100 nm, and together with micropores constitute the adsorption volume of coal;

Mesopores: the pore size is between 100 and 1000nm, and methane penetrates slowly through laminar flow in coal;

Macropores: The pore size is between 1000 and 100,000 nm, and the methane laminar flow penetrates the motion area vigorously;

Visible pores and fissures: the permeation area of laminar and turbulent methane in coal with a pore size greater than 100,000nm.

**2.3 Low-temperature liquid nitrogen adsorption method to measure pore structure**

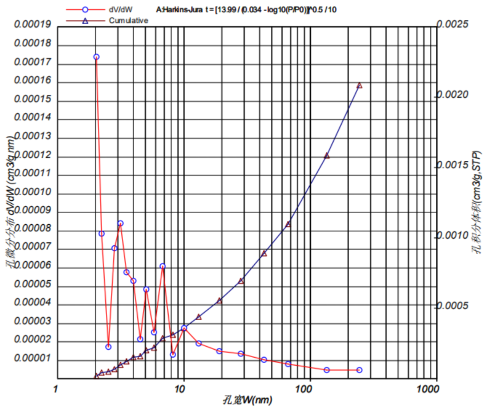
The equipment used in the experiment is the V-Sorb 2800TP specific surface area and pore size analyzer produced by Beijing Jine Spectrum Technology Co., Ltd., as shown in Figure 1. The instrument uses liquid nitrogen with a temperature of 77k as the adsorbate for adsorption experiments, and the measured pore size range is 2-375nm. The specific surface area of coal was measured by Langmuir method and BET method, and the pore volume and pore size distribution of coal were analyzed by BJH method.


*Figure 1: V-Sorb 2800TP specific surface area and aperture analyzer*

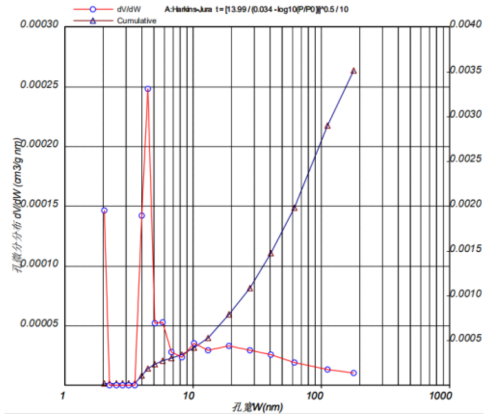
The coal samples of HB, LS, and JLS 0.18-0.25mm were selected, and after vacuum treatment at 150 ºC for 6h, the low temperature liquid nitrogen adsorption experiment was carried out on the three coal samples. The specific surface area and liquid nitrogen adsorption-desorption measured by the experiment The curves are shown in Table 3 and Figure 2 respectively:

**Table 3:** Pore development of coal samples (liquid nitrogen method)

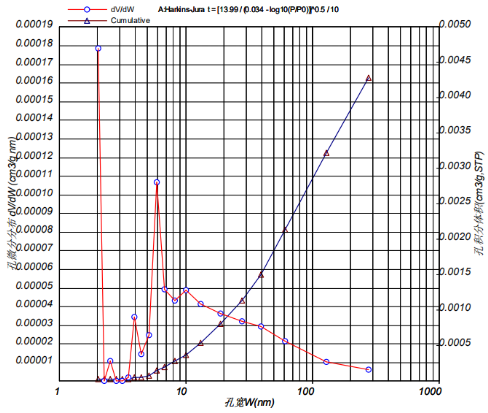
| Coal sample name | BET Specific surface area ($m^2/g$) | BJH Pore volume ($cm^3/g$) | BJH Average pore diameter (nm) | Pore volume ratio (%) | | | Specific surface area ratio (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Micro pores | Small pores | Middle pores | Micro pores | Small pores | Middle pores |
| HB | 0.344 | 0.00208 | 18.583 | 17.18 | 58.73 | 24.09 | 73.11 | 25.06 | 1.83 |
| JLS | 0.719 | 0.00351 | 24.918 | 11.88 | 70.48 | 17.64 | 56.36 | 41.21 | 2.43 |
| LS | 0.988 | 0.00428 | 33.01 | 8.3 | 66.91 | 24.79 | 45.64 | 51.43 | 2.93 |




(a) Adsorption curve of liquid nitrogen and pore size distribution of HB coal sample




(b) Adsorption curve of liquid nitrogen and pore size distribution of JLS coal sample




(c) Adsorption curve of liquid nitrogen and pore size distribution of LS coal sample

*Figure 2: Adsorption - desorption of low temperature liquid nitrogen and pore size distribution curve of coal sample*

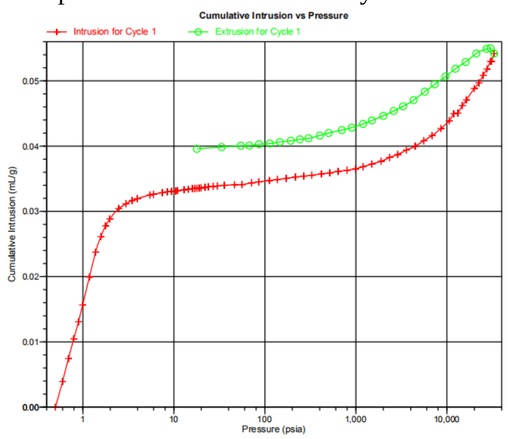
The research shows that the isothermal adsorption curves of the three coal samples to liquid nitrogen belong to the type II adsorption isotherms. As can be seen from the adsorption curve in Figure 2, the entire adsorption process can be roughly divided into three stages: when the relative pressure is below 0.4, the isotherms of the three coal samples are convex upward, which shows that all three coal samples There is a certain amount of micropores. At this time, the coal sample is mainly single-layer adsorption and gradually transitions to multi-layer adsorption. When the relative pressure is between 0.4 and 0.8, the adsorption capacity of the three coal samples will increase slowly with the increase of pressure, indicating that the nitrogen molecules have entered the multi-layer adsorption stage in the coal body. When the relative pressure is greater than 0.8, as the pressure increases, the adsorption isotherm is significantly convex and rapidly rising, indicating that capillary condensation occurs inside the coal sample pores, indicating that there is a certain amount of mesopores and macropores in the coal sample.

### 2.4. Measurement of pore structure by mercury intrusion method

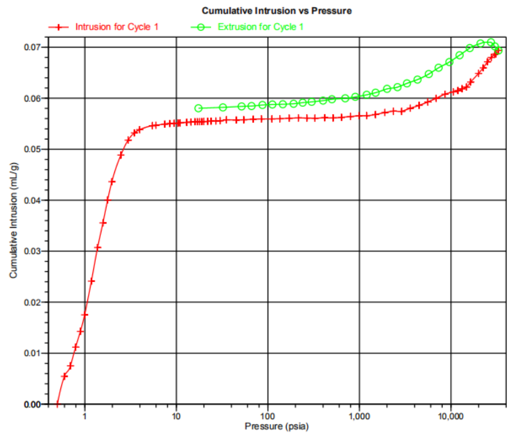
The experiment uses the AutoPore IV9500 mercury intrusion instrument. As shown in Figure 3, the instrument has 2 high-pressure stations and 4 low-pressure stations. The mercury inlet pressure range is 0.5-33000 psia, and the measured pore size range is 0.003μm-1000μm. , The pore volume, specific surface area, pore size and pore structure distribution in coal can be obtained.

*Figure 3: AutoPore IV9500 mercury injector*

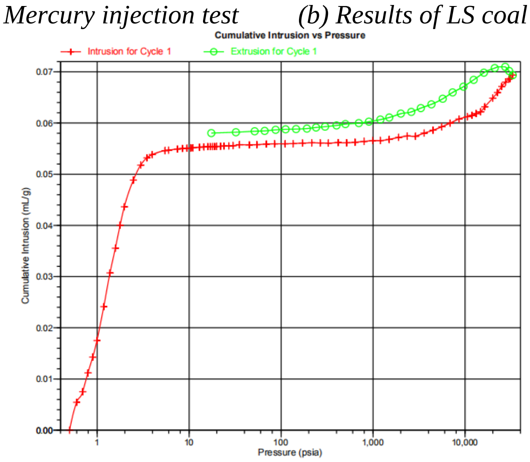
The experimental results of mercury intrusion of three coal samples are shown in Figure 4 and Table 4.




*(a) Results of HB coal sample Mercury injection test*




*(b) Results of LS coal sample Mercury injection test*




(c) JLS results of J LS coal sample Mercury injection test

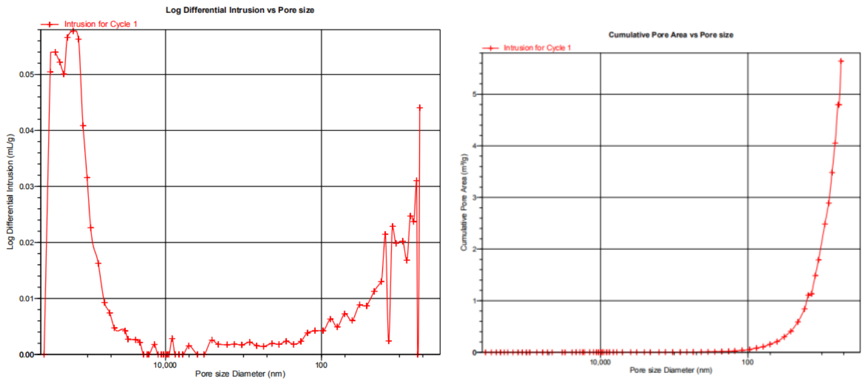
*Figure 4: Mercury injection and mercury withdrawal curves of coal samples*

**Table 4:** Pore structure characterization of coal samples in mercury injection experiment

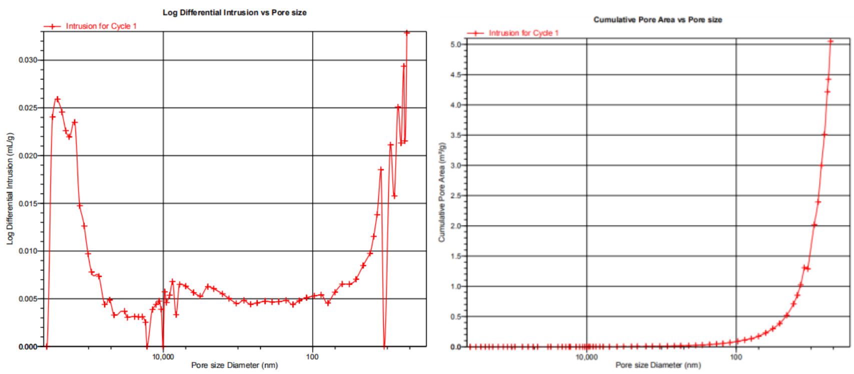
| Coal sample name | Specific surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Pore volume ratio (%) | | | | Specific surface area ratio (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Micro pores | Small pores | Middle pores | Big pores | Micro pores | Small pores | Middle pores | Big pores |
| HB | 5.640 | 0.0542 | 13.1 | 17.34 | 4.98 | 64.58 | 68.25 | 31.06 | 0.62 | 0.07 |
| JLS | 4.347 | 0.0693 | 8.8 | 9.24 | 1.01 | 80.95 | 73.73 | 25.88 | 0.32 | 0.07 |
| LS | 5.051 | 0.0399 | 17.54 | 19.05 | 11.28 | 52.13 | 74.1 | 24.53 | 1.19 | 0.18 |

As the mercury inlet pressure increases, mercury will preferentially fill large pores in coal pores and then enter mesopore pores. As the pressure further increases, mercury gradually enters the micropores and pores. The measured mercury ingress and demercuration curves of the three coal samples are shown in Figure 4. When the pressure is less than 0.035MPa, the mercury ingress curves of the three coal samples rise rapidly, indicating that the large pores in the coal sample are well developed. The mercury entry curve grows slowly in the medium pressure area (0.035 ~ 35MPa), which indicates that the number of pores in the hole is small, making the mercury entry curve rise slowly. When the mercury inlet pressure is greater than 35MPa, the curve rises rapidly and steadily, which indicates that there are more micropores and small pores in the pores. The hysteresis loop in the mercury withdrawal process indicates that the pore connectivity of the LS coal sample and the JLS coal sample is stronger than that of the HB coal sample. The three coal samples are mainly open pores, and the pores above the large pores are continuously distributed. The three coal samples showed a slight increase in the curve during the mercury removal process. It may be that as the pressure decreased, a small number of closed micropores in the coal body reopened under the action of high pressure, indicating that the number of micropores measured during the experiment It is less than the actual number of micropores.

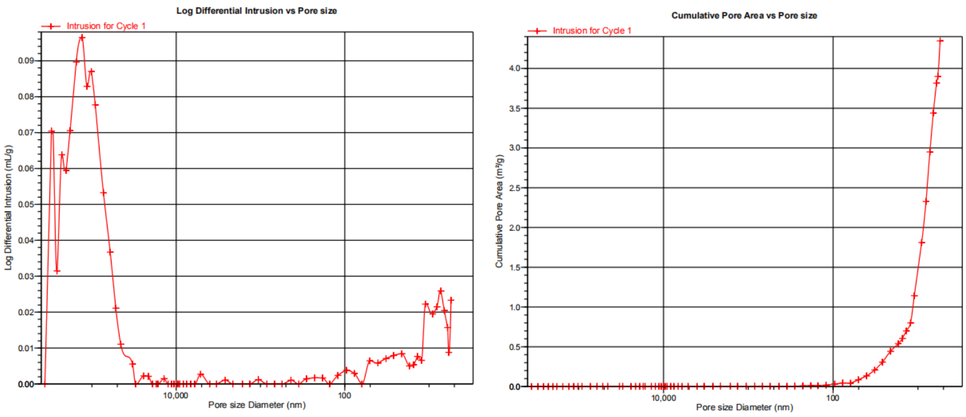
Under the action of external pressure, mercury can invade the capillary channels of the coal body. During the intrusion process, the capillary channels of coal will cause resistance to mercury. Given the pressure P of mercury entering the outside world, the corresponding pore size r can be calculated according to formula. Different pressures correspond to different pore sizes. The pore volume and specific surface area distribution are shown in Figure 5.




*(a) Diagram of mercury injection volume increment, specific surface area and pore diameter of HB coal sample*




*(b) Diagram of mercury injection volume increment, specific surface area and pore diameter of LS coal sample*




*(c) Diagram of mercury injection volume increment, specific surface area and pore diameter of JLS coal sample*

*Figure 5: Distribution curves of coal sample volume and specific surface area with pore size*

It can be seen from Figure 5: from the perspective of the volume increment of mercury inlet, the pore volume increment of the three coal samples in the mercury inlet process all presents a "concave" shape distribution, the mercury volume increment is mainly concentrated in the pore size of 50nm In the range below and above 20000nm, the volume of the LS coal sample increases from 100 to 10000nm, indicating that there are some pores with a pore size of 100 to 10000nm in the LS coal sample. From the distribution diagram of pore size and specific surface area, when the pore size is above 100nm, the increment of the specific surface area of the three coal samples is basically 0, and the growth of the specific surface area of the three coal samples is mainly concentrated in the micropores and pores below 100nm Among them, this indicates that the micropores and pores of the coal sample provide the specific surface area of the coal, and the micropores and pores are more abundant in the coal sample.

## 3. Conclusions

From the industrial analysis results of the experimental coal samples, the volatilization of LS, JLS and HB is divided into: 5.58%, 6.43% and 15.33%. The three coal samples are all highly metamorphic coals, and the metamorphisms are HB (lean thin coal), JLS (No. 3 anthracite), and LS (No. 2 anthracite) from low to high.

The results of low temperature liquid nitrogen adsorption experiments on coal show that the three types of coal samples have slit flat pores and ink bottle pores, and the pores have good connectivity. At the same time, there are also semi-closed micropores with poor connectivity. From the analysis of the experimental results, the adsorption capacity of the coal sample to liquid nitrogen is LS> JLS> HB, and the specific surface areas of HB, JLS and LS measured by the experiment are: 0.344$m^2$/g, 0.719$m^2$/g, 0.988$m^2$/g, The pore volume is: 0.00208 $cm^3$/g, 0.00351 $cm^3$/g, and 0.00428 $cm^3$/g. The experimental results show that as the degree of metamorphism increases, the larger the specific surface area and pore volume of the coal measured in the experiment, the stronger the adsorption capacity of the coal for liquid nitrogen.

From the results of mercury intrusion experiments, the ratios of mesopore and macropore volume to total pore volume in HB, LS, and JLS coal samples are: 69.56%, 63.41%, and 81.96%, respectively, and the proportion of micropore surface area is 99.31, respectively, %, 98.63%, 99.61%. The experimental results show that the pore volume in coal is mainly concentrated in mesopores and macropores, and micropores and small pores provide the specific surface area of coal. Mercury-removal curves show that there are a large number of micropores and small pores and a certain amount of macropores in the three coal samples. The connectivity of macropores is good, and the connectivity of micropores and small pores is poor.

Based on the analysis of the results of the mercury injection test and the low temperature liquid nitrogen adsorption experiment, when describing the pore distribution of coal samples, the pore characteristics of micropores and small pores can be characterized by liquid nitrogen, and mesopores and macropores can be characterized by mercury injection The pore structure is characterized. From the results of the joint characterization of the two, it can be seen that micropores and pores with a pore volume accounting for 4.14% to 11.23% of the total pore volume provide a specific surface area of 92.84% to 96.23% in coal, and a specific surface area of 3.77% to 5.16% The pores and macropores occupy 88.77% ~ 95.86% of the pore volume in coal. Experimental results show that micropores and small pores provide the specific surface area of coal, which is the main place for methane adsorption, and mesopores and macropores provide the pore volume of coal, and the main storage place for free methane. The experimentally measured specific surface areas of HB, JLS, and LS were 0.356 $m^2$/g, 0.729 $m^2$/g, and 1.033 $m^2$/g, respectively, which indicated that with the increase of the degree of metamorphism, the specific surface areas of the three coal samples also increased, and the Kong Xiaokong is also more developed.

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