

Utilization of Coal-bed Methane and Oilfield Associate Gas in Carbon Black Industry

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Abstract

The major component of coal-bed methane and oilfield associate gas is methane. The first economic utilization of these gases is to use them as citizen's fuel. The second is to use them as an industrial fuel or raw material in a power plant or a chemical plant. But while the site of the gas source is far from the city or industrial district, and the gases can not or temporary can not be transferred into the network of pipelines. The gas is often vented to the atmosphere directly or through a flare. As an unfortunate result, the energy of the gas is wasted and the atmosphere is polluted by the gas. The scale of a carbon black plant is small and variable, the consumption of electric power and process water is very low, and the transport amount in plant operation is negligible other than the transportation of carbon black product. The investment is relative small and the construction period is short for building of a carbon black plant. It is a good choice for utilization of a scattered and remote gas source with economical and environmental benefit.

China Carbon Black Institute (abbreviated as CCBI hereafter) have successfully developed the technology for using coal-bed methane and oilfield associate gas in carbon black production. There are several commercial plants, designed by CCBI, in operation. The process, product grade and quality, raw material and utility consumption, investment and benefit are introduced briefly in following related projects.

- As raw material in gas furnace carbon black process
- As fuel of reactor in oil furnace carbon black process
- Utilization or incineration of carbon black tail gas
- Use of oxygen-enriched air in gas furnace process,

1. Introduction

The major component of coal-bed methane and oilfield associate gas are methane. Also some air i.e. oxygen and nitrogen is contained in coal-bed methane as coal-bed methane is generally suctioned under negative pressure. Its methane content and heat value are lower. In case of oilfield associate gas, alkane from ethane to pentane, in addition to methane, is also contained in it when it is separated from liquid hydrocarbon. Its heat value is higher as a result.

The first economic utilization of these gases is to use them as citizen's fuel. The second is to use them as an industrial fuel or raw material in a power plant or a chemical plant. But while the site of the gas source is far from the city or industrial

district, and the gases can not or temporary can not be transferred into the network of pipelines. The gas is often vented to the atmosphere directly or through a flare, for the sake of petroleum production and coal mine safety. As an unfortunate result, the energy of the gas is wasted and the atmosphere is polluted by the gas.

As reported by SPDC⁽¹⁾, a hundred million cubic meters of oilfield associate gas are flared every day worldwide in 1996.

Coal-bed methane and oilfield associate gas may be used as feedstock in synthetic ammonia, methanol or formaldehyde plants. But the capacity of these chemical plants must be built in a sufficient large scale with sufficient supply of utilities, communications and transport in the site. The investment is too large and the construction period is too long. So the project of building such plants for utilization of scattered or remote gas source are often infeasible. Compared to the chemical plants mentioned above, the scale of a carbon black plant is small and variable, the consumption of electric power and process water is very low, and the transport amount in plant operation is negligible other than the transportation of carbon black product. The investment is relative small and the construction period is short for building of a carbon black plant. It is a good choice for utilization of a scattered and remote gas source with economical and environmental benefit.

China Carbon Black Institute (abbreviated as CCBI hereinafter) has successfully developed a series of carbon black production technology, as follows, by using coal-bed methane or oilfield associated gas.

- As raw material in gas furnace carbon black process
- As fuel of reactor in oil furnace carbon black process
- Utilization or incineration of carbon black tail gas
- Use of oxygen-enriched air in gas furnace process,

Now several commercial plants are in operation properly by using the technology mentioned above. Thus the direct emission of a large amount of methane has been avoided. Environmental and economical benefit are both achieved. Please see details as follows.

2. Gas Furnace Carbon Black Process

2.1 Using coal-bed methane as raw material

The technology for gas furnace carbon black process using coal-bed methane as raw material has been commercialized in Baijigou Coal Mine, at Shitanjing, Ning Xia. Baijigou Coal Mine, at Shitanjing, Ning Xia, in which the reserve of coal-bed methane is very rich, is located to the north of Yinchun City at the distance of 115km. It is reported, in 1991, in Verification Report of Baijigou Coal Mine Coal-bed Methane Resource made by Fushun Branch of China Coal Science Institute, that the coal-bed methane reserve is $26.6 \times 10^8 \text{m}^3$, among which, $15.96 \times 10^8 \text{m}^3$ is valuable and $3.2 \times 10^8 \text{m}^3$ can be suctioned. A coal-bed methane suction system was begun to set up in Baijigou Coal Mine in 1991. Coal-bed methane sent in pipes, after being suctioned out from drill holes distributed over the upper layer of the coal-bed by water-ring type vacuum pump, to gas-consumption points through gas-water separator. The suction capacity of the coal-bed methane was

50m³/min (7.2×10⁴m³/d, 0.238×10⁸m³/a) in 1996. The suction of coal-bed methane provides the production safety in the coal mine. On the other side, for geographical reason, the demand for coal-bed methane as domestic fuel, particularly in summer, is very limited, the remainder coal-bed methane is vented as waste to the atmosphere, resulting in environment pollution.

Therefore, a 1000t/a Semi-Reinforcing Gas Furnace Black(abbreviated as SRF hereinafter) Plant was designed by CCBI with entrustment of Baijigou Coal Mine. The construction of the 1000t/a carbon black plant was begun in August, 1994 and put into operation in March, 1995. Up to now, the plant has been in operation for more than 8 years, and the actual capacity has been increased up to 1300t/a. The products from the plant meet related National Standards of PRC and consumer's requirement, and sell well.

Further, as coal-bed methane capacity to be suctioned increases, CCBI was contracted to design another 1300t/a SRF Plant in July 2000. This plant was put into operation in June 2001.

This carbon black plant is briefly introduced as follows.

2.1.1 Composition And Heat value of Coal-bed Methane

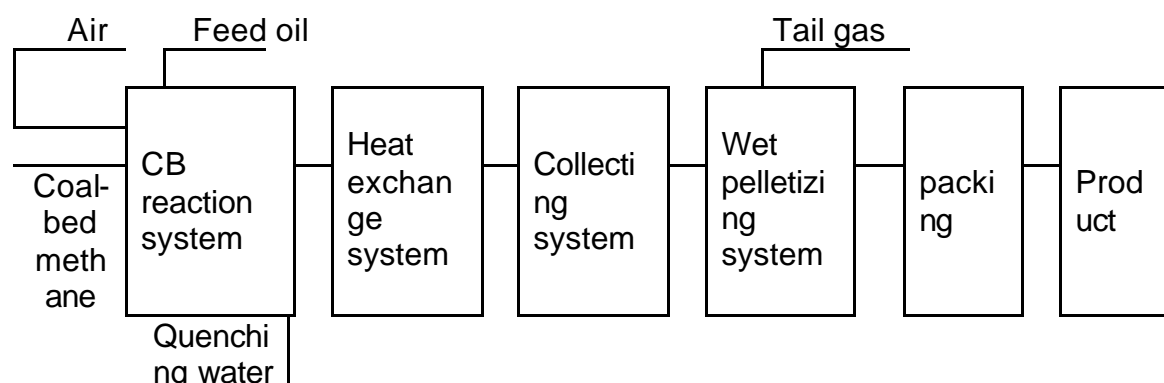
Table 1 Composition of Coal-bed Methane in Baijigou Coal Mine

Composition	O ₂	N ₂	CO	CH ₄	CO ₂	Other
Content (vol.%)	1.54	6.48	--	84.42	1.68	5.88

The heat value is 7226kcal/Nm³.

2.1.2 Process Flow

Flow diagram as follows:



Coal-bed methane and air are sent through special designed-injector to reactor respectively, in which a part of coal-bed methane is combusted and another part is decomposed into carbon black suspended in the hot smoke gas. The carbon black is cooled, collected, pelletized and packaged to be finished products.

Efficient pulse bag filter, which is designed by CCBI, is adopted for collecting system which can efficiently filter and separate carbon black product from the smoke gas to make the carbon black particle content in the tail gas be lower than 18mg/m³ specified in the National Standard of PRC, and it also makes contribution to further utilization of the low heat value tail gas.

2.1.3 Product Quality And Application

According to the data from China National Quality Inspection Center in July 2001, product quality of Baijigou Coal Mine can meet the quality requirement specified in National Standard GB3778-94 Specification of Carbon Black for Use in Rubber Industry, and according to the excellent grade of Natural Gas Semi Reinforcement Furnace Black(SRF). Please see Table 2.

SRF made in China is similar to N724 had been listed in ASTM D1765 ,and close to oil furnace black N754 or Fine Thermal black FT. SRF is characterized by larger particle size and lower structure and suitable for natural rubber and synthetic rubber. Vulcanizate filled with SRF has high elongation, low heat generation, high elasticity and superior aging resistance, and often used in buffer layer and ply of tire carcass, mechanical rubber products for automobile, hose, belt and extruded parts and sheathing for wire and cable.

Table 2 Quality data of SRF produced by Baijigou Plant

Inspection Item			Specification ^a	Tested value
Iodine g/kg	Adsorption	Number,	14±3	16
DBP cm ³ /100g	Adsorption	Number,	47±4	51
pH Value			8.0~10.5	10.2
Heating %		Loss,	≤1.0	0.3
Ash %		Content,	≤0.3	0.3
45µm %	Sieve	Residue,	≤0.10	0.01
150µm %	Sieve	Residue,	---	0.00
500µm %	Sieve	Residue,	≤0.001	0.000
Impurity			None	None
Tensile MPa	Strength	^b ,	≥-4.5	-2.5
Elongation %		^b ,	≥+110	+122
Modulus at 300% Elongation MPa		^b ,	-8.5±1.0	-7.0

*Note : **a** Specification of excellent grade. **b** The physical property data of rubber compound refer to the difference of those between Chinese Industrial Reference Black SRB2.

2.1.4 Raw Material And Power Consumption

According to the operation data of Baijigou plant, if the operation hours of single plant are 7,200h/a and the output is 1,300t/a, the process consumption norm per unit of carbon black product: coal-bed methane (methane content 84% min.) is $6,600\text{m}^3/\text{t}$, equal to $8.58 \times 10^6\text{m}^3/\text{a}$, $1,192\text{m}^3/\text{h}$ and $19.86\text{m}^3/\text{min}$, water is $13\text{m}^3/\text{t}$ and electric power is $645\text{kwh}/\text{t}$. If calculated into pure methane, it would be equal to $7.2 \times 10^6\text{m}^3$. $14.4 \times 10^6\text{m}^3$ of methane emission is reduced per year.

2.1.5 Investment And Benefit



Figure 1 Beihai Carbon Black Plant

Construction capital investment (excluding interests during construction period and active money) for a 1,300t/a SRF plant is about 5.33 million RMB. Calculated on the basis of sale price of 4,000RMB/t, annual sale income is 5.20 million RMB. The cost is about 2,918RMB/t, if calculated as $0.15\text{RMB}/\text{m}^3$ of coal-bed methane (it should be vented even if it is not be used), $1.0\text{RMB}/\text{m}^3$ of water and $0.45\text{RMB}/\text{kwh}$ of electric power. The total cost is 3.79million RMB/year and the gross profit is 1.41 million RMB/year. It can be seen that the carbon black plant is characterized by less investment and higher benefit.

2.2 Using oilfield associate Gas As Raw Material

With gradual development of oil field in China, the source of oilfield associate gas increases. However, a great part of oil fields are located at jumping-off. Oilfield associate gas has to be vented to atmosphere with exploitation of oil.

So it is feasible to use oilfield associate gas to produce carbon black. In recent ten years, CCBI designed progressively five SRF plants for Xinjiang, Guangxi, Mongolia and Shaanxi, total capacity is 20,600T/a. Now Beihai Carbon Black Plant, the largest one, is introduced briefly as follows. Refer to Figure 1. It can be seen that a small part of remainder oilfield associate gas is vented by flare.

China Offshore Oil Nanhai Corporation exploits oil on the sea in Beibu Gulf for more than ten years. At the beginning, oil-gas separation was performed on an oil tanker anchored near the oil field. Oilfield associate gas is emitted on site. In 1999, this Corporation set up an oil-gas separating plant on Weizhou Island, to south of Beihai City in Guangxi Province. Daily output volume of oilfield associate gas is more than 300,000m³. People had suggested several methods to utilize the gas, for example, supplying it to Beihai city to use as citizen gas. But, conveying pipeline on the sea with a distance of 50km should be at priority constructed, it would cause a large investment. Furthermore the oilfield associate gas of Weizhou has a relative quick decreasing tendency. Construction of chemical plant was also considered, but fresh water was not sufficient in the island. In this case, CCBI was contracted to design and construct a SRF plant with capacity of 10,500T/a in 1999. Now it operates properly since being put into operation. As a result, the oilfield associate gas emission of 63×10⁶m³ has been avoided every year.

Composition of oilfield associate gas in Weizhou Oil Field is seen in Table 3.

Table 3 Composition of Oilfield Associate Gas in Weizhou Oil Field

Compositi on	CH ₄	C ₃ H ₆	C ₃ H ₈	IC ₄	NC ₄	N ₂	CO ₂
Volume %	83.9	10.2	1.28	0.02	0.01	2.53	2.0
	1	5					

Process flow of SRF plant in Weizhou is similar to the one in Baijigou. As the scale of plant in Weizhou is much bigger, environment protection condition is of exigency in Weizhou Island when constructing, CCBI made many improvements in design. For example, cooling tower which consumes much fresh water is improved, high efficient improved bag filter is adopted, product is centralized to be packed, DCS is used for automatic control etc. With these measures, more advanced level is achieved for this plant.

Since power from local power station in Weizhou Island is excessive, the tail gas of Wetzhou plant is vented out after being combusted completely in a special incinerator which is designed by CCBI.

3. As Fuel of Reactor in Oil Furnace Black Process

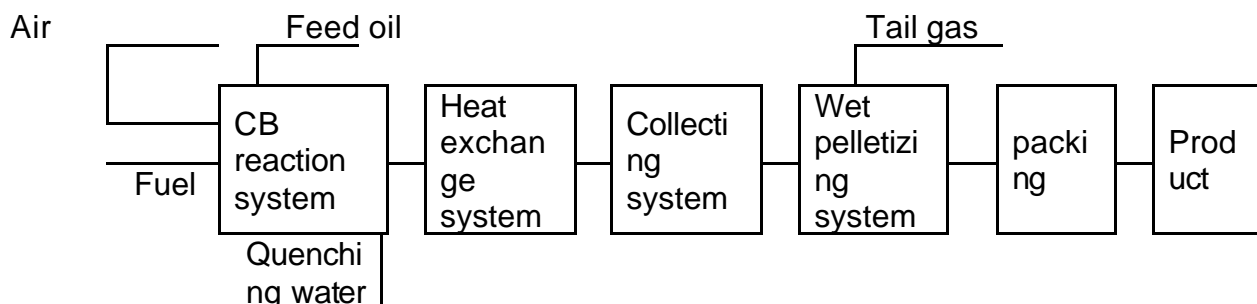
3.1 Using Coal-bed Methane in a 5000t/a Oil Furnace Black Plant

Taking into consideration the local demand for carbon black and feed oil supply, Baijigou Coal Mine entrusted CCBI to design a 5,000t/a new technology oil furnace black plant in September 1995. In this plant, a new technology reactor is used, in this reactor, combustion of fuel and decomposition of feed oil are separated.

The principle of process is as follows: Fuel and preheated air flow, in axial direction, into the upstream of the reactor to produce high speed high temperature combustion gas stream in the combustion chamber. And then, feed oil is injected, in radial direction, into the reactor through the throat, and the oil drops are sheared, vaporized, and decomposed into carbon black by the high speed high temperature combustion gas. In such a way that the output and yield of carbon black will be increased evidently as compared with the traditional

carbon black reactor. Generally, the oil of higher price is used as fuel in the most oil furnace black plant in China. In order to utilize coal-bed methane of Baijigou sufficiently, coal-bed methane is used as fuel in the carbon black reactor, and some improvements have been made, such as the development of a new burner and regulating of some process parameters, in this plant designed by CCBI.

Brief flow diagram as follows:



Quality and yield of carbon black product by using coal-bed methane as fuel are not inferior to the one by using oil as fuel in similar plant. According to the inspection data from China National Carbon Black Quality Inspection Center in July 2001, quality of carbon black product N326 of Baijigou Coal Mine meet the quality requirement specified in National Standard GB3778-94 Specification of Carbon Black for Use in Rubber Industry. Please see Table 4.

According to production of different grade of carbon black, coal-bed methane demand is 300~500m³/h. Coal-bed methane consumption is about 430~500 m³ per ton of carbon black. Coal-bed methane consumption is totally about 2.325×10⁶m³ for a 5000t/a plant, corresponded to 2.0×10⁶m³ pure methane emission is reduced per year.

According to the heat balance, the substituted carbon black feed oil will be 2,000 ton per year. Generally, the same oil is used as feed oil and fuel oil of a carbon black plant. Since the feed oil price is 1,300RMB/t at present time, the coal-bed methane price is 0.15RMB/m³, then 2.25 million RMB will be saved per year, the economic benefit is significant.

Table 4 Quality data of N326 produced by Baijigou plant

Inspection Item			Specificatio n ^a	Data
Iodine	Adsorption	Number, g/kg	82±5	79
DBP	Adsorption	Number, cm ³ /100g	72±5	69
CTAB,		10 ³ m ² /kg	78~88	89
Tinting Strength,		%	107~117	109
Heating Loss,		%	≤2.5	0.3
Ash Content,		%	≤0.5	0.1
150μm Sieve Residue,		%	--	0.01

Impurity		None	None
Tensile Strength ^b ,	MPa ≥	+1.0	+1.6
Elongation ^b ,	% ≥	+40	+76
Modulus at 300% Elongation ^b ,	MPa	-3.0±1.0	-4.6

**Note : a Specification of excellent grade. b The physical property data of rubber compound refer to the difference of those between Chinese Industrial Reference Black SRB2.*

3.2 Using Natural Gas in a 15,000t/a New Technology Carbon Black plant

Technology for using natural gas in more than 10,000t/a New Technology Carbon Black plant was developed by CCBI. The first 15,000t/a commercial plant applied this technology was constructed in CCBI, and successfully operated from March 2001. It was technically certified by State Economy & Trade Committee. After operation for more than two years, it is proved that the process parameters and product quality are more stable, the impurity content of carbon black product is very few compared with the process using oil as fuel. If calculated as per heat value, the price of natural gas is lower than oil in Sichuan, so cost can be reduced. Because the major composition of natural gas is methane too, hence there is no technic problem to use coal-bed methane or oilfield associate gas as a substitute of natural gas.

Typical (N339 taken as example) process parameters and consumption norm of this plant are as follows :

--- Major process parameters

Natural gas: 465Nm³/h

Feed oil: 2,850kg/h

--- Consumption norm of raw material and utilities:

Natural gas: 265Nm³/t

Feed oil: 1,654kg/t

Additive: 0.008kg/t

Water: 10.25m³/t

Electric power: 480kwh/

4. Utilization or Incineration of Carbon Black Tail Gas

Carbon black tail gas is a combustible gas with low heat value. It contains CO, H₂ and a small amount of other contaminates such as carbon black particulate. Emission of this gas directly into atmosphere is not appropriate for the environment protection. So CCBI has developed the technology of utilization and incineration of carbon black tail gas. The major part of this technology is development of a specialty boiler using low heat value carbon black tail gas, to generate steam for supply of steam or power generation. This work was completed by boiler manufacturers and CCBI.

CCBI has designed 16 sets of power plant or boiler using the tail gas. 12 sets of them are in operation and others are in construction.