Technology and application of concentrating methane from low-concentration coal mine gas to produce natural gas

Sichuan DKT Energy Technology CO., LTD.
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As a clean and eco-friendly high-quality energy, natural gas’s proportion in China’s energy consumption structure is low (the world average is 23.9%), conventional natural gas production is far below market demand, and the contradiction between supply and demand is obvious.
In 2013, natural gas consumption in China was 167.6 billion cubic meters, of which import volume was 53 billion cubic meters, accounting for 31.6%.
Introduction

Its safe recovery means a great supplement to conventional natural gas.
Introduction

20-30 billion cubic meters of gas has been discharged each year along with coal mining. Equivalent to approximately 350-525 million tons of CO2 greenhouse gas. If fully recovered to produce clean energy, it is equivalent to 20-30 million tons of refined oil.

2000m-deep shallow CBM geological resource is approximately 36.8 trillion cubic meters, mainly distributed in the north and northwest China. CBM drainage methods are sorted to pre-drainage before mining and draining while mining. CBM content of pre-drainage before mining exceeds more than 90%, but the drainage volume is small, the method draining while mining is mainly used, thus the most drained CBM is featured by low methane content and high oxygen & nitrogen content, safety factor becomes the bottleneck restricting its application.
Introduction

Main Research Direction

Pressure swing adsorption

Cryogenic separation

Gas hydrates

Membrane separation

Solvent absorption

Better choice!
- low energy consumption
- simple technological process
- low capital investment
- low operation cost
After striving to make technological breakthrough for years, Sichuan DKT Energy Technology Co., Ltd successfully developed efficient special adsorbents DKT-612 and DKT-613 for gas adsorption deoxidization and methane separation, as well as a whole set of process safety measures. With such a technology, the company has built an industrial demonstration plant for producing oxygen-containing concentrated CNG and LNG at Sijiazhuang Mine in Xiyang County, Shanxi Province, which has been running safely and stably for nearly two years and a half.
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Characteristics of oxygen-containing gas

High gas content in raw material—the content of underground drained coal mine gas reaches 50000Nm³/h

Low methane content—methane content of most drained methane gas is 10-30%

High oxygen content—oxygen content is generally above 12%, it is necessary to enhance the safety

High dust content—contains a variety of dusts, which are easy to plug pipes and equipment, thus impacting service performance and life of adsorbent materials, and may contain harmful substances such as sulfur and water.

Remote geographic position—other users featured by easy and direct application are unavailable nearby
Process technologies

Process safety guarantee

- Low pressure of the raw material
- Contains lots of impurities, Hydrogen sulfide
- Low methane content in the oxygen-containing methane gas, high flow
- Oxygen: a dangerous factor
  - How to remove $O_2$?
  - How to guarantee safety?
- Concentration needed
- Compression needed

CBM
Process technologies

Process safety guarantee

Deoxidation process technologies

Coke combustion

High Temperature (It is strong exothermic reaction, which needs a 200-300℃ initial temperature. For per 1% oxygen reacted, system temperature would rise by about 150℃)

Catalytic oxidation

Safety (When temperature is higher than a certain value, methane begins to split, and even burn spontaneously, so the safety is not guaranteed.)

PSA and explosion suppression technology

Better choice!!!

√High recovery rate of CH4
√Simple technological process

No Consumption of Methane (Methane and oxygen react at a ratio of 2:1, which will consume 20-30% methane in gas, and even higher, and therefore the natural gas production rate of low content methane gas is low.)
Process technologies

Process safety precautions

Passed safety evaluation of Safety Evaluation Center, Nanjing University of Technology (Grade B qualification) and Chongqing Branch of China Coal Research Institute (Grade A qualification)

Adsorption separation safety: guaranteed by the adsorbents with good thermal and electrical conductivity which can timely transfer the static electricity and adsorption heat

Pipelines and buffer tanks safety: guaranteed by the explosion suppression material with excellent thermal and electrical conductivity

Compression process safety: guaranteed by the special compressors, very small temperature rise and no sparks during compression process.

PSA processes: the former process guarantees the latter process safety, they are closely interrelated.
Process technologies

Process safety precautions
Process technologies

Process safety precautions
The developed special efficient adsorbent for methane separation is nearly 50% higher than the conventional adsorbent for methane separation.
Process technologies

R&D of special adsorbent for methane separation

Adsorption isotherm of DKT-612-type special adsorbent for CH₄ and O₂

High performance deoxidizing adsorbent is able to quickly remove oxygen from gas to ensure safety of methane separation.
Experimental units
It was passed Chinese coal industry technological achievements identification organized by China National Coal Association On December 25, 2010, the technological achievements reached the international advanced level.
Process technologies

Process technology flow

Determined by concentration of methane in CBM
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Industrial demonstration units

Industrial demonstration project on the above process technologies is carried out by Shanxi Ruiyang CBM CO., LTD, size of phase-I is 35 million square meters / year of CNG products, size of phase-II is 50,000 tons / year of LNG products. Currently phase-I has been put into operation, phase-II is under construction. The project is the key project supervised by SASAC Shanxi Branch in 2012, total investment is 310 million Yuan, investment of phase-I is 130 million Yuan, total construction area is about 100,000 m². In June 2011, the project was started, and achieved **successful one-time test run** on September 10, 2012, **official commercial operation** started on September 20.
Industrial demonstration units
Industrial demonstration units
## Industrial demonstration units

### Composition of the low concentration oxygen-containing CBM feed gas

<table>
<thead>
<tr>
<th>Component name</th>
<th>Normal content/vol%</th>
<th>Abnormal content/vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>35 (no less than 30)</td>
<td>20~30</td>
</tr>
<tr>
<td>N₂</td>
<td>53.3</td>
<td>65.3~57.3</td>
</tr>
<tr>
<td>O₂</td>
<td>11.0</td>
<td>12~14</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>saturated</td>
<td>saturated</td>
</tr>
</tbody>
</table>

After concentrating through PAS methane enrichment, PAS deoxidation and PAS denitrification, the feed gas is produced to CNG sale (unit CNG's integrated power consumption is 0.98KWH), **overall methane yield exceeds 95%**, the test results are: **methane content was 98.14vol%, oxygen content was 0.15vol%, nitrogen content was 1.71vol%**, all indexes met or exceeded the design criteria, and successfully realized the goal of concentrating low concentration oxygen-containing gas to produce CNG.
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Technological innovations

(1) Adopt adsorption deoxidation for the first time, the adsorbing materials adsorb oxygen only, but not the methane, methane yield reaches 98% during deoxidation;

(2) as special material, the adsorbent could effectively isolate oxygen and methane during the adsorption deoxidation, as adsorption continues, oxygen content in gas phase decreases, the safety is more effectively guaranteed;

(3) the special adsorbent for separating methane and nitrogen is 40% higher than the traditional ones, featured by low energy consumption in methane separation, high methane content and high methane yield;
Technological innovations

（4）Deoxidation adsorbent and special adsorbent for concentrating methane are featured by good explosion protection and suppression functions, the safety performance is recognized by relevant authority, they are designed to be filled in most non-standard equipment of the unit to ensure intrinsic safety of the separation equipment;

（5）Install explosion suppression materials approved by fire department on the pipelines and buffer devices to ensure safety of the whole unit;

（6）Apply 3-stage (or 2-stage) process integration technology recovering and applied by methane in low concentrations gas to produce CNG or LNG.
Benefit analysis

Phase-I project (separate methane from low concentration gas to produce CNG)

Phase-II project (oxygen-containing CBM liquefy LNG 50,000 tons / year)

Remarkable benefits

Environmental protection benefit
Annually use of 70 million Nm$^3$ of coal mine gas can reduce greenhouse gas emission (converted to 750,000 tons of CO$_2$, 500 tons of SO$_2$, 600 tons of NO$_2$, and 18,300 tons of coal dust)

Economic benefit
After the project is fully completed and put into operation, the annual sales revenue is expected to reach 280 million Yuan, profit is 140 million Yuan, tax is 35 million Yuan

Social benefit
After completion, the project can directly solve local employment for about 100 people, and indirectly solve employment for about 250 people
Benefit analysis

All cost of phase-I

- **Annual amortization of house property and land, amortization period is 30 years**: 125 million
- **Raw materials, management, financial and other cost**: 1650 million
- **Staff cost**: 275 million
- **Power consumption**: 2450 million
- **Equipment annual depreciation, depreciation period is 10 years, net residual value is 2%**: 882 million

Analysis based on all cost of actual production operation of phase-I project.

Annual output of CNG is 35 million square meters, production cost of unit product is 1.538 Yuan / Nm³.
 Benefit analysis

According to actual output of phase-I project, annual output of CNG containing 98% methane is 34.77 million square meters, sales revenue is \(34.77 \times 2.5 = 86.925\) million Yuan.

Annual sales revenue is 86.925 million Yuan

Profit: 33.105 million Yuan
Rate of profit: 38.1%

All cost is 53.82 million Yuan
Conclusions

The world’s first application of PSA technology to remove oxygen in low concentration gas;

Adopt PSA enrichment, PSA deoxidation and PSA denitrification integrated process to obtain CNG products with purity greater than 95vol%;

As oxygen contained in low concentration gas, safety of technology process could be effectively ensured through process design optimization, main process equipment selection, special adsorbent selection, analysis equipment control instrument selection and the use of explosion suppression materials, flame arresters and other measures;

Apply this technology to build a set of industrial demonstration unit for concentrating low-concentration oxygen-containing gas to produce CNG for the purpose of commercial safety operation, and benefit analysis shows that it has significant economic and social benefits.
**Problems**

Efficiency of recovery unit is severely affected by gas flow and content. The raw gas covers a small proportion in the production cost, large construction scale will not reach the desired effect, and small one will easily lead to intermittent direct gas venting;

The overall output value of gas utilization covers a small proportion in output value in coal mines, most coal mines fail to place enough stress on it;

Local government of construction needs to increase support, the corresponding regulations are not sound;

National support for the industry is not enough. Currently, there is no construction units like gas generation obtaining corresponding policy subsidies from the state;

Investment for initial construction is large, financial support for project construction also needs to be put in place.