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Design and security analysis for the liquefaction and distillation process of oxygen-bearing coal-bed methane

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Abstract: Coal-bed methane (CBM) is a new clean energy. Because of the limitation of treating technologies, most of the oxygen-bearing coal-bed methane is not used efficiently and is evacuated immediately, which cause waste of resource and severe pollution of the environment. In order to use oxygen-bearing coal-bed methane efficiently, in this paper, a new liquefaction and distillation process has been proposed. However, the existing research shows that there may be explosion hazard in the liquefaction and distillation process. Therefore, the formulas of the methane explosion limit proposed by Li et al, which is appropriate for low temperature condition, is adopted to analyze the security of the process. Then, in order to guarantee the security of the process, nitrogen as a dilution is added to the distillation column to reduce the oxygen content. At the same time, the flow rate and the inlet location of nitrogen are optimized. Research results indicate that this process can remove nitrogen and oxygen thoroughly. The purity of the LNG product can reach up to 99.91%, the recovery rate of methane is 97.21%, and the energy consumption of per unit LNG production is $0.94 \text{ kW}\cdot\text{h}/\text{m}^3$. In the stages of compression, liquefaction and cold energy recovery, no explosion hazard exists. However, explosion hazard may occur at the top of the distillation column. When a nitrogen flow rate of $50000 \text{ Nm}^3/\text{h}$ is added from the 7th plate of the distillation column, the mole fraction of oxygen in the whole column is less than 8% which is the minimum oxygen concentration. The product purity is 99.87% and the methane recovery rate is 91.35%. However, the energy consumption of per unit LNG production can increase by 38% at the same time.

Key words: oxygen-bearing CBM; liquefaction; explosion limit; safety analysis

Nomenclature

CBM: coal-bed methane	LEL: lower explosion limit
UEL: upper explosion limit	MIX: mixer
C-1, C-2, C-3, C-4, C-5, C-6, C-7, C-8: compressors	LNG: liquid natural gas
E-1, E-2, E-3, E-4, E-5, E-6, E-7, E-8, E-9: coolers	P-1, P-2: pumps
VLV-1, VLV-2, VLV-3, VLV-4, VLV-5: throttle valves	
LNG-100, LNG-101, LNG-102, LNG-103: heat exchangers	
T-100: distillation column	V-1, V-2, V-3: separators
U : upper explosion limit at a certain pressure and temperature, %	
U_{CH_4} : upper explosion limit of methane at normal pressure and temperature, %	
P : initial pressure, MPa	t : initial temperature, °C;
L : lower explosion limit at a certain pressure and temperature, %	
L_{CH_4} : lower explosion limit of methane at normal pressure and temperature, %	
U' : upper explosion limit at a certain pressure and temperature when inert gas exists, %	
L' : lower explosion limit at a certain pressure and temperature when inert gas exists, %	
n_I : the required oxygen mole number when 1 mole methane is consumed	
c_I : mole fraction of methane;	r : mole ratio of inert gas to methane
Exp-Li: explosion limits tested by Li et al.	t_0 : room temperature, °C;
Exp-Karim: lower explosion limit tested by Karim et al.	
Exp-Wierzba: upper explosion limit tested by Wierzba et al.	
Cal: explosion limits calculated by empiric formulas	
a, b, c, d, e, f, g: correlated parameters determined by experimental values	

Introduction

China is rich in coal-bed methane¹ and is the third largest coal-bed methane reserves after Russia and Canada all over the world. The coal-bed methane resources whose burial depth is smaller than 2000 m can be as high as $36.8 \times 10^{12} \text{ m}^3$, which is about thirteen percent of the resources in the whole world. There are mainly two types of coal-bed methane for exploiting: One is the surface extracted coal-bed methane before the coal mining. The methane content is high with the volume fraction exceeding 95%. As a result, it can be transported directly by pipeline or stored in a liquid state, but on a smaller scale. The main cause which influences the surface extraction of CBM is the permeability of the coal seam. The best permeability of the coal seam is $(3\sim 4) \times 10^{-3} \text{ mD}$ but it cannot be lower than 10^{-3} mD . However, in China, most of the coal seams have a low permeability with a range of $10^{-4} \sim 10^{-3} \text{ mD}$ which is lower than 10^{-3} mD . At present, before mining, the surface extraction of the coal-bed methane in this type of coal seam is a technical problem at home and abroad. Another is the extracted coal-bed methane during the coal mining for the safety production of

the coal mine ². The methane content is low with volume fraction of 30%~80% and other content is mainly carbon dioxide and air. The coal-bed methane containing much air is called oxygen-bearing coal-bed methane. Most of them will be evacuated on the spot or burnt by the neighbor plant or resident, resulting in the waste of resource and the pollution of environment. Therefore, there are many benefits to explore oxygen bearing coal-bed methane. One benefit is improving the prevention level of methane accident to guarantee the safety production of the coal mine. Another one is reducing carbon emission to achieve energy conservation and better global atmospheric environment. Meanwhile, as an efficient and clean energy, to commercialize the coal-bed methane can produce large economic benefit.³⁻⁵

The deoxidation of coal-bed methane is a technical problem at home and abroad. At present, the deoxidation technologies mainly include pressure swing adsorption (PSA) ⁶, membranes separation ^{7,8}, combustion ⁹ and cryogenic distillation ¹⁰. Among these, the cryogenic distillation is a rather common method because of the high product purity. The gas composition changes in the stages of liquefaction and distillation. When the gas comes across spark generated by the collision between residual heavy hydrocarbon liquid droplets and dust, or the outside heat source, a combustion accident may occur. The existing research shows that a higher danger stage is the distillation with temperature of -160~-170 °C and pressure of 0.1~0.3 MPa. Particularly, in the top of the distillation column, the methane concentration maybe within the explosion limit which makes the whole equipment has a danger of explosion. Thus, in order to improve the security of the real production, it is necessary to study the explosion risks in the whole liquefaction and distillation process and then adopt safety measures.

Thus, on the basis of the exploitation status of the oxygen-bearing coal-bed methane, firstly, a new liquefaction and distillation process is designed. Then, the formulas of the methane explosion limit proposed by Li et al. ¹¹ which is suitable for low temperature conditions are adopted to evaluate the security of the process. At last, in order to ensure the security of the operation, nitrogen as a dilution is added to the distillation column to reduce the oxygen content. The simulation results can offer

significant guidance for the oxygen separation from oxygen-bearing CBM, the analysis of explosion limits and the security measures for the operation process.

1. New coal-bed methane liquefaction and distillation process design

1.1 Liquefaction and distillation process introduction

An oxygen-bearing CBM liquefaction and distillation process is designed for a typical coal-bed methane gas source, of which content is shown in Table 1. When the oxygen-bearing coal-bed methane is extracted, the gas pressure is about 0.11 MPa which is a little higher than atmospheric pressure and the temperature is 40 °C. After some special handling technologies such as dehydration and deacidification, the gas composition contains only methane, nitrogen and oxygen.

Table 1 Parameters of the oxygen-bearing coal-bed methane

Mole fraction of components/%			Temperature/	Pressure /	Flow rate/
CH ₄	N ₂	O ₂	°C	MPa	kmol/h
40	47.4	12.6	40	0.11	1760

Fig. 1 demonstrates the liquefaction and distillation process which is mainly composed of the liquefaction system as well as the refrigerant system for the CBM. In the liquefaction system, oxygen-bearing CBM is first compressed by compressor C-1 and then cooled by cooler E-1. Secondly, it is compressed again by compressor C-2 and cooled by cooler E-2. As a consequence, the CBM has a high pressure and initial temperature. Thirdly, the high pressure CBM is sequentially cooled and liquefied by heat exchangers LNG-100 and LNG-101. After that, the CBM enters the distillation column T-100, in which the oxygen and nitrogen are separated from the CBM. The liquefied methane from the bottom of the distillation column is first cooled by heat exchanger LNG-101 and then flows through the throttle valve VLV-1. Finally, it will be stored in separator V-2. To reduce the energy consumption of the whole process, the cold energy of the impurity gas is recovered. The impurity gas from the top of the column is first cooled by heat exchanger LNG-103 and then fed into separator V-1. The gases from the top of the separator V-1 is then fed into the heat exchangers LNG-102, LNG-101 and LNG-100 in series to cool the CBM and the refrigerant.

In the refrigeration system, the nitrogen gases are first compressed by four compressors (C-3, C-4, C-5 and C-6) and cooled by water coolers. Then they are fed

into the heat exchanger LNG-100, LNG-101 and LNG-102 in series for further cooling. After that, the nitrogen gases are extracted from VLV-2 to reach a lower pressure and temperature. The low pressure, low temperature nitrogen gases are then fed into the four heat exchangers (LNG-103, LNG-102, LNG-101 and LNG-100) to cool the CBM and the refrigerant. Finally, the temperature of nitrogen returns to ambient temperature and the nitrogen gases are compressed again to finish the refrigeration cycle.

In the mixed refrigerant refrigeration cycle system, the mixed refrigerant is first compressed by compressor C-7 and then fed into separator V-3. In separator V-3, the separation of refrigerant gas and liquid is achieved. The flow rate of the refrigerant liquid is 245.3 kmol/h while the total flow rate of the mixed refrigerant is 2920 kmol/h. The refrigerant gas from the top of the separator V-3 is compressed by compressor C-8 and then mixed with the refrigerant liquid in MIX. After that, the mixed refrigerant is fed into heat exchangers (LNG-100 and LNG-101) and extracted by throttle valve VLV-3 in sequence. Then, the cold mixed refrigerant is fed into heat exchangers (LNG-101 and LNG-100) to cool the CBM and the refrigerant. Finally the mixed refrigerant returns to ambient temperature and a mixed refrigerant refrigeration cycle is finished.

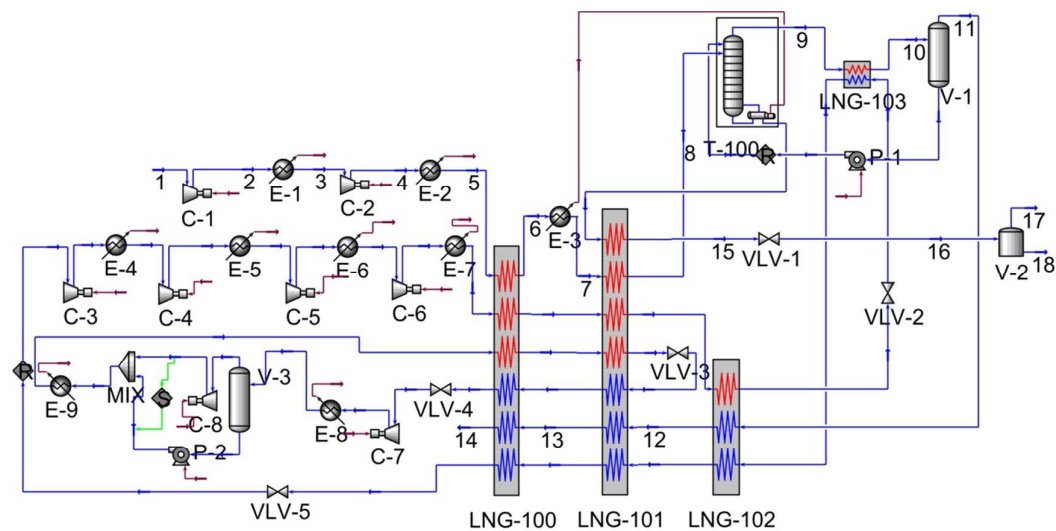


Fig.1 Liquefaction and distillation process of CBM

1.2 Critical device description and main parameter Settings

Multi-steam heat exchanger is the main device in the oxygen-bearing coal-bed methane liquefaction and distillation process. In the heat exchanger, the heat is transferred from the heat flux (CBM in this study) to the cold flux (nitrogen and mixed refrigerant in this study). Therefore, the temperature of the CBM decreases after flowing through the heat exchanger. The performance of the heat exchanger has significant influence on the effect of the whole process. Plate-fin heat exchanger has a mainly copper aluminum structure and is composed of plate, fin and seal. The plate-fin heat exchanger is widely used in the cryogenic system because of the compact structure, light weight, large heat transfer area and high design pressure. Therefore, in this liquefaction and distillation process, plate-fin heat exchanger is used. During simulation, the pressure drop of LNG-100 and LNG-101 are set as 30 kPa, respectively. The pressure drop of LNG-102 is set as 10 kPa. In LNG-103, the pressure drop of the hot flux is set as 0 while the cold flux is set as 20 kPa.

In the oxygen-bearing coal-bed methane liquefaction and distillation process, the distillation column is the key device in which the methane and impurity gases are separated. The principle of distillation is the different boiling point of the composition. The vapor is fed from the bottom of the distillation column and flow to the top of the column. The liquid is fed from the upside of the column and flow to the bottom of the column. When the downward liquid comes across the upward vapor, the composition with low boiling point in liquid will transfer into the vapor and the composition with high boiling point in the vapor will transfer into the liquid. Therefore, the purpose of components separation is achieved. In the liquid CBM, the methane has a high boiling point while oxygen and nitrogen have a low boiling point. Thus, when the liquid CBM flow downward, the oxygen and nitrogen transfer into the upward vapor. As a consequence, the liquid CBM at the bottom of the distillation column has a high purity of methane. During simulation, the parameters set in the distillation column are important. The pressure of the inlet CBM is 0.5 MPa and the temperature is -160°C . CBM is fed into distillation column from the middle plate. In the distillation column, the number of distillation plates is 10 which is the optimized value and the reflux ratio is 1.21. The pressure of the liquid product (LNG) at the bottom and the impurity gas

at the top of the column are assumed to be 0.31 MPa and 0.27 MPa, respectively.

In refrigeration system, the parameters of nitrogen (as refrigerant) and mixed refrigerant are shown in Table 2. The reason of using a mixed refrigerant in such a composition is the lowest energy consumption of per unit LNG production. In the HYSYS simulation software, PR (Peng-Robinson) equation is used to calculate the phase equilibrium of the oxygen-bearing CBM, refrigerant, and nitrogen. As we know, in the calculation of the vapor liquid equilibrium, the PR equation is basically appropriate no matter what the pressure and temperature are. From the HYSYS software, the results calculated by PR equation have a high accuracy when the temperature is higher than $-271\text{ }^{\circ}\text{C}$ and the pressure is smaller than 10^5 kPa . According to the practical operating condition of the liquefaction stage, adiabatic efficiency of the compressor is set as 80% and the pressure drop of water cooler is set as 30 kPa.

Table 2 Parameters of refrigerant

Category	Mole fraction of components /%					Flow rate/ kmol/h
	CH ₄	C ₂ H ₄	C ₃ H ₆	C ₅ H ₁₂	N ₂	
Mixed refrigerant	42.12	15.07	8.90	17.12	16.78	2920
Throttling refrigerant					100	1960

1.3 Applicability analyses

The range of methane concentration and oxygen concentration of the raw coal-bed gas which are suitable for the liquefaction and distillation process designed in the present paper has been studied. It has been stated in this paper that the oxygen-bearing coal-bed methane has a methane content range of 30%~80%. Therefore, two gas sources are studied: a gas source composed of methane with 30%, nitrogen with 55.3% and oxygen with 14.7%; another gas source composed of methane with 80%, nitrogen with 15.8% and oxygen with 4.2%. The temperature and pressure of the two gas sources are the same which are $40\text{ }^{\circ}\text{C}$ and 0.11 MPa, respectively. For the first gas source composed of methane with 30%, simulation results show that the purity of LNG is 99.91% and the recovery rate of methane is 95.03%. Energy consumption of per unit LNG production is $0.876\text{ kW} \cdot \text{h}/\text{m}^3$. For the second gas source composed of methane with 80%, simulation results show that the purity of LNG is 99.96% and the recovery rate of methane is 98.98%. Energy

consumption of per unit LNG production is $1.21 \text{ kW} \cdot \text{h}/\text{m}^3$.

We can conclude that for different gas sources, the purity of LNG and the recovery rate of methane are high while the energy consumption of per unit LNG production is low enough. Therefore, the liquefaction and distillation process designed in the present paper has good applicability for different gas sources.

2. Explosion limit analysis

2.1 The empirical formula and validation

There are many factors which can affect explosion limit, for instance, initial temperature, initial pressure and ignition energy. When the content of coal-bed methane is a mixture of methane and air, considering the influence of temperature and pressure, the calculation formulas of explosion limit are expressed as follows¹²:

$$U=[U_{CH_4}+20.6(\lg p+1)][1+8 \times 10^{-4}(t-25)] \quad (1)$$

$$L=L_{CH_4}[1-8 \times 10^{-4}(t-25)] \quad (2)$$

In the compression and cold energy recovery stage of the liquefaction and distillation process, methane is gaseous phase and no phase change occurs. While in the stages of liquefaction, throttling and distillation, because of the phase change, the methane concentration will change a lot. At this moment, gas composition will also affect the explosion limit in addition to temperature and pressure. When there are inert gases in the methane and air mixture, the explosive mixed gases can be regarded as methane and air mixture diluted by inert gas¹³. Based on the Extended Le Chatelier formula¹⁴, the explosion limit of the explosive mixed gases can be expressed as:

$$U' = [100c_1 - \frac{(100 - U_{CH_4})c_1^2 n_1}{c_1 n_1 + (100 - U_{CH_4})(0.00122c_{in} + 0.00187c_{in}^2 - 0.00242c_{in}^3)} + 20.6(\lg p + 1)] [1 + 8 \times 10^{-4}(t - 25)] \quad (3)$$

$$L' = \frac{L_{CH_4}c_1[1 - 8 \times 10^{-4}(t - 25)]}{c_1 - 0.00187c_{in}L_{CH_4}} \quad (4)$$

$$c_{in} = 1 - c_1 \quad (5)$$

The methane explosion limits are calculated by the equation (3) and (4) for normal pressure, different low temperature and different nitrogen content. The

calculated results are compared with the experimental data which is shown in Fig.2.

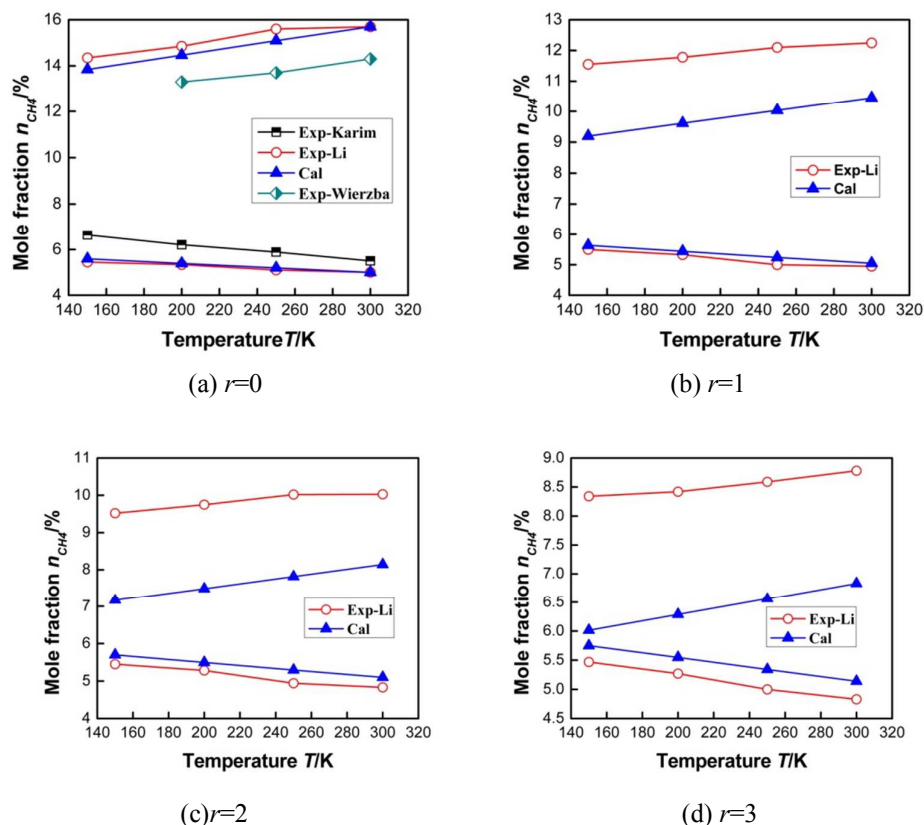


Fig.2 Comparison between calculated results and experimental results

The comparison result shows that when $r=0$ i.e. pure methane, under cryogenic conditions, the lower explosion limit calculated by empiric formula is in good agreement with the experimental data tested by Li et al. But the calculated results are much less than the experimental data tested by Karim et al. The upper explosion limit calculated by empiric formula shows great difference with the experimental data. The difference of the experimental data tested by Li et al., Karim et al., and Wierzba et al. is mainly caused by explosion vessels and explosion criteria. In Karim's and Wierzba's experiment, the explosion vessel is a cylindrical stainless steel tube with a diameter of 5 cm and length of 1 m, and the criterion of explosion is flame spread. While in Li's experiment, the explosion vessel is a cylindrical explosion vessel with inner diameter of 100 mm and height of 200 mm, and the criterion of explosion is pressure rise. According to many researchers^{17, 18}, because of the wall effect and buoyancy effect, the different vessel diameter and the different explosion criteria can

cause big differences in the explosion limits.

With the increase of r , i.e. with the increase of inert gas, the difference between calculated results by empiric formula and experimental data increases. Additionally, the difference of the upper explosion limit is bigger than that of the lower explosion limit. Therefore, we can conclude that the existing empiric formula is never applicable when calculating the explosion limit of methane under low temperature conditions.

2.2 Formula fitted by Li et al

In Li's study¹¹, high-order and temperature terms are introduced into the extended Le Chatelier's formula to improve the correlation accuracy and predict the explosion limits at each temperature from 150 to 300 K. The independent variable is the molar ratio of inert gas to methane instead of the molar fraction of inert gas in the oxygen-bearing coal-bed methane. The calculation is illustrated in Equation (6) to (8).

The LELs correlation is written as follows:

$$\frac{c_1}{L} = \frac{c_1}{L_{CH_4}[1+a(t-t_0)]} + br + cr^2 \quad (6)$$

Similarly, the UEL correlation can be expressed as:

$$\frac{c_1 n_1}{100 - \left(\frac{U'}{c_1}\right)} = \frac{c_1 n_1}{100 - U_{CH_4}[1+d(t-t_0)]} + er + fr^2 + gr^3 \quad (7)$$

The value of n_1 is determined by the following equation:

$$n_1 = \frac{0.21\{100 - U_{CH_4}[1+d(t-t_0)]\}}{U_{CH_4}[1+d(t-t_0)]} \quad (8)$$

The resulting parameter values are presented in Table 3. After calculations, the average absolute deviation is 0.08 vol% for the LEL and 0.23 vol% for the UEL. The maximum absolute deviation is 0.27 vol% for the LEL and 0.98 vol% for the UEL. The calculated values are in agreement with the experimental results for both the LEL and the UEL.

Table 3 Parameter values resulting from fitting calculation to explosion limits

Case	Parameter values			
	a,d	b,e	c,f	g
LEL	-6.0857×10^{-4}	2.049×10^{-4}	3×10^{-5}	-

UEL	5.323×10^{-4}	7.748×10^{-4}	-1.7×10^{-4}	1.09×10^{-5}
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3. Calculation results and discussions

3.1 Liquefaction and distillation process simulation results

The flow rate and methane content of CBM are assumed to be $9.6 \times 10^5 \text{ m}^3/\text{d}$ (1760 kmol/h) and 40%, respectively. The simulation results indicate that the output of LNG product is 684.7 kmol/h and the impurity nitrogen is removed from the CBM thoroughly. Furthermore, the purity of LNG is 99.91%, the volume fraction of oxygen is merely 0.09% and the recovery rate of methane is 97.12%. Energy consumption of per unit LNG production is $0.94 \text{ kW} \cdot \text{h}/\text{m}^3$. The main parameters of the process are listed in Table 4.

Table 4 Main parameters of the process

Stream number	Temperature/ $^{\circ}\text{C}$	Pressure/MPa
1	40	0.11
4	130.4	0.63
6	-51	0.57
7	-146.6	0.54
10	-181.1	0.27
14	28	0.2
15	-158	0.28
18	-160.1	0.115

3.2 Security evaluation results

3.2.1 Compression stage (stream 1-5)

In the compression stage, the CBM keeps in gas state and no phase change occurs. The methane content is 40% all the time. The CBM is compressed by the compressor and cooled by the cooler. Therefore, the temperature and pressure change a lot in the compression stage. Both the temperature and pressure reach to the maximum at the exit of the compressor C-2. After calculations, the lower explosion limit of methane is 4.58% while the upper explosion limit is 34.11%. As a consequence, no explosion hazard exists in the compression stage because the methane content is always higher than the UEL value.

3.2.2 Liquefaction stage (stream 5-8)

There is no phase change in the heat exchanger LNG-100. The temperature of the CBM decreases when it flows through the heat exchanger LNG-100 and the cooler

E-3. The upper explosion limits decrease which is lower than the methane content in CBM. Therefore, no explosion hazard exists in LNG-100. Phase change occurs in the heat exchanger LNG-101. After simulation and calculation, the variations of explosion limits and methane content as functions of temperature in liquefaction stage are obtained which are shown in Fig.3. Fig.3 shows that in gas phase, methane content decreases gradually with the decrease of the temperature. However, the upper explosion limit also decreases with the decrease of the temperature. In the whole temperature ranges, methane content is always higher than the UEL. Therefore, the possibility of the CBM explosion in the heat exchanger LNG - 101 does not exist.

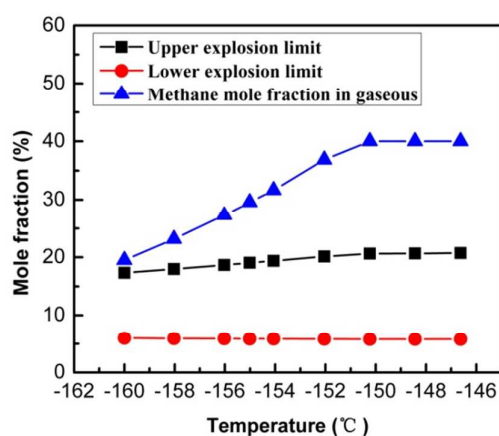


Fig.3 Variations of explosion limits and methane content as functions of temperature in liquefaction stage

3.2.3 Distillation stage (steam 8-9)

After compression and liquefaction stages, the CBM from the LNG-101 is then fed into the distillation column T-100. On each plate of the distillation column, heat transfers between methane, nitrogen and oxygen happen. Because of the high boiling point, the phase of methane changes from gaseous to liquid gradually. The liquid flows to the bottom while the impurity gases composed of nitrogen and oxygen flow out from the top of the column. After simulation, variations of gas composition along different plates of the column are obtained which are shown in Fig.4. Fig.4 shows that for different plates, the ratio of nitrogen to oxygen is always less than that in air. Therefore, the environment of the distillation column is oxygen enrichment. After simulation and calculation, the variations of explosion limits and methane content as

function of plates in distillation column are obtained which are shown in Fig.5. It should be noted that the plates are numbered from the top to the bottom. The 11th plate represents the reboiler which is located at the bottom of the column. Fig.5 shows that from the reboiler to the 6th piece of plate, in the gas phase, methane content is much higher than the upper explosion limit which indicates no explosion hazard. From the 6th piece of plate to the top of the column, methane content decreases a lot. However the calculated UEL and LEL also decrease slowly. The methane content is still higher than the UEL until the 2th piece of plate. On the 1th piece of plate, the methane content reaches to the minimum which is less than the LEL. The methane content is within the explosion limits between the 1th and 2th piece of plate and an explosion hazard may exist.

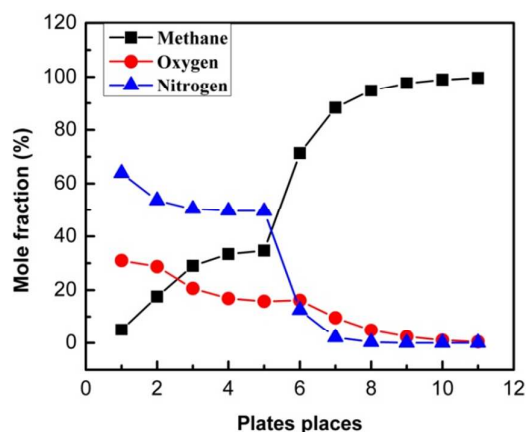


Fig.4 Variations of gas composition on different plates of the column

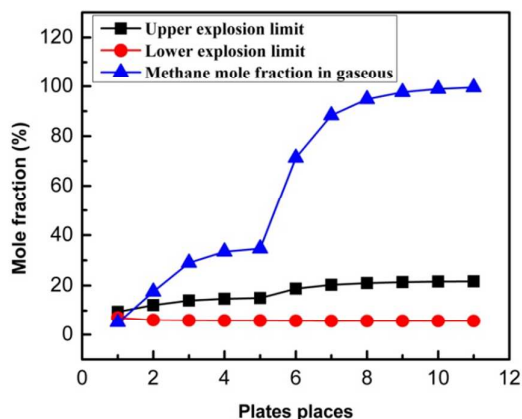


Fig.5 Variations of explosion limits and methane content as functions of plates in distillation

column

3.2.4 Condenser reflux stage (stream 9-11)

The impurity gas from the top of the column is first cooled by heat exchanger LNG-103 and then fed into separator V-1. For the impurity gases from the top of the column, methane content is less than the lower explosion limit. The lower explosion limit of methane increases because of the decrease of the temperature when the impurity gases are condensed in the heat exchanger LNG-103. The composition of the stream 11 is also obtained by simulation. The methane content is only 0.86% which is far below the lower explosion limit and thus no gas explosion hazard exists.

3.2.5 Cold energy recovery stage (stream 11-14)

The impurity gases from the top of the separator V-1 is fed into the heat exchangers LNG-102, LNG-101 and LNG-100 in series to cool the CBM and the refrigerant. Finally, the temperature of the impurity gases increases to the ambient temperature. In this stage, the impurity gases keep in gas phase still and the composition remains unchanged. Methane content is 0.86% which is far below the lower explosion limits and thus no gas explosion hazard exists.

3.2.6 Stream 15-18

The liquefied methane from the bottom of the distillation column is first cooled by heat exchanger LNG-101 and then flows through the throttle valve VLV-1. Finally, it will be stored in separator V-2. The stream 15 is the liquid LNG which is composed of methane with 99.88%, nitrogen with 0.02% and oxygen 0.1%. There is no gas exists in stream 15 and the oxygen content is 0.1% which is far below 8%, therefore, no gas explosion hazard exists. Stream 16 and 18 are also liquid LNG and no gas explosion hazard exists. Stream 17 is composed of methane with 99.5% and oxygen with 0.5% which indicates no explosion hazard.

4. Security measures and performance analysis

4.1 Security measures

Through the above analysis we can conclude that in the stages of compression, liquefaction and cold energy recovery, methane content is higher than the UEL or lower than the LEL. Thus, no explosion hazard exists. However, in the distillation

stage, the methane content is within the explosion limits at the top of the distillation column, probably resulting in an explosion hazard. In order to guarantee the safety in the whole process, security measures should be taken.

Methane explosion limits are influenced by many factors such as temperature, pressure and gas composition. When the basic parameters of the CBM liquefaction and distillation process are determined, the temperature and pressure will hardly be changed. Therefore, the gas composition is a key parameter which affects the explosion limits. At present, for the CBM liquefaction and distillation process, the safety is achieved by controlling the oxygen content in the coal-bed methane below the required minimum oxygen concentration, or controlling the methane concentration out of the explosion limits range. There are mainly 3 ways in detail: deoxidization of the CBM in advance, production control at the bottom of the column and adding inert gas N_2 . The deoxidization of CBM requires an additional device which leads to expensive budget. Production control at the bottom of the column affects the methane recovery rate and LNG output, and a lot of methane will flow out from the top of the column.

As we all know, methane explosion needs enough oxygen. Coward explosive triangle theory believes that the minimum oxygen concentration in the air is about 10%. When the oxygen concentration is lower than 10%, regardless of the methane content, the methane and air mixture will not be ignited. In this study, considering the variations of pressure and temperature, the minimum oxygen concentration is set to 8%. The security measure is to add nitrogen into the distillation column and make the oxygen concentration in the distillation column less than 8%. The nitrogen content in the impurity gases which come from the top of the distillation column is high. After cold energy recovery, it can be sent back to nitrogen-making device to recycle the nitrogen.

The plate location where N_2 is fed into and the flow rate of N_2 both have influence on the distribution of the oxygen concentration in the column. For simulation, the parameters of the coal-bed methane are set as: flow rate $40000 \text{ Nm}^3/\text{h}$, temperature $-150 \text{ }^\circ\text{C}$ and pressure 0.5 MPa . The number of the distillation column

plates is 10 and the coal-bed methane is fed into the column from the middle plate. Nitrogen which is added into the column has the same temperature and pressure with the inlet coal-bed methane.

N_2 is added from the 5th piece of plate of the distillation column. In the simulation, the flow rate of nitrogen is set as 0, 10000, 20000, 30000, 40000, 50000, 60000, 80000, 200000 Nm^3/h , respectively. In gas phase composition, oxygen concentration varies with the change of plate number, and the curve is shown in Fig.6. From the diagram, when the flow rate of N_2 is 0, it is observed that oxygen concentration gradually reduced from top to bottom in the distillation column. Among them, from the 7th piece of plate to the top of the column, oxygen concentration is higher than 8%. When N_2 is added to the column from the 5th piece of plate, with the increase of the flow rate of nitrogen, oxygen concentration decreases a lot between the top and the 5th piece of plate, while remains basically unchanged between the 7th piece of plate and the bottom of the column. This is because nitrogen is fed into the column from the 5th piece of plate and then it flows to the top. The mixture between the 5th piece of plate and the top of the column is diluted by nitrogen directly, so oxygen concentration decreases a lot. For mixture between the 7th piece of plate and the bottom, it only relies on medium heat transfer to reach the equilibrium, so it cannot be diluted immediately and oxygen concentration remains unchanged.

An interesting phenomenon can be seen from Fig.6 that when a flow rate of nitrogen i.e. 30000 Nm^3/h exists, the mole fraction of oxygen decreases gradually from the top plate to the 5th plate. However, between the 5th plate and the 6th plate, the mole fraction of oxygen increases a lot which is higher than 8%. The mole fraction of oxygen decreases again from the 6th plate to the bottom of the column. In practical production, an oxygen concentration which is below 8% should be reached in the whole column. As a consequence, the flow rate of nitrogen will reaches up to 200000 Nm^3/h , which is as 5 times as the flow rate of feed gas. Therefore, we can conclude that when N_2 is added to the column from the 5th piece of plate, the consumption of nitrogen is very high, in other words, poor economy.

Then nitrogen is added from the 7th piece of plate. In the simulation, the flow rate

of nitrogen is set as 0, 10000, 20000, 30000, 40000, 50000 and 80000 Nm^3/h , respectively. In the gas phase composition, oxygen concentration varies with the change of the plate number and the curves are shown in Fig.7. When N_2 is added to the column from the 7th piece of plate, with the increase of the flow rate of nitrogen, oxygen concentration decreases a lot between the top and the 7th piece of plate, while remains basically unchanged between the 9th piece of plate and the bottom of the column. The reason is the same with the previous study. For a flow rate of nitrogen i.e. 20000 Nm^3/h , the mole fraction of oxygen decreases gradually from the top plate to the 7th plate. However, the mole fraction of oxygen increases a bit between the 7th plate and the 8th plate. It decreases again from the 8th plate to the bottom of the column. When the flow rate of nitrogen reaches up to 50000 Nm^3/h , the mole fraction of oxygen in the whole column is less than 8% and there is no explosion hazard. In the stage of cold energy recovery, for the impurity gases, methane concentration is 2.7% while oxygen concentration is 7%, which are lower than the explosion limit and the minimum oxygen concentration, respectively. In conclusion, a nitrogen flow rate of 50000 Nm^3/h fed from the 7th plate is recommended.

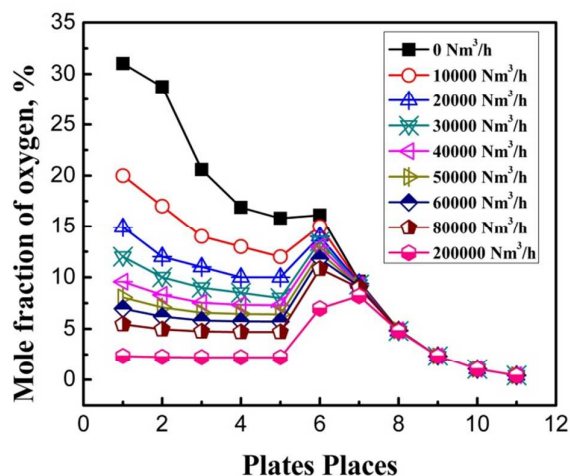


Fig.6. Variations of oxygen content along the plates when nitrogen is added from the 5th plate

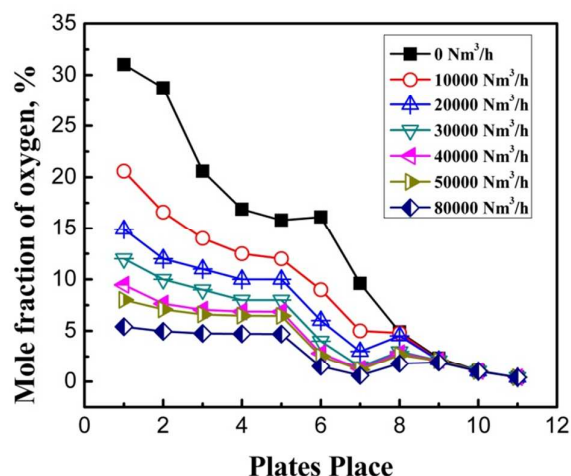


Fig.7. Variations of oxygen content along the plates when nitrogen is added from the 7th plate

4.2 Performance analysis

According to the simulation results, for oxygen-bearing coal-bed methane gas source in Table 1, by adding nitrogen from the 7th piece of plate in the distillation column with a flow of 50000 Nm³/h can ensure the security of the whole distillation stage and no explosion danger exists. Under this condition, after taking security measures, bottom product purity is 99.87%, the methane recovery rate is 91.35%, and energy consumption of per unit LNG product is 1.3 kW·h/m³. Compared with the simulation results which are no security measures, as shown in Table 5, the bottom product purity basically remain unchanged. The LNG production of the bottom decreases slightly and the methane recovery decreases but in an acceptable range. When nitrogen with a flow rate 50000 Nm³/h is fed, the load of the condenser gets bigger. The energy consumption of per unit LNG production increases by 38%. Although methane recovery rate is reduced and production energy consumption increases, the liquefaction and distillation process can be kept in a safe state.

Table 5 Comparison between the performance of the process considering the security measures and that without N₂ dilution

Items	Purity of LNG product, %	Recovery rate of methane, %	Energy consumption, kW·h/m ³
No dilution	99.91	97.21	0.94
With security measures	99.87	91.35	1.3

Conclusions

After simulations and calculations, we draw some conclusions which are shown below.

(1) For a typical oxygen-bearing coal-bed methane source, we propose a new liquefaction and distillation process which has good applicability for different gas sources. When the methane content is 40%, the purity of LNG production is 99.91% and the volume fraction of oxygen is only 0.09%. In addition, the methane recovery rate is as high as 97.12% while the energy consumption of per unit LNG product is only 0.94 kW·h/m³.

(2) In the compression, liquefaction, condensation and cold energy recovery stages of the liquefaction and distillation process, there are no explosion hazard. Only in the top of the distillation column, it has a danger of explosion.

(3) For safety measures, a nitrogen flow rate of 50000 Nm³/h fed from the 7th plate is recommended. This method can make the oxygen content in all the plates of the column less than 8% which is the required minimum oxygen content. Additionally, when the nitrogen is added into the column, the methane recovery rate is 91.35% and the energy consumption increases by 38%.

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References

- 1 Z. Q. Sun, J. H. Wu, M. Haghghi, J. Bromly, E. Ng, H. L. Wee, Y. Wang and D. K. Zhang, *Energ. Fuel*, 2007, **21**, 1601-1605.
- 2 S. Kedzior, *Int. J. Coal Geol.*, 2009, **80**, 20-34.
- 3 T. Gao, W. S. Lin, A. Z. Gu and M. Gu, *Appl. Energy*, 2010, **87**, 2141-2147.
- 4 K. Gatnar and A. Tor, *Appl. Energy*, 2003, **74**, 331-341.
- 5 J. Hetland, Z. Li and S. S. Xu, *Appl. Energy*, 2003, **86**, 219-229.
- 6 Q. B. Liu, H. Hong and J. L. Yuan, *Appl. Energy*, 2009, **86**, 155-162.
- 7 B. Pal Uday, C. Adam and I. V. Powell, *JOM-J. Mineral Metal Mater. Soc.*, 2007, **59**, 44-49.

- 8 K. Qiu and A. C. S. Hayden, *Appl. Energy*, 2009, **86**, 349-354.
- 9 D. A. Yagodnikov and A. V. Voronetskii, *Combust. Explo. Shock+*, 1997, **33**, 49-55.
- 10 T. C. Nguyen, Thomas and J. J. Bergman, US Patent, 2002, 6351971.
- 11 Z. M. Li, M. Q. Gong and E. Y. Sun, *Energy*, 2011, **36**, 5521-5524.
- 12 M. Q. Yan and M. L. Lian, Beijing: China Architecture & Building Press, 2005, 10-13.
- 13 S. Kondo, K. J. Takizawa and K. A. Takahashi, *J. Hazard. Mater.*, 2006, **138**, 1-8.
- 14 S. Kondo, K. J. Takizawa and K. A. Takahashi, *Fire Safety J.*, 2006, **41**, 406-417.
- 15 G. A. Karim, I. Wierzba and S. Boon, *Cryogenics*, 1984, **24**, 305-308.
- 16 I. Wierzba, K. Harris and G. A. Karim, *J. Hazard. Mater.*, 1990, **25**, 257-265.
- 17 M. Gieras, R. Klemens, G. Rarata and P. Wolanski, *J. Loss Prevent. Proc.*, 2006, **19**, 263-270.
- 18 F. Van den Schoor, R. T. E. Hermanns, J. A. van Oijen, F. Verplaetsen and L. P. H. de Goey, *J. Hazard. Mater.*, 2008, **150**, 573-581.

A new liquefaction and distillation process for oxygen-bearing CBM has been proposed. Safety evaluation and safety measures are also studied.

