Analysis of Methane Explosion Limit under Cryogenic Conditions

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Abstract: During the past several years, the explosion risk analysis of each stage in oxygen CBM liquefaction process has been carried out by a large number of domestic scholars. In this work, firstly, safety evaluation of the coalbed methane liquefied process was summarized. Then, the experiment of the explosion limit test under cryogenic condition was introduced. At last, the explosion limit calculated by the empiric formula was compared with the experiment data. The result shows that there are big differences between the calculated result and the experiment data. The existing empiric formula is never applicable when calculating the explosion limit of methane under low temperature conditions. The method of safety evaluation of coalbed methane liquid process using the empiric formula is wrong. It is advised to build a new experimental device to test the explosion limit of methane under cryogenic conditions. The test condition should include initial temperature of 0~-170°C and initial pressure of 0.1~0.9 MPa.

Keywords- CBM liquefied process; explosion limit; methane; empiric formula; cryogenic

I. INTRODUCTION

China is rich in coalbed methane [1] and is the third largest coalbed methane reserves after Russia and Canada all over the world [2]. The coalbed methane resources whose burial depth is smaller than 2000 m can be as high as 36.8×10^{12} m³, which is about thirteen percent of the resources in the whole world [3]. There are mainly two types of coalbed methane for exploiting [4]: One is the extracted coalbed 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. Another is the extracted coalbed methane during the coal mining for the safety production of the coal mine [5]. The methane content is low with volume fraction of 30%~50% and other content is mainly carbon dioxide and air. The coalbed methane containing much air is called oxygen bearing coalbed 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 coalbed methane. One benefit is improving the prevention level of methane accident to guarantee the safety production of the coal mine. Another is reducing carbon emission to achieve energy conservation and better global atmospheric environment. Meanwhile, as an efficient and clean energy, to commercialize the coalbed methane can produce large economic benefit.

The deoxidation of coalbed methane is a technical problem at home and abroad. At present, the deoxidation technologies mainly include adsorption method, separation membrane method, combustion method and low temperature processing method. Among these, the low temperature processing method is a rather common method because of the high product purity [6]. A typical liquefied process of oxygen bearing coalbed methane is shown in Fig.1. The gas composition changes in the process of liquefaction. 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 [7]. The existing research shows that a higher danger stage is the fractionation process with temperature of -160~-170 °C and pressure of 0.1~0.3 MPa [8]. Particularly, in the top of the fractionation tower, 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 liquefied process and then adopt safety measures.

II. SAFETY EVALUATION OF THE COALBED METHANE LIQUEFIED PROCESS

A. Summarize of the evaluation

The explosion risk analysis of each stage in oxygen CBM liquefaction process has been carried out by a large number of domestic scholars. According to the current state of coalbed methane development, Yu et al. [9] put

forward a new mix refrigerant cycle technology with the methane pressurized by liquid ring pump. They analyze the explosion limits among the whole liquefied process using the existing empirical formula of the methane explosion limit. As for the safety problems of the low temperature liquefied and purification process, Wu et al. [4] come up with three technical measures to prevent explosion: controlling the lowest smog exit temperature, adding flame retardant composition and coarse deoxidation in advance. Combined with the feature of the low temperature liquefied process, they then propose detailed implementation method of the above three anti-explosion methods using the explosion triangle theory. Li et al. [10] describe a simple liquefied process of the oxygen bearing coalbed methane deoxidation. On the basis of theoretical analysis, they analyze the explosion hazard of all the stages in liquefied process. As a consequence, the corresponding safety measurements are proposed. Based on the gas source condition and composition characteristic of coalbed methane, Li et al. [3] design a new liquefied rectification technological process. They analyze and calculate the explosion limit of the rectification technological process combined with the simulation results and the explosion limit theory. The results show that methane concentration is higher than the upper explosion limit during the compress, liquefaction and throttling process. However, in the top of the rectifying column, the methane concentration will get lower than the upper explosion limit and thus cause potential safety hazard in the distillation process. Ma et al. [11] analyze the safety characteristic of a cryogenic liquid - fractionation process using the extended explosion triangle theory. By comparing the component content with the explosion limit, the evaluation of the process safety is realized.

B. The existing empirical formula for the safety evaluation

All the evaluation method is based on the HYSIS simulation of the liquefied process and then acquires the working condition parameters including methane concentration, temperature and pressure in every stage. Because the methane explosion limit 5%~15% [4] under normal temperature and pressure is never applicable under low temperature, they use the methane explosion limit data under cryogenic conditions calculated by the existing formula which is applicable under normal temperature and pressure, or elevated temperature and pressure.

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 follows [12]:

$$U = [U_{CH4} + 20.6(\lg p + 1)][1 + 8 \times 10^{-4}(t - 25)] \quad (1)$$

$$L = L_{CH4}[1 - 8 \times 10^{-4}(t - 25)] \quad (2)$$

Here, U- Upper flammability limit at a certain pressure and temperature, %; U_{CH4}- Upper flammability limit of methane at normal pressure and temperature, %; P-Initial pressure, MPa; t-initial temperature, °C; L-Lower flammability limit at a certain pressure and

temperature, %; L_{CH4} - Lower flammability limit of methane at normal pressure and temperature, %.

In the compression and cold energy recovery stage of coalbed methane liquefied process, methane is gaseous phase and no phase change occurs. While in the stage of liquefaction, throttling and rectification, 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 gas and air mixture diluted by inert gas [13]. The gas in the liquefied process can be regard mixed gases diluted by nitrogen. Based on the Extended Le Chatelier formula [14], the explosion limit of gas can be expressed as:

$$U' = [100c_1 - \frac{(100 - U_{CH4})c_1^2 n_1}{c_1 n_1 + (100 - U_{CH4})(0.00122c_{in} + 0.00187c_{in}^2 - 0.00242c_{in}^3)} + 20.6(\lg p + 1)]$$
$$[1 + 8 \times 10^{-4}(t - 25)]$$
$$(3)$$

$$L' = \frac{L_{CH4}c_1[1 - 8 \times 10^{-4}(t - 25)]}{c_1 - 0.00187c_{in}L_{CH4}} \quad (4)$$

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

Here, U' -Upper flammability limit at certain pressure and temperature when inert gas exists, %; c_1-Mole fraction of methane; L' - Lower flammability limit at certain pressure and temperature when inert gas exists, %; n_1- The required oxygen mole number when 1 mole methane is consumed.

III. SUMMARY OF THE METHANE EXPLOSION LIMIT UNDER CRYOGENIC CONDITIONS

There are limited studies on the methane explosion limit under cryogenic conditions at home and abroad. Karim et al. [15] tested the lower explosion limit of methane at initial temperature of 143~298 K and normal pressure. The criterion of explosion was flame spread and the refrigerating method was liquid nitrogen. The experiment facility is shown in Fig.1. The explosion vessel was a cylindrical stainless steel tube with a diameter of 5 cm and length of 1 m. In Fig.1, 14 represented liquid nitrogen coilers. The temperature of the explosive gas would decrease by the evaporation of liquid nitrogen in the coilers. 15 represented insulating layer and had a function of thermal insulation. There were six temperature sensors inside the explosion vessel. By comparing the values of the temperature sensors, the temperature inside the vessel would be estimated that whether the temperature was uniform or not. Wierzba et al. [16] studied the upper explosion limit of explosive gases under normal pressure and low temperature using the same experiment device and test method. The low temperature ranged from room temperature to -60 °C. Then, Wierzbaet al. studied the explosion limit of hydrogen and other fuel gas mixtures under low temperature [17].The initial temperature range for upper explosion limit test was from room temperature to -60 °C, while for the lower explosion limit was from room temperature to -100 °C。Li et al. from Chinese Academy

of Sciences [18] built a cylindrical explosion vessel with inner diameter of 100 mm and height of 200 mm. The explosion limit of methane and nitrogen mixture under normal pressure and low temperature was tested. The range of initial temperature was from 150 K to 300 K. The experiment equipment schematic diagram was shown in Fig.2. In Fig.2, the air in cryostat was decreased to a low temperature by evaporator. Then, the explosion vessel would be cooled down by heat conduction and convection of the air.
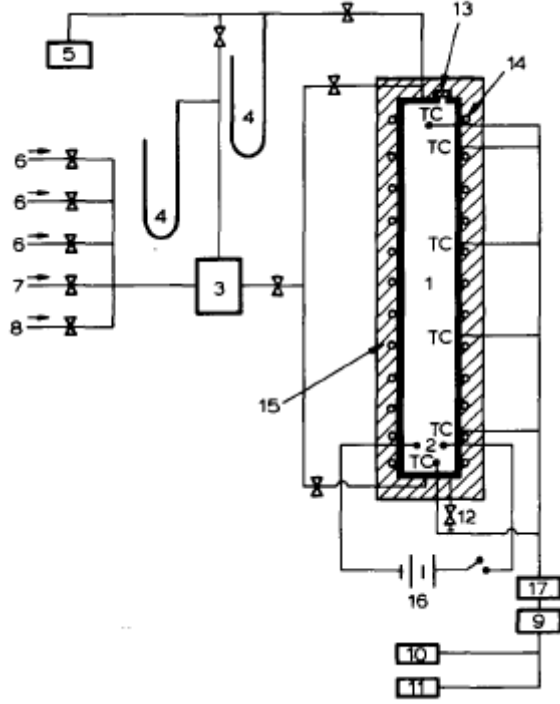

Figure 1 Laboratory equipment schematic diagram of Karim et al.

1-explosion vessel; 2-ignition electrode; 3-mixer; 4- pressure gauge; 5- vacuum pump; 6，7，8-admission line; 9, 10, 11-display component; 12-valve; 13-evacuation diaphragm; 14-refrigeration coiler; 15-insulating layer; 16-power source; 17-voltmeter; TC-thermocouple
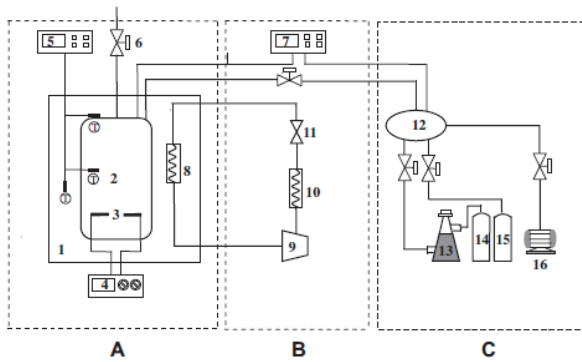

Figure 2 Laboratory equipment schematic diagram of Li et al.

1-cryostat; 2-explosion vessel; 3-electrode; 4-igniting circuit; 5-temperature measurement system; 6-safe valve; 7-pressure measurement system; 8-evaporator; 9-compressor; 10-condenser; 11-throttle; 12-mixing vessel; 13-desiccator; 14-air; 15-testing sample (methane & nitrogen); 16-vacuum pump; A-measurement area; B-refrigeration area; C-mixture preparation area.

IV. COMPARISON OF THE EXISTING EMPIRIC FORMULA WITH THE EXPERIMENT DATA
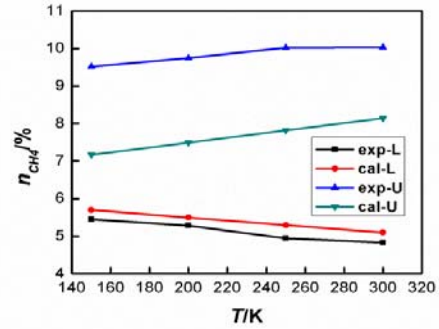
The methane explosion limit was calculated by the equation (3) and (4) for normal pressure, different low temperature and different nitrogen content. The calculated results are compared with the experimental data which is shown in Fig.3.
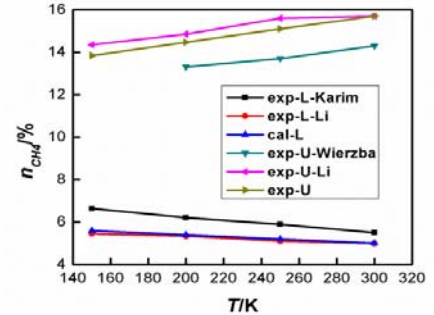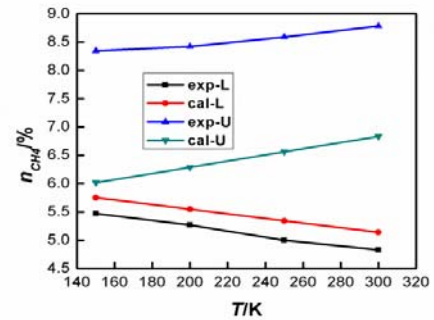

(a) r=0
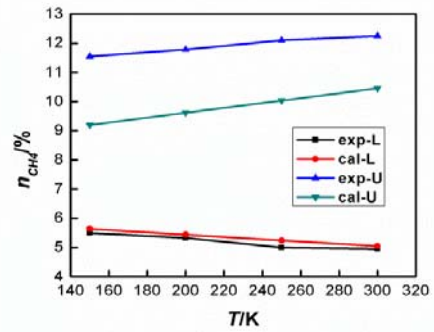
(b) r=1

(c) r=2

(d) r=3

Figure 3 Comparison between calculated results and experimental results

In Fig.3, exp-L(-Li) and exp-U(-Li) represent lower explosion limit and upper explosion limit tested by Li et al., respectively. Exp-L-Karim represents lower explosion limit tested by Karim et al. Exp-U-Wierzba represents upper explosion limit tested by Wierzbaet al. Cal-L and cal-U represent lower explosion limit and upper explosion limit calculated by empiric formula, respectively. Here, r represents mole fraction ratio of inert gas and methane in combustible gas.

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. With the increase of r, i.e. with the increase of inert gas, the difference between calculated 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. The method of safety evaluation of coalbed methane liquid process using the empiric formula is wrong.

V.   CONCLUSIONS

At present, safety evaluation of the coalbed methane liquid process is based on the existing empiric formula. However, the methane explosion limit calculated by empiric formula shows big difference with the experimental data. With the increase of inert gas content, the difference gets bigger. Therefore, the evaluation result is unbelievable and can cause potential safety hazard.

The initial pressure of the explosion test under low temperatures is normal pressure and the lowest initial temperature is 143 K. There is no relevant experimental data aimed at the fractionation distillation stage which has the most danger in the coalbed methane liquid process. In fractionation distillation stage, the temperature is -160～-170 °C and pressure is 0.1～0.3 MPa. As a consequence, it is impossible to evaluate the safety of all the stages in the liquefied process. We then advise to build a new experimental device to test the explosion limit of methane under cryogenic conditions. The test condition should include initial temperature of 0~-170 °Cand initial pressure of 0.1~0.9 MPa.

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