



Study on the Solution of Heavy Hydrocarbon Caused Frozen Stoppage in LNG Factory

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Abstract: This paper focus on the characteristics of heavy hydrocarbon frozen stoppage, which is based on the investigation of current problems of liquefied natural gas factory. Combined with the causes of frozen study, the paper analyzes the four kinds of technological schemes, such as "adsorption", "heavy hydrocarbon washing", "gas stripping + heavy hydrocarbon backflow" and "low temperature distillation" in a LNG project in Inner Mongolia of CNPC. It analysis the merits and drawbacks of every proposals from process simulation, process description, applicability, temperature parameters, liquefaction energy consumption, major equipment, investment etc. Finally this paper selects a heavy hydrocarbon removal process proposal, which is suitable for a LNG factory in Inner Mongolia, and is more simple process, low energy consumption, easy to operate. After the project is put into operation, the comparison between actual operation data and designed data proves the feasibility of this proposal. The results provide a guidance and reference for the subsequent LNG factory designing

Keywords: LNG factory; heavy hydrocarbon; frozen stoppage; process proposal

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1 Introduction

1.1 Research purpose and significance

Liquefied natural gas (LNG) is a clean and efficient energy source. As a rising star in the global energy industry, LNG import and export is expanding, which mainly depends on two aspects. For energy consuming countries, importing LNG can achieve energy diversification, reduce energy costs, and ensure energy security. For LNG exporting countries, it is beneficial to the full development of natural gas energy, increase the foreign exchange income, and promote economic growth.

2006 is the first year of country's natural gas imports, with 90 million cubic meters of imported natural gas. By 2010, the import volume will be 17 billion cubic meters. With the rapid development of country's economy and society, the demand for natural gas has gradually increased. The demand will be increased by 2020. It will reach 400 billion cubic meters, accounting for one-tenth of the entire energy consumption. It is estimated that the gap will be about 200 billion cubic meters, and the degree of external dependence is 50%. Due to the limitation of domestic resources, it is necessary to import from abroad to meet the growth. Imported natural gas enters China by two channels: pipeline gas and LNG. According to relevant statistics, two resource channels have contributed approximately 50% of China's total natural gas imports.

Liquefied natural gas (LNG) has the characteristics of safe use and environmental friendliness, and it precisely meets

the requirements of state's economic and social development plans. With increasing environmental protection pressure and environmental protection requirements become higher than before, LNG will become more widely used. At the same time, LNG is conducive to improving the utilization efficiency of natural gas, which is in line with the country's strategy of replacing coal and oil with natural gas. The LNG market has broad prospects, high added value and good benefits. Although the price of LNG is higher than that of pipeline gas, it still has a advantage compared with oil. Coupled with the advantages of cleanliness and flexible use, the price is stable under the current market situation and will rise slightly in the long run. According to market rules, fluctuations in oil prices have little impact on LNG prices. In the field of vehicle fuels, LNG is cheaper and less polluting than gasoline and diesel.

Heavy hydrocarbons generally refer to C_5+ (above C_5) hydrocarbons. Generally, there are heavy hydrocarbon components in natural gas extracted from underground, which makes the hydrocarbon dew point of natural gas higher. When the temperature and pressure of natural gas change, the temperature of natural gas is lower than the hydrocarbon dew point under a certain pressure, heavy hydrocarbon components in the natural gas will precipitate to form a liquid phase, and the precipitated liquid hydrocarbon will accumulate in the low-lying part of the pipeline, which will reduce the cross-sectional area of the pipeline increases energy consumption and the cost of gas transmission and distribution. The condensate precipitated when the temperature is lower than the ambient temperature is likely to

cause ice blockage. On the other hand, the condensate combines with the acid gas in the natural gas, which is easy to damage the pipeline, valve and other Equipment causes corrosion. In order to facilitate the storage and transportation of natural gas, heavy hydrocarbon components in natural gas should be removed to reduce the hydrocarbon dew point.

In hydrocarbon components, when the relative molecular mass changes from small to large, the corresponding molecular boiling point changes from low to high. In the cycle of condensing natural gas, heavy hydrocarbons are always condensed first. Especially in the natural gas liquefaction process, since heavy hydrocarbons are liquefied before methane, if they are not cleaned, they will solidify first, and even cause ice blockage and block the flow path of the heat exchanger. Therefore, it must be condensed before or during the condensation process. Although the content of C₅+ in natural gas is very small, small changes in its characteristics will significantly affect the changes in natural gas phase characteristics. The main reason is that the hydrocarbon dew point or water dew point of the natural gas mixture is greatly affected by the heaviest component, and slight changes in the heavy component will directly affect the dew point temperature or dew point pressure. Above -183.3°C, ethane and propane can be dissolved in LNG at any concentration, while C₆+ hydrocarbons, CO₂ and water are difficult to dissolve. In the natural gas liquefaction process, if the extraction is not complete, the heat exchanger flow channel will be blocked in the low temperature section of the liquefaction and the cold box will freeze up, which reduces the liquefaction rate and increases energy consumption. Therefore, it is necessary to deeply remove the heavy hydrocarbon components in the feed gas in the LNG process to meet the requirements of liquefaction.

1.2 LNG impurity requirements

Natural gas processing is to remove undesirable components of natural gas according to different requirements to make it meet the quality requirements of commercial natural gas and to recover or process the required components to be used in industrial production. Natural gas treatment refers to those processes adopted to make natural gas meet the requirements of commodity quality or pipeline transportation, such as removing acid gas (removing acidic components such as H₂S, CO₂, organic sulfur compounds such as COS, etc.) and other impurities (water, Hydrocarbons, solid particles, etc.) processes such as calorific value adjustment, sulfur recovery and tail gas treatment (environmental protection requirements). In China, it is also customary to call natural gas purification such as dehydration of natural gas, acid gas removal (desulfurization and decarbonization), sulfur recovery and tail gas treatment (environmental protection requirements). Natural gas processing is the process of separating and recovering certain components from natural gas to make them into products. For example, natural gas condensate recovery, natural gas liquefaction and extraction of rare gases from natural gas are all within the scope of natural gas processing. Natural gas treatment and processing are important links in the midstream field of natural gas. Some processes have both treatment and processing purposes.

The quality indicators of commercial natural gas include calorific value (calorific value), hydrocarbon dew point, water dew point, sulfur content, and carbon dioxide content. If only to

meet the requirements of pipeline transportation, the processed natural gas is called pipeline natural gas, or pipeline gas for short. The local requirements for the water dew point and hydrocarbon dew point in natural gas pipelines are the water dew point should be 5°C lower than the lowest possible ambient temperature of the gas in the gas pipeline (that is, the lowest pipeline gas temperature). The hydrocarbon dew point should be lower or equal to the lowest possible ambient temperature of the gas in the gas pipeline.

The pretreatment of liquefied natural gas refers to the removal of impurities such as hydrogen sulfide, carbon dioxide, moisture, heavy hydrocarbons, and mercury in natural gas. In order to prevent CO₂, water vapor, heavy hydrocarbons from freezing at low temperatures and blocking equipment and pipelines, H₂S, mercury, which will cause corrosion. When natural gas contains impurities such as high zeolite, naphthenic hydrocarbons and aromatic hydrocarbons, solids may form during the cryogenic process and cause blockage of equipment and pipelines, which should be removed from the system. The maximum allowable impurity content requirements for raw gas treatment are shown in Table 1.1 From the table, it can be seen that the treatment degree is higher than that of pipeline gas.

Table 1.1 The quality requirement of raw material gas to the natural gas liquefaction device

Impurity Components	Allowable Content, ×10 ⁻⁶ (V)	Impurity Components	Allowable Content
H ₂ O	<0.1	Total S	10~50 mg/m ³
CO ₂	50	Hg	<0.01 μg/m ³
COS	<0.1	H ₂ S	3.5 mg/m ³
Aromatics	10	C5+	<70 mg/m ³

It can be seen from the above table that the content of heavy hydrocarbon should be less than 70 mg/m³, about 70 ppm, and that of aromatic hydrocarbon should be less than 10 mg/m³, about 10 ppm.

1.3 The development status of natural gas removal technology

In the process of natural gas treatment, dehydration and dehydrogenation are often carried out simultaneously for the process with low degree of desorption. The technology of natural gas dehydration and dehydrocarbonization tends to be energy-saving, safe and efficient. There are some traditional processes such as the optimization and transformation of some process technologies of low-temperature dehydration and dehydrocarbon. At the same time, there are also new dehydration and de hydrocarbon technologies, such as supersonic separation technology, ifpex-1 technology, and the combination of traditional technology and new technology.

In addition, there are also low-temperature separation combined with washing or distillation process for heavy hydrocarbon removal, but the application is less. Usually in the day

A heavy hydrocarbon separator is set up after the natural gas liquefaction precooling. However, when the gas quality of the feed gas changes and the heavy hydrocarbon component increases, the heavy hydrocarbon separator can not separate the heavy hydrocarbon that meets the liquefaction requirements.

It can be considered to add a scrubbing tower or a rectifying tower behind the heavy hydrocarbon separator to extract the condensate with lower temperature from the natural gas channel from the liquefaction section of the cold box and inject it into the benzene and heavy hydrocarbon in the scrubbing natural gas at the top of the tower. Before the general project is put into operation, the design of heavy hydrocarbon removal unit should be carried out according to the feed gas composition, treatment load and treatment capacity requirements.

In the initial stage of design and construction, the influence of feed gas change on process and equipment shall be fully considered, especially the imported process package technology or engineering projects participated by foreign engineering companies, such as feed gas quality, feed gas source, water source, etc.

In order to improve the operation adaptability of LNG plant process and equipment to different factors and avoid load reduction due to device problems, the characteristics of its change should be fully considered. Before the general project is put into operation, the design of heavy hydrocarbon removal unit should be carried out according to the feed gas composition, treatment load and treatment capacity requirements.

According to the principle of heavy hydrocarbon removal in natural gas, the absorption method, low temperature separation method and washing method are used to remove heavy hydrocarbon. In actual production, different heavy hydrocarbon removal methods can be selected according to different process packages and liquefaction processes. According to the content of heavy hydrocarbon in feed gas, several methods can be combined to remove heavy hydrocarbon. For several heavy hydrocarbon removal schemes, the best scheme can be selected by comparing economic advantages, and the first scheme is more reasonable. As long as the appropriate heavy hydrocarbon removal process is selected according to the number of heavy hydrocarbon components in the feed gas, the accuracy of heavy hydrocarbon removal can be ensured, the freezing and blocking problem of cold box can be solved, the normal operation of liquefaction process can be ensured, and the long-term stable operation of the unit can be promoted, the liquefaction rate can be increased, the LNG production can be increased and the specific power consumption of the unit can be reduced.

1.3.1 Current status of foreign research on natural gas dewatering technology

In 1997, T.Naheiri et al. used a PVDC carbonized layer with porous aluminum tube as a support layer as a selective composite membrane to conduct laboratory and field tests on the mixed gas of hydrogen and light hydrocarbons. This inorganic composite membrane is more than C_2 . The hydrocarbons show a selectivity of more than 90%, and the stability is very good.

In 2000, AntOniO et al. used carbonized phenolic resin to carry out the above-mentioned similar experimental research on the surface active layer, and tested the multi-component mixture containing nitrogen and CrC_4 alkanes. When the $n-C_4H_{10}$ content was 20%, the separation factor reached 98. It is also found that the strongly adsorbing components in the multi-component gas have a decisive effect on the adsorption process, and the increase of its concentration will inhibit the penetration

of other components.

In 2001, Marmebo et al. used zeolite membranes to recover heavy hydrocarbon components from natural gas, and found that the relative adsorption of different hydrocarbon substances to zeolite membranes can be used to separate hydrocarbon components, even if heavy hydrocarbon components are in natural gas. In the case of low content, the zeolite membrane still shows good selectivity. In addition, OnumaCarmody et al. used organoclays to adsorb hydrocarbon components, and the results showed that organoclays had a large adsorption capacity for heavy hydrocarbons.

In 2007, Mitariten's patent invented integrated removal of heavy hydrocarbons, CO_2 , H_2S and water from the feed gas. It designed multiple absorption/adsorption steps to selectively separate heavy hydrocarbons and water, and prepared an aqueous amine solution to absorb and remove CO_2 and H_2S , while simultaneously adsorbing and dehydrating. In this method, the raw natural gas feed is first passed through an adsorption bed that selectively adsorbs heavy hydrocarbons and water to remove part of water and heavy hydrocarbons; in the second step, amine liquid is used to absorb and remove acid gases such as carbon dioxide and hydrogen sulfide. In the first step, the adsorption device adsorbs the remaining neutralization weight and then enters the next process.

In 2014, the heavy hydrocarbon removal patent invented by Chen, Fel et al. proposed a method and device for removing heavy hydrocarbons from a natural gas feed stream. The method uses one or more adsorption beds and uses gas-liquid separation equipment (including steam). The two heavy hydrocarbon removal systems composed of stripping tower, scrubber or gas-liquid separator remove heavy hydrocarbons above C_6 in natural gas. The first part makes natural gas depleted in heavy hydrocarbon natural gas, and the second part deeply removes heavy hydrocarbons to the natural gas liquefaction requirement. Three different working conditions are described separately, each of which has detailed explanations of various situations, and a detailed overview of various heavy hydrocarbon removal processes. Including the selective adsorption bed to remove heavy hydrocarbons before removing part of the heavy hydrocarbons with separation equipment, and then enter the liquefaction process, the natural gas after precooling and de-heavy hydrocarbons undergoes a deep adsorption and then enters the liquefaction section. The liquefaction pre-cooling section uses different adsorption methods to remove heavy hydrocarbons step by step, or adsorption and removal of some heavy hydrocarbons before liquefaction, and low temperature removal of heavy hydrocarbons in the liquefaction section.

1.3.2 Current status of domestic research on natural gas removal technology

In China, the low pressure difference throttling refrigeration de hydrocarbon technology designed by Li Shixuan et al. Was applied in Yulin gas field of Changqing in 2005. The heavy hydrocarbon was removed by $1.1m^3/d$, which completely solved the low-temperature dehydrocation technology of natural gas in well block 141, and made the dew point of natural gas exported meet the requirements.

In 2006, Zhang Kongming et al. Proposed the method

of using heavy hydrocarbon to absorb and remove heavy hydrocarbon from natural gas. After removing hydrocarbon, most of the heavy gas will enter the top of heavy phase scrubbing tower to remove the heavy hydrocarbon from the top of the heavy phase scrubbing tower. By simplifying the heavy hydrocarbon removal process and reducing energy consumption, the molar content of heavy hydrocarbon in the purified natural gas can be reduced to less than 10ppm.

In 2014, he Zhenyong et al. Proposed a device combining adsorbent and low-temperature separation to remove heavy hydrocarbons in natural gas. Most of the heavy hydrocarbons in the gas were removed from the adsorbent bed of the heavy hydrocarbon removal tower, and then the remaining heavy hydrocarbons were further separated and separated in the cold box at low temperature. The C_6 and $C_6 +$ heavy hydrocarbon components in the treated natural gas were removed to the extent that LNG could be dissolved.

In 2014, Dong Xianying et al. Proposed a device and method for removing heavy hydrocarbon from natural gas by distributed condensation. After decarbonization and dehydration, the natural gas first enters the shallow cooling separation system for heavy hydrocarbon separation, and then enters the deep cooling box for the second step of heavy hydrocarbon separation. After the dehydration, the natural gas can meet the requirements of cryogenic liquefaction for heavy hydrocarbon content. The separation system includes heat exchanger, refrigeration unit and heavy hydrocarbon separator. Finally, the heavy hydrocarbon condensate separated from the shallow cooling heavy hydrocarbon separator and the cryogenic heavy hydrocarbon separator is combined. After throttling and reheating, the gas phase is used as fuel and the liquid phase heavy hydrocarbon is recovered. At the same time, the process reduces the temperature of natural gas entering the liquefaction system after shallow cooling, reduces the load of the liquefaction system and improves the liquefaction capacity of the unit.

Three kinds of traditional heavy hydrocarbon removal technologies of natural gas mainly include adsorption separation method, isopentane dissolution method and cryogenic separation method. The adsorption separation method mainly uses porous solid such as silica gel, molecular sieve and activated carbon as adsorbent. Aiming at the difference of adsorption capacity of hydrocarbon components, the separation of hydrocarbon gas is suitable for the situation that the content of heavy components in feed gas is not high and the design scale is small, but it has the disadvantages of high energy consumption and high cost. There are two tower process and three tower process. The adsorption process is divided into three stages: adsorption, heating desorption and regeneration. However, it is often used to separate the medium and cold components. Isopentane dissolution method is mainly used for high benzene content in hydrocarbon components. Benzene rich natural gas enters into the debenzylization tower and contacts with isopentane washing solution in reverse, and isopentane solution dissolves and dehydrocarbonates. Cryogenic separation and de hydrocarbon, also known as low-temperature distillation, mainly uses the different boiling points of hydrocarbon components to achieve the purpose of gas-liquid separation. It is to cool the natural gas to the low temperature required below the hydrocarbon dew point temperature to obtain part of the condensate rich in $C_5 +$ hydrocarbons for heavy hydrocarbon separation and removal.

The throttling expansion method can be used to separate the gas after compression and cooling, which is commonly used in the process of LNG production.

The application of liquefied natural gas (LNG) is more and more widely used, which promotes the rapid development of liquefaction technology. Through the optimization and transformation of traditional dehydrocarbon process, new technologies such as supersonic separation technology and ifpex-1 new technology have been formed. There are also combination technologies of traditional technology and new technology, such as throttling separation method.

Supersonic separation technology is a new technology of condensing and separating water and liquid hydrocarbon from natural gas. Its equipment is mainly composed of hydrocyclone, Laval nozzle, vortex separation blade and diffuser. During the process of gas injection, the temperature decreases and the speed increases. At this time, water and heavy alkanes in natural gas are condensed into liquid to achieve the purpose of separation. The principle of throttling separation is that when the gas is throttled from high pressure to low pressure, the temperature of actual gas changes before and after throttling. Different components are separated in the process of cooling by taking advantage of the different condensing temperatures of hydrocarbon components in hydrocarbon containing feed gas.

Zhang Kongming et al. Put forward the method of heavy hydrocarbon absorption and removal of heavy hydrocarbon in natural gas, that is, after the heavy hydrocarbon rich natural gas enters the bottom of the heavy hydrocarbon removal tower, the gas phase enters the lower process, and the liquid phase is pressurized and sent to the top of the heavy hydrocarbon removal tower to contact with the rich hydrocarbon gas countercurrent as the washing liquid, so as to realize the separation of heavy hydrocarbon, and the molar content of heavy hydrocarbon after purification can be reduced to less than 10×10^{-6} . He Zhenyong et al. Proposed to use adsorbent combined with low-temperature separation device to remove heavy hydrocarbons in natural gas, that is, first use adsorbent to absorb most of the heavy components in the feed gas, and then enter the cold box to further separate the remaining heavy hydrocarbons at low temperature. The heavy components above $C_6 +$ can be fully separated to meet the product requirements for $C_6 +$, but the removal effect of neopentane in hydrocarbons is not obvious. Dong Xianying et al. Put forward a device and method of distributed condensation for heavy hydrocarbon removal. First, the shallow cooling separation is carried out, and then the secondary hydrocarbon removal is carried out in the cryogenic cold box. However, this method is only applicable to the case of less hydrocarbon content. Zhang Dejun et al. Put forward a kind of heavy hydrocarbon removal system of precooling box. The method of scrubbing and cryogenic separation was used to remove heavy hydrocarbon. Benzene and neopentane were removed by adding precooling small cooling box. Zhang Jingtao et al. Proposed an adsorption dehydration and heavy hydrocarbon removal system. Through adsorption to remove water in the regeneration gas and deep removal of heavy hydrocarbon, the content of water and heavy hydrocarbon in the returned regeneration gas is greatly reduced. Hou Wengui et al. Proposed a process for removing heavy hydrocarbon from liquefied natural gas, that is, the purified natural gas enters the scrubbing tower, and the gas phase at the top of the scrubber enters the

liquefaction cold box. After condensation and separation, the gas returns to the cold box again. This method can effectively prevent the cold box from blocking and can utilize part of the heat capacity of heavy hydrocarbon. Li Junfang et al. Proposed a liquefied natural gas (LNG) heavy hydrocarbon removal device and its method. The purified natural gas enters the scrubbing tower to remove benzene and heavy hydrocarbon components. The overhead gas phase enters the LNG liquefaction cold box and is condensed and separated. The separated gas phase returns to the liquefaction cold box again. This process is repeated to remove benzene and heavy hydrocarbon. Zeng Fanping and others analyzed the status and problems of heavy hydrocarbon removal in the $100 \times 10^4 \text{ m}^3 / \text{D}$ unit of Guangyuan liquefaction plant, compared the advantages and disadvantages of heavy hydrocarbon removal scheme, and adopted a new set of heavy hydrocarbon removal unit to reduce flash steam volume of heavy hydrocarbon, reduce power consumption and improve LNG yield. Hu Zhouhai et al. Proposed a new LNG process for heavy hydrocarbon removal. Supercooled LNG was used to condense and distill the light natural gas to realize calorific value adjustment. HYSYS software was used to simulate the liquid nitrogen reliquefaction process. It was considered that the liquid nitrogen re liquefaction process experiment could be extrapolated to the LNG rehydration process, but it was only a theoretical inference, but not verified in practice.

1.3.2.1 Methods for deep removal of heavy hydrocarbons in LNG plants

According to the investigations, in order to meet the removal of heavy hydrocarbons in natural gas and meet the requirements of natural gas liquefaction, there are generally four mainstream processes at local and abroad, namely silica gel adsorption, solvent absorption, heavy hydrocarbon washing, and optimized operation methods. Table 1.2 lists common natural gas removal processes. Brief introduction of heavy hydrocarbon process plan and typical examples of domestic application.

Since optimizing the operation method is essentially heating up, dissolving the frozen part and re-liquefying, it does not fundamentally solve the problem. It depends on increasing

energy consumption and reducing efficiency which can only be used as a stopgap measure for thawing. Thus it is not used as a common scheme, the first three common processes are analyzed below.

In some plants that produce LNG by injecting natural gas, the design of deviation value of gas source components in LNG production may always be changed due to the complexity of raw material gas source, unstable mixing ratio and user's gas consumption. This situation has happened in most domestic LNG plants, and some LNG plants have Factories even change frequently in days. Among these changed components, the change of heavy hydrocarbon has the greatest impact on the system. In the process of heavy hydrocarbon removal, the natural gas channel of cold box will be frozen and blocked to a certain extent, which will cause the temperature difference between cold and hot ends more than 20°C , which will lead to a sharp decline in the production efficiency of LNG plant. When the LNG plant is shut down due to freezing and blocking, it is necessary to keep the natural gas channel unblocked. This will affect the production progress of the plant, and will cause a large number of natural gas flare. At the same time, many refrigerant before restart will be vented, which will bring huge waste of resources and economic losses to the LNG plant. For many reasons, the LNG plant needs to change the deviation value of the gas source components in normal operation, which may lead to a series of problems, such as some naphthenic hydrocarbons, aromatic hydrocarbons and some or more alkanes, which are very easy to cause the cold box to cool down in the low temperature environment, resulting in freezing and blocking of the circuit. To solve this problem, three kinds of traditional heavy hydrocarbon removal processes are listed and studied. The following is a brief introduction and analysis.

(1)Cryogenic separation process

When the domestic natural gas industry is still in the development stage and there is no perfect natural gas pipeline network, the pit gas is usually used as the feed gas in China's LNG plants, and the pit gas has relatively fixed and less volatile natural gas components, so the cryogenic separation process is

Table 1.2 The technology proposal of heavy hydrocarbon removal from natural gas

Number	Solution	Contents	Situation
1	Adsorption method	A silica gel adsorption bed is added to the outlet of the molecular sieve dehydration unit, with two tower processes, one tower for adsorption and one tower for regeneration and cold blowing.	The method was used in a LNG plant in Ningxia, but the effect was not good
2	Solvent absorption method	A washing tower is added after the heavy hydrocarbon separator, and a special absorption solvent is used to wash the benzene and heavy hydrocarbon components in the natural gas. Need to purchase absorption solvent.	The method is applied to an LNG plant in Yan'an
3	Cryogenic separation	A scrubber is added after the heavy hydrocarbon separator, and the principle of similar compatibility is adopted, and the removed heavy hydrocarbons are returned to the scrubber for washing without the need to purchase special solvents.	The method is applied to a LNG plant in Jilin
4	Optimize operation method	By reducing the operating pressure of the heavy hydrocarbon separator, the separation temperature of the heavy hydrocarbon is lowered, which can temporarily alleviate the freezing and blocking problem of the cold box.	This method is used in Guang'an LNG project.

the best. This method of heavy hydrocarbon removal is mainly to reduce the pressure of natural gas at the extraction point in the middle of the cold box, and at the same time, the temperature of the natural gas will drop below 50 °C, so that the heavy components in the feed gas will be separated out from the cold box separation tank in the form of liquid, which is still in the gas state in this environment. Then, it is divided into two phases by the foam net in the separator, and then the heavy components in the feed gas are separated to avoid freezing and blocking in the cold box channel.

The cost of this method is less and the operation is relatively simple. However, if the content of various components in the feed gas exceeds 1000ppm, it is required to lower the temperature at the extraction point of the cold box, which will lead to a lot of liquefaction ahead of time and cause the loss of LNG products. When the content is small, it is difficult to effectively remove the heavy hydrocarbon, and then freeze plugging occurs.

(2) Low temperature washing process

When the natural gas is precooled at - 40 °C above the cold box, it is allowed to enter the low-temperature scrubber. Some LNG products are used as reflux of tower top to ensure that there is no residue of heavy component in natural gas at the outlet of tower top; liquid phase refrigerant or feed gas is used to supply heat to reboiler at bottom of tower to improve heavy hydrocarbon content of separated components and reduce flash capacity.

The advantage of low temperature scrubbing process is that it can adjust the top reflux of LNG tower based on the content of heavy components in feed gas, so it has strong adaptability to component changes and has a large adjustment range, and the initial input cost of this process is low. However, LNG reflux is adopted in this process, so the heavy components do not have high solubility in LNG, and the temperature change is more used for separation. When the content of toluene, benzene and other aromatic hydrocarbons in the heavy component is large, a large amount of reflux LNG will be consumed. Moreover, the low-temperature distillation tower is used in this process, so the operation is more complex.

(3) dry adsorption process

In this process, the heavy components in the pretreatment stage of feed gas can be absorbed by adsorbent, and then the heavy components can be separated out, so as to avoid the freezing and blocking of the heavy components in the cold box at low temperature. The adsorption process is usually carried out by two or three towers. The two tower adsorption process has the advantages of low cost and simple operation, but the regeneration and desorption time is relatively long, which affects the heavy hydrocarbon removal efficiency; the cost of three tower adsorption process is relatively high and the operation is relatively complex, but because one bed is in adsorption work, the other two beds are heating and cold blowing, so the weight is removed. The efficiency of hydrocarbon is high.

The main advantage of the dry adsorption process is that it can fully remove the heavy components in the feed gas for the content of heavy components within the design range, and it requires less additional cooling capacity for the cold box when

separating the heavy components, which can effectively reduce the power consumption of the refrigerant compressor. However, if the heavy components in the feed gas exceed the design range, it is very easy to cause the penetration of heavy components in the adsorption bed, and it is usually easy to penetrate the removed feed gas, and aromatic hydrocarbons are difficult to be removed by using the temperature change in the cold box, so it is easy to cause the freezing and blocking of the cold box.

(4) summary

To sum up, the three traditional heavy hydrocarbon removal processes of LNG plant have their own advantages and disadvantages in removing heavy components in feed gas. Combined with the actual production situation of the plant, the heavy hydrocarbon removal process should be reasonably used to improve the heavy hydrocarbon removal efficiency and ensure the normal operation of the LNG plant.

1.3.2.2 Silica gel adsorption method

The main adsorbents are activated carbon, zeolite molecular sieve, alumina, silica gel and ion exchange resin. The good adsorption performance of adsorbent is the basic condition of adsorption and separation process. The following problems should be paid attention to when selecting adsorbent

(1) The adsorbent should have a large amount of adsorbed impurities, and the adsorbed impurities are easy to desorb, so as to achieve the balance between adsorption and desorption in a short period of time, so as to ensure the separation and purification.

(2) The separation coefficient between components should be as large as possible. The higher the separation coefficient of the gas component is, the easier the separation is, the higher the purity of the product and the higher the recovery rate.

(3) The adsorbent used should have sufficient strength to reduce crushing and wear.

(4) A variety of adsorbents can be selected for the separation of gas mixtures with complex components and various categories. These adsorbents can be loaded in the same adsorbent bed layer by layer according to the adsorption and separation performance, or they can be loaded in multiple adsorption beds.

Silica gel is a silica xerogel. It is a porous solid with a large specific surface area. The surface is covered with a large number of active silanol groups. It can be used as a desiccant, adsorbent, catalyst, and catalyst carrier, which is widely used in industrial production. The key to the removal of heavy hydrocarbons is that there are no heavy components in the raw gas components used as the basis for the design of the liquefaction unit. If the heavy hydrocarbon content is small, there is no need to install a heavy hydrocarbon removal unit for the treatment of this feed gas. However, if feed gas containing excessive benzene and other heavy hydrocarbons (C_6+) may enter the plant in the future, heavy hydrocarbon removal units need to be installed to avoid freezing and related operation failures in the liquefaction part. The heavy hydrocarbon components above C_6 in the feed gas must be removed to the trace level to ensure that the facilities of the liquefaction unit are free from blockage, barrier-free and meet the requirements of the cooling part of the liquefaction unit. If the raw material gas contains less than C_6 components but still reaches the highest allowable content.

The main process is as follows:

Heavy hydrocarbons are removed by two silica gel beds, which is called heavy hydrocarbon removal bed. The design includes the combined use of molecular sieve (MS), activated carbon and silica gel (SG) in the adsorption bed. The MS layer mainly removes any vapor phase water, so the MS layer is placed on top of the SG layer as a protective layer. Generally, the recommended adsorbent grade is: molecular sieve adsorbent is 4A type small particle grade produced from high-purity 4A zeolite crystals. Its large particles can increase the crushing strength, maintain the ability to absorb water molecules, and further distribute the gas flow. Benzene, toluene, xylene (BTX) and a small amount of C_8 and above are all removed to trace level (usually a small amount of PPMV) in the silica bed. Activated carbon is also granular and has a strong adsorption pore structure, which can adsorb a large number of aliphatic hydrocarbons.

Under normal operating conditions, one bed is in adsorption state, one bed is in heating regeneration state, and one bed is in cooling regeneration/standby state. After natural gas passes through the bed, heavy hydrocarbons are adsorbed and removed. Before the heavy hydrocarbon components adsorbed by the adsorption bed are saturated, the silica gel bed must be switched to the analytical state. The feed gas enters another silica gel bed that has been regenerated and is waiting to adsorb heavy hydrocarbons. The saturated bed is regenerated to precipitate heavy hydrocarbons. The total regeneration cycle time is to be provided by the supplier after confirmation. The switching of the entire adsorption, heating, cooling, and standby process is completed by the switching time of the DCS system control program switching valve. These shut-off valves are also used to isolate the adsorption and Regenerate two different circuits to avoid mixing of the two streams.

The high-temperature circulating hot oil heats the regeneration gas to 280°C. The high-temperature regeneration gas then takes away the adsorbed heavy hydrocarbons. Then air-cooled in a cooler. The condensed heavy hydrocarbon is collected in the storage tank, and the gas from the regeneration gas cooler is sent to the external pipeline of the factory. The liquid collected in the heavy hydrocarbon storage tank is sent to the condensate tank

intermittently through the liquid level control valve store, and then load the truck for export. The adsorption bed will be cooled after heavy hydrocarbons are taken away and enter the next cycle. The air source in the cooling stage is the same as the hot blowing air source, but the regeneration gas heater is not used at this stage, and at least 5-10% of the flow is maintained through the regeneration gas heater to avoid surface high temperatures. The cold regeneration air flows through the bed, then through the regeneration gas cooler, and finally into the outer tube.

After the regeneration cycle is completed, the adsorption bed is to be used until another adsorption bed completes its adsorption stage.

The specific flowchart is shown in the [Figure 1.1](#):

The performance of adsorbent determines the application of adsorption separation technology, so in practice, the development of new adsorbents has always been the focus of research and development of adsorption separation technology. To improve the existing adsorbents to improve the economy and effect of the process; to synthesize new adsorbents and materials for adsorption and separation, such as the synthesis of different types of new molecular sieves which have been applied in the process of adsorption and separation; to develop adsorption materials and adsorption separation processes with new application characteristics based on the characteristics of existing adsorption materials, For example, using the characteristics of alumina, silica gel, molecular sieve and other commonly used desiccants, there is a wide space to develop various desiccants that meet the specific application field according to the drying conditions of different fluids; the main direction of adsorbent development is to develop the application specific adsorption separation technology by using some properties of adsorbent and adsorbate.

1.3.2.3 Isopentane absorption method

The main process of isopentane absorption method is as follows: The pre-treated natural gas is first pre-cooled to -55°C, then flows out of the cold box and enters the gas-liquid separator to separate C_5 and above heavy hydrocarbon components, and the natural gas after the heavy hydrocarbons are removed

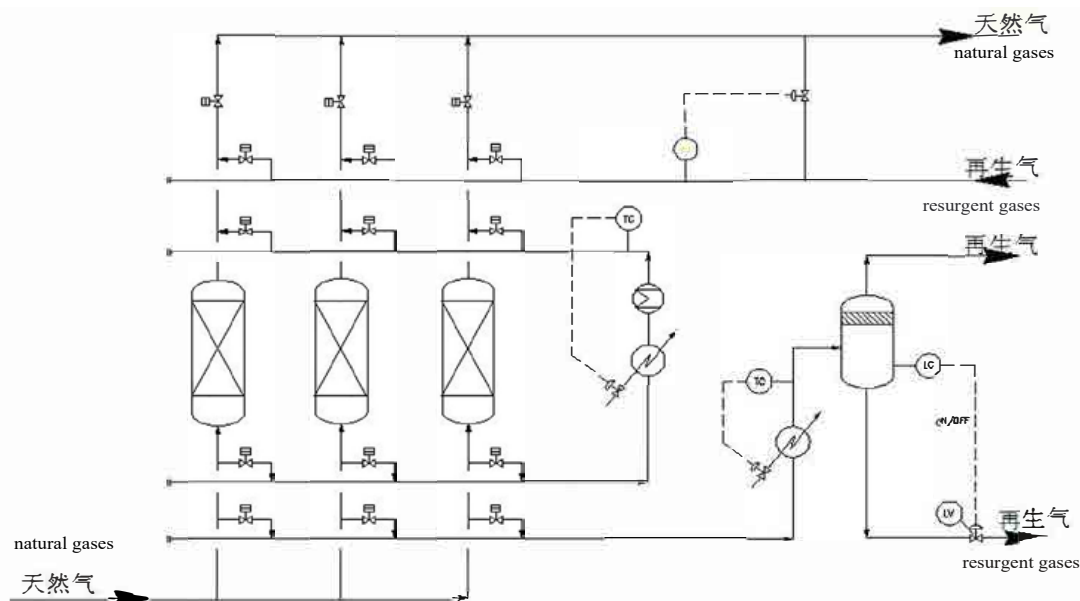


Figure 1.1 The flow chart of heavy hydrocarbon removal in the way of Silica gel adsorption method

enters the isopentane scrubber, passing through the isopentane scrubber from bottom to top, and come into contact with the isopentane liquid from top to bottom in countercurrent. Use isopentane to remove heavy hydrocarbons, benzene and aromatic hydrocarbons in natural gas. Isopentane comes from an isopentane storage tank and is pressurized by an isopentane booster pump. Isopentane can remove benzene and aromatic hydrocarbons from natural gas. After the heavy hydrocarbons are removed, the natural gas enters the cold box and continues to be cooled to -160°C , and then throttling by the J-T valve to obtain the LNG product (-166.64°C).

The heavy hydrocarbon (-55°C) separated from the heavy hydrocarbon separator enters the heat exchanger for heat exchange, after passing through the liquid level regulating valve, and then after heat exchange, it exchanges heat with the refrigerant liquid again, and the two liquids are reheated until 20°C , it enters the heavy hydrocarbon separation tank. The liquid separated from the heavy hydrocarbon separator tank (the main components are benzene-rich isopentane and heavy hydrocarbons) is stored in the heavy hydrocarbon tank, and then transported out of the tanker. The process flow chart is as follows in the Figure 1.2:

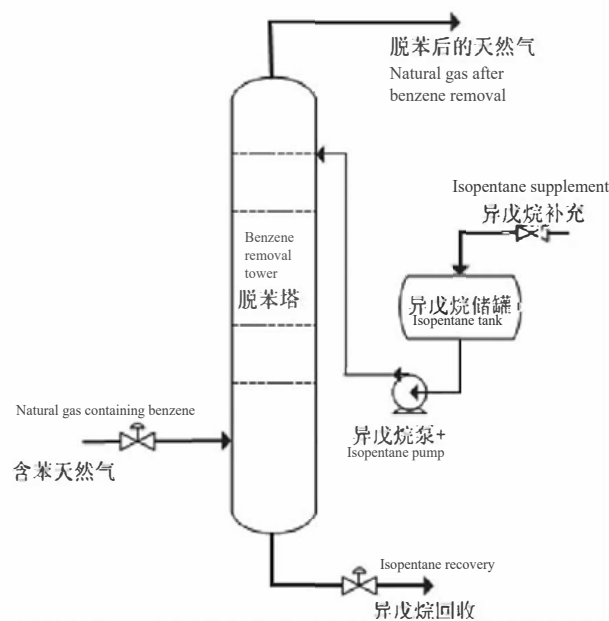


图2 溶解法流程图

1.3.4 Low-temperature separation method

The principle of the cryogenic separation method is to use the different melting and boiling points of different components for

Figure 1.2 The flow chart of heavy hydrocarbon removal in the way of Isopentane adsorption method

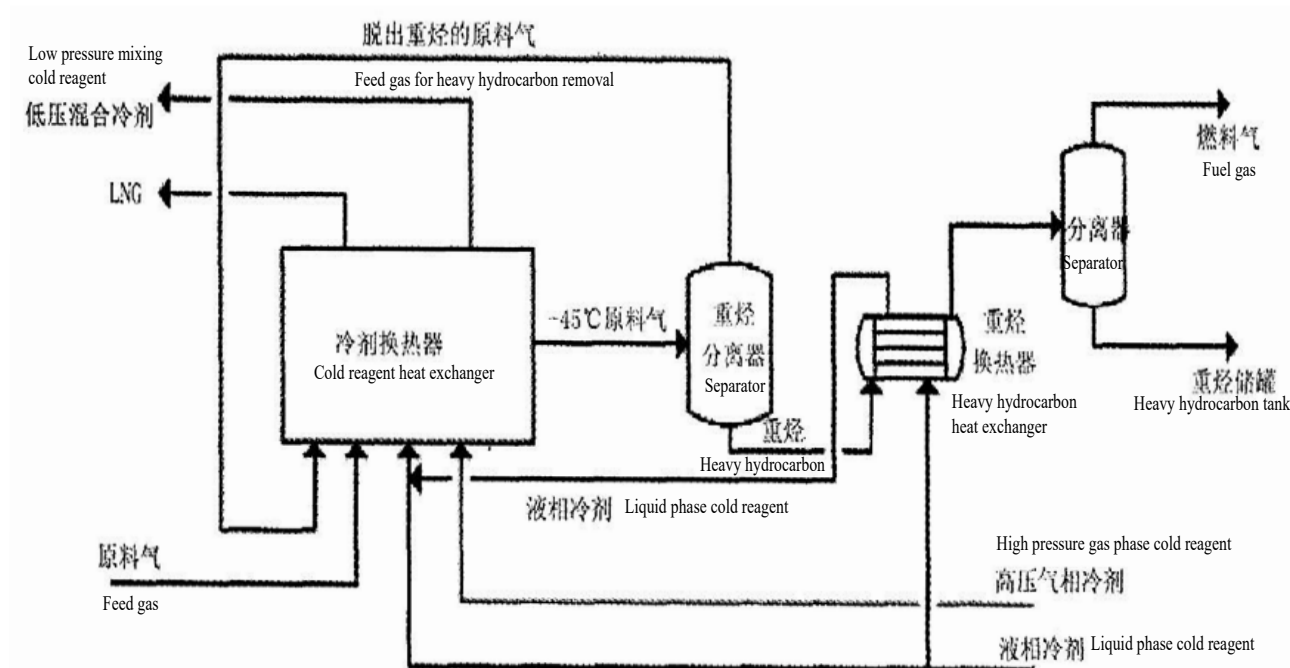


Figure 1.3 The flow chart of heavy hydrocarbon removal in the way of low temperature separation method

gas-liquid separation. It cools natural gas to a low temperature below the hydrocarbon dew point temperature to obtain a part of the condensate rich in heavier hydrocarbons and separates it from the gas at this low temperature. The main process is shown in the Figure 1.3:

1.3.5 Problems in the three processes

All three processes have certain disadvantages.

Disadvantages of the adsorption method: mainly for the main natural gas feedstock is heavy hydrocarbon (C_5^+) pipe network

gas and gas field gas with less components (less than 200ppm). It also uses natural gas to regenerate. If the natural gas plant is a base plant, the heavy hydrocarbons in the regenerated gas need to be separated, otherwise the regenerated gas will have nowhere to go. This method requires two or more adsorption towers for switching operations at the same time, and a heating furnace for regeneration needs to be added, which results in high energy consumption.

Disadvantages of the absorption method: solvents need to be purchased outside, and absorption solvents need to be

supplemented during the production operation. The source isopentane is expensive in the market and cannot be regenerated during absorption. When the absorption of isopentane is saturated, it can only be used as waste liquid deal with.

Disadvantages of the cryogenic separation method: Generally, the size of the separator is small, the separation is not complete when the heavy hydrocarbon content is high, and the heavy hydrocarbon content cannot be separated at a certain temperature when the heavy hydrocarbon content is low. If it is too high or too low, it will still cause ice blockage in the cold box. The bottom of the rectification tower needs to be heated by a heat source, and the top of the tower needs to be cooled by a cold source. Therefore, it is necessary to add a bottom heating system and a cooling system at the top of the rectification tower. The energy consumption is large and the investment is high, which is not conducive to saving investment and reducing energy for LNG plants consumption.

Taking a project as an example, based on the above comparative analysis, the 1.2 million tons/year natural gas liquefaction process technology has selected the cryogenic separation method. The natural gas containing heavy hydrocarbons enters the bottom of the heavy hydrocarbon scrubber, and most of the heavy hydrocarbon is removed in the heavy hydrocarbon scrubber. After the hydrocarbons, they are discharged from the top of the heavy hydrocarbon scrubber and cooled into a gas-liquid two-phase. The gas phase enters the next cooling process, and the liquid phase is pumped to the top of the heavy hydrocarbon scrubber by a heavy hydrocarbon reflux pump so that the heavy hydrocarbons and natural gas are in countercurrent mass transfer contact, thereby washing down most of the heavy hydrocarbons in natural gas. At the same time, in order to improve the quality of heavy hydrocarbon products, reduce the flash steam flow rate of heavy hydrocarbons and the saturated vapor pressure of heavy hydrocarbon products, a stripping line is installed in the heavy hydrocarbon scrubber, and normal temperature natural gas is used as the heating medium for the stripping to directly contact the heavy hydrocarbons. Reduce the content of light components in heavy hydrocarbons.

The composition comparison before and after the heavy hydrocarbons of natural gas removed is shown in Table 1.3.

It can be seen from the above that the removal effect of heavy hydrocarbons in natural gas is better, and the content of C6 and above components in natural gas after heavy hydrocarbon removal is less than 1 ppm. The heavy hydrocarbon scrubbing method is used to remove heavy hydrocarbons in natural gas, which not only ensures that subsequent equipment does not freeze up, but also the removed heavy hydrocarbons can also be exported as products, resulting in economic benefits.

1.4 Research content and key issues to be solved

1.4.1 Research content

This subject is based on a natural gas liquefaction plant with a daily processing capacity of 1 million cubic meters in Sichuan. The cold box freezing problem caused by the unclean removal of heavy hydrocarbons has led to the study of different heavy hydrocarbon removal technologies, which is a later stage of the Inner Mongolia LNG project designed and provided technical support.

Table 1.3 The comparison of natural gas components before and after heavy hydrocarbon removal

Component	Before heavy hydrocarbon removal	After heavy hydrocarbon removal
Nitrogen	0.025298	0.025374
CO ₂	0.000005	0.000005
Methane	0.939321	0.941545
Ethane	0.028604	0.028532
Propane	0.004332	0.004046
i-Butane	0.000544	0.000322
n-Butane	0.000897	0.000172
22-Mpropane	0.000071	0.000004
i-Pentane	0.000191	0
n-Pentane	0.000212	0
n-Hexane	0.000232	0
n-Heptane	0.000075	0
n-Octane	0.000018	0
n-Nonane	0.000004	0
Benzene	0.000067	0
E-Benzene	0.000002	0
Toluene	0.000024	0
Mecyclopentan	0.000022	0
Cyclohexane	0.000042	0
Mecyclohexane	0.000039	0

1) Collect raw gas on-site at an LNG plant in Sichuan, analyze it with chromatographic methods, and analyze the components and content of natural gas, focusing on the content of aromatic hydrocarbons;

2) Collect the DCS operation data of a factory in Sichuan to analyze the temperature range of the freezing block and the reasons for the freezing block;

3) Use HYSYS software to simulate the data analyzed by a certain LNG plant in Sichuan, obtain the condensation characteristic curve, calculate the boundary conditions and boundary parameters of the frozen blockage of the LNG composition, and obtain the technical indicators of whether the heavy hydrocarbons are frozen or not;

4) Conduct research on three heavy hydrocarbon removal processes, including heavy hydrocarbon scrubbing, gas stripping + heavy hydrocarbon scrubbing, and cryogenic rectification, analyze the applicable conditions and operating conditions of different processes, and conduct technical feasibility studies to achieve the "no-freeze index";

5) Carry out energy consumption analysis, equipment investment analysis for heavy hydrocarbon scrubbing, gas stripping + heavy hydrocarbon scrubbing, and cryogenic distillation to calculate the best plan or the best applicable conditions for different plans through process simulation;

6) Limit the output of liquefied natural gas liquefied products, and optimize the temperature control analysis of heavy hydrocarbon removal according to the energy consumption of the refrigerant under the given constraints;

7) Research on the influence of the composition of natural gas on the three process schemes for heavy hydrocarbon removal;

8) To research the influence of process parameters such as pressure and temperature on the efficiency of cryogenic distillation.

1.4.2 Key issues to be solved

Based on the investigation of the freezing and blocking problems of existing heavy hydrocarbon freezing and blocking LNG plants, the characteristics of heavy hydrocarbon freezing are studied. Combined with the research on the causes of freezing and blocking problems, relying on an LNG project in Inner Mongolia of PetroChina, a set of process schemes suitable for heavy hydrocarbon removal in country's LNG plants with simple process, low energy consumption and convenient operation are studied. The liquefaction plant is not shut down due to the freezing of heavy hydrocarbons.

2 Plate-fin heat exchanger

Before natural gas is liquefied, the heavy hydrocarbons contained in it need to be removed to prevent heavy hydrocarbons from freezing at low temperatures and blocking equipment and pipelines. The lighter ones cause the factory to stop production, the more serious ones have safety accidents. In LNG projects, cold boxes generally adopt a compact, lightweight, and efficient plate-fin structure. As natural gas is cooled and liquefied, cyclic aromatic hydrocarbons, mainly benzene and benzene derivatives, are easy to solidify and block the narrow cold box. This chapter introduces the occurrence point of freezing blockage in LNG plant, the principle, classification, structural characteristics, fluid flow direction, and heat transfer principle of the key equipment heat exchanger. On this basis, the problem of fin selection and heat exchanger combination mode is analyzed to exchange the structure optimization of the heat exchanger reduces the probability of freeze blockage.

2.1 Overview

The aluminum plate-fin heat exchanger has the following advantages. The first is the lightweight of the equipment, because it is mainly constructed of aluminum alloy, and the weight is about 10% of the tube heat exchanger. The second is the high pressure resistance, generally domestic plate-fin. The pressure resistance of the type heat exchanger can reach 8.0MPa. The third is to support the simultaneous heat exchange of multiple streams. The same heat exchanger can support up to 20 streams of heat exchange at the same time and can pump fluids from different temperature points. Because of the above advantages, aluminum plate-fin heat exchangers are often used as cold boxes of LNG liquefaction plants.

However, it has two shortcomings at the same time. The first is that it is not resistant to corrosion, that is, it cannot be used where it is corrosive to aluminum alloy. The second is that it is easy to block. Since the pitch of the fins is mostly only 1.0mm–4.2mm, the circulating medium without solid impurities, if the circulating liquid freezes, it is easier to cause partial blockage.

2.1.1 Conditions and direction of heat transfer

In daily life and the production of industrial products, there are various forms of heat transfer phenomena. Such as heating or cooling a certain fluid, boiling of liquid and condensation of gas.

People have summed up many practical experiences and come to this conclusion wherever there is a temperature difference between different objects or different parts of the same object ($t_1 - t_2 > 0$), there must be heat transfer. The heat transfer is always automatically caused by high temperature. The object is transmitted to the cold object. For example, the combustion of natural gas makes the water boil, the air conditioner makes the air in the room cooler (or warmer), the cooling water tower water cools, etc. From the above phenomenon, it can be concluded that $T_{f1} - T_{f2} > 0$, "Where there is a temperature difference, there is heat transfer."

2.1.2 The importance of plate-fin heat exchangers in the cryogenic process industry

Typical low-temperature process industrial equipment (such as cryogenic separation air separation complete equipment, cryogenic multi-component gas (oil field gas, natural gas, coke oven tail gas, synthetic ammonia tail gas, coal bed methane, coal-to-synthetic natural gas, etc.) separation and liquefaction equipment, Large-scale ethylene cryogenic separation device, synthetic ammonia cryogenic liquid nitrogen washing device), it is necessary to efficiently recover cold energy and use a large number of aluminum plate-fin heat exchangers. As an important part of a complete set of equipment, depending on the size of the equipment, its investment accounts for 10% to 40% of the total amount of the complete set of equipment. The heat transfer performance of the heat exchanger directly affects its investment and operating costs. It is a complete set of equipment technology. An important evaluation index for performance and economy.

2.1.3 Features of low-temperature heat exchanger

The heat exchanger of low-temperature process industrial equipment is characterized by deep low temperature and small temperature difference.

1) The vast majority of heat transfer processes in the cryogenic process industry are carried out under small temperature differences. The smaller the heat transfer temperature difference, the smaller the irreversible loss of the process. For example, in an air separation plant, calculation and analysis show that the temperature difference at the hot end of the main heat exchanger is reduced by 1°C, and the energy consumption of the whole plant can be reduced by about 2%; the temperature difference between the condensation evaporator in the main tower and the argon tower is reduced by 1°C, energy consumption can be reduced by about 5%.

2) In the low-temperature process, the required heat exchanger flow resistance is small. In an air separation plant, the flow resistance of each fluid flowing back from the main heat exchanger increases by 10Kpa, the air compressor discharge pressure needs to be increased by 30Kpa, and the energy consumption of the device is greatly increased. Therefore, a small flow rate is generally selected and a larger heat exchange area is required, thus heat exchange elements with compact heat exchange surfaces should be selected.

3) In the low-temperature process, when the gas temperature is close to the critical temperature, its physical properties change greatly. Therefore, the integral average temperature difference should be used to calculate the heat transfer temperature difference to improve calculation accuracy.

6) The cold loss of the heat exchanger during the low-temperature process directly affects the energy consumption of the equipment, so effective cold preservation measures should be taken.

Heat exchangers can be classified in many ways. As the structure is the main factor that affects the freezing and blocking, the analysis is focused on the different classifications of the structure, which can be divided into shell-and-tube heat exchangers (also subdivided into coil, tube, and sleeve) and plate-type heat exchangers (also subdivided into plate-fin type, plate type, spiral plate type).

Local successfully developed this product on air separation equipment in the late 1970s. After the 1990s, the introduction of American technology led to the rapid development of local plate-fin heat exchanger manufacturing technology. The main domestic manufacturers include Hangyang, Sichuan Air Separation and Kaifeng Air Separation Company. Hangyang began designing and manufacturing ethylene cold boxes in the 1990s and providing products to companies such as Yanshan Petrochemical. The ZH-2060 large vacuum brazing furnace

On the basis of plate bundle, the upper head, nozzle and support are combined to form a complete PFHE, as shown in Figure 2.2.

2.5 The flow direction of the plate-fin heat exchanger fluid

The flow of fluid in the plate-fin heat exchanger can be realized by designing different flow channels to achieve co-current (two fluids flow in parallel and in the same direction), counter-current

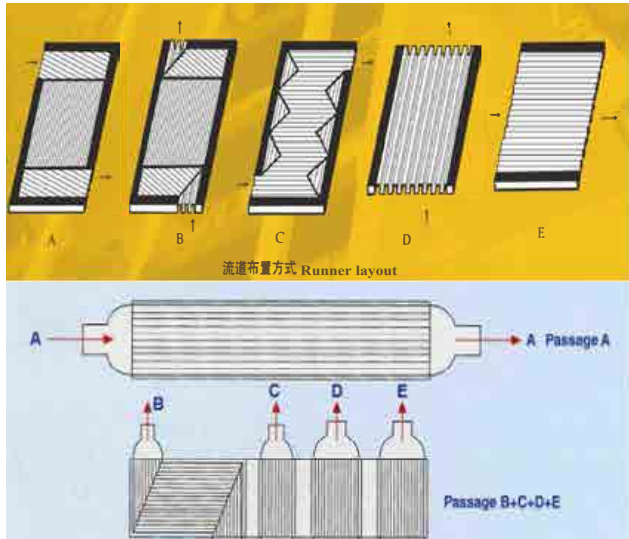


Figure 2.3 The fluid flow diagram of heat exchanger

(two fluids flow in opposite directions and parallel), cross-flow (two fluids are perpendicular to each other), and mixed flow (part of counter flow, part of crossflow), etc. As shown in Figure 2.3:

The heat exchanger preferentially adopts countercurrent arrangement and adopts mixed flow when countercurrent cannot be used. Mixed flow should be adopted when multiple fluids are required to exchange heat at the same time.

2.6 Heat transfer temperature difference of plate-fin heat exchanger

The heat transfer temperature difference is the power for the heat

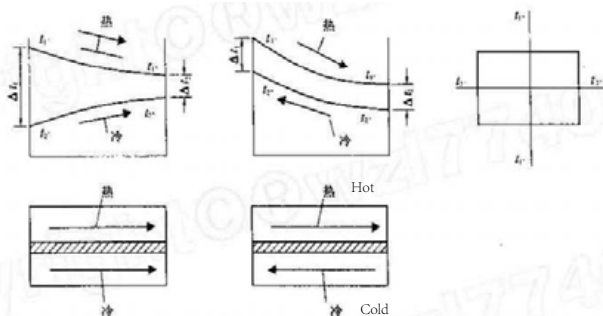


Figure 2.4 The temperature changes under different flow directions in heat exchanger

transfer of the heat exchanger. The flow direction of the fluid in the heat exchanger has different temperature changes, as shown in Figure 2.4:

The average heat transfer temperature difference of the heat exchanger is determined by the temperature change and flow direction of the fluid. Generally, there are three models of arithmetic, logarithm, and integral to calculate the average heat

transfer temperature difference.

The arithmetic average temperature difference is the simplest, that is, the calculation model considers the temperature change to be linear, so the result is the arithmetic average of the cold and hot ends. This calculation result has a large deviation and is generally not used.

$$\Delta t_{\text{算}} = \frac{\Delta t' + \Delta t''}{2}$$

When the specific heat, heat transfer coefficient and flow rate of the fluid are stable, the logarithmic average temperature difference is used to calculate.

In the LNG liquefaction process, the phase change or supercritical state, the specific heat capacity changes drastically. At this time, the logarithmic average temperature difference is used to calculate, and the error is also large. Therefore, the integral average temperature difference calculation is used, and the result is more accurate. The calculation process is rough as follows:

1. Make temperature-enthalpy diagrams of cold and hot fluids (T-Q diagram);
2. Divide the curve into several intervals, so that the curve in each interval is approximately a straight line;
3. Calculate the logarithmic average temperature difference of each interval separately;
4. Weighted calculation MTD:

$$MTD = \frac{\sum Q}{\sum \frac{Q}{MTD}}$$

The accuracy of the calculation depends on the frequency of the segments. The more segments, the more accurate the temperature difference calculation. When calculating the temperature difference in the fourth chapter of this article, the HYSYS software is used on the computer to simulate the thermal calculation of the heat exchanger, and the calculation points are 60~100 points.

2.7 The form and selection of fins of the plate-fin heat exchanger

2.7.1 The form of the fin

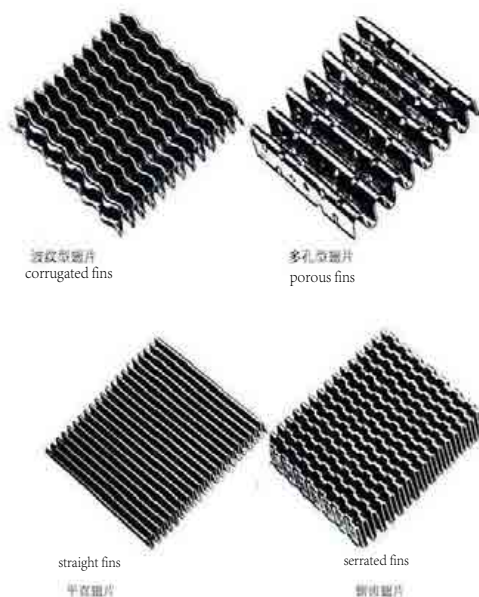


Figure 2.5 The common forms of fins

There are 4 common fin forms: straight fins, porous fins, serrated fins and corrugated fins, as shown in Figure 2.5.

The straight fin is rectangular, and its main function is to expand the heat transfer surface. The heat transfer principle is similar to that of fluid flowing through a circular pipe.

The serrated fin has more serrations based on straightness, which increases the disturbance to the fluid. Under the same pressure drop, the heat transfer coefficient is 30% higher than that of the straight fin.

The porous fin is also a modification of the straight fin, adding many holes. Also in order to increase disturbance and improve heat transfer performance, the opening rate is generally 5-10%.

The corrugated fin is stamped into a certain wave shape on a straight fin, which breaks the heat transfer boundary layer. The denser the corrugation, the better the heat transfer performance.

2.7.2 Selection of Fins

The area of the fin in the heat transfer of the heat exchanger contributes more than 90%, and its choice is very important. Generally need to choose according to pressure, fluid, pressure drop limit, etc.

When the fluid contains suspended solids, flat fins are often used; corrugated fins are used when the fluid has a high viscosity liquid; porous fins are used when there is a phase change in the heat transfer process.

2.8 Combination of the plate-fin heat exchanger

When the plate-fin heat exchanger is manufactured, its cross-sectional size and length are restricted by the process equipment (vacuum brazing furnace) and the manufacturing process level, so in large-scale installations, the heat exchanger usually needs to be combined in series and parallel to meet the requirements. When multiple units are combined, reducing and preventing the uneven distribution of fluid is a very important issue. Poor handling will seriously affect the heat exchange performance

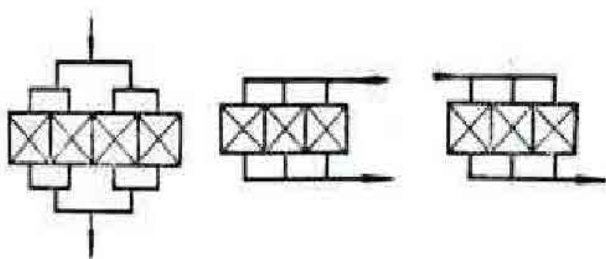


Figure 2.6 The common combination of heat exchangers

of the heat exchanger. There are mainly three modes of unit combination: symmetrical, convective, and parallel, as shown in Figure 2.6:

In order to distribute the fluid evenly, the symmetrical method should be selected as much as possible when selecting the heat exchanger. At the same time, as strictly as possible based on the reference results of the channel resistance test of each heat exchanger unit, matching the resistance, and comprehensively considering the piping of the processing pipeline. In the design of the collecting pipe, comprehensive consideration should be given to make the total circulation area of the collecting pipe larger than the total circulation area of the inlet pipes of each unit, so as to minimize the phenomenon of non-distribution.

3 Analysis of the Causes of Freeze Blocking of the Cold Box in LNG Plant

3.1 Overview

Natural gas liquefaction is a low-temperature process. When the pressure of natural gas is constant and when the liquefaction reaches a certain temperature, the C_5+ in the natural gas is first condensed, so that the separation of C_5+ can be realized. A plant in Sichuan uses a cryogenic separator outside the cold box to separate heavy and aromatic hydrocarbons separated from the liquefaction project. That is, natural gas enters the cold box after pretreatment. After being cooled to a certain temperature in the cold box, it is drawn out of the cold box and enters the heavy hydrocarbon separator. After the heavy hydrocarbons are separated, the natural gas enters the cold box to continue cooling and liquefying into LNG. The heat exchanger in the cold box uses a plate-fin heat exchanger. The heat exchanger is characterized by narrow circulation channels, a large amount of heat exchange material, and high heat exchange efficiency. When the heavy hydrocarbon aromatics or CO_2 in the natural gas is not cleaned and does not reach the allowable value of liquefaction, the heavy hydrocarbon aromatics or CO_2 slowly solidify during the liquefaction process of natural gas, blocking the passage of the cold box, thereby reducing the heat exchange area and flow, the factory cannot run continuously.

3.2 Freeze blockage of the cold box

According to statistics, the freezing of natural gas channels in the cold box caused by the solidification of heavy hydrocarbons, benzene and their derivatives during the natural gas liquefaction process is a common phenomenon in the LNG industry. The current research direction of most people is mainly concentrated on natural gas liquefaction process refrigeration technology, refrigeration equipment, liquefaction equipment, and automatic control. In the face of freezing and blocking of cold boxes and pipelines in the process of natural gas liquefaction, there is only a description of the blockage on the spot, without substantive research and analysis of the reasons for freezing and blocking. In order to find the reason for the blockage of the cold box and pipelines of natural gas in the operation of the liquefaction plant, and to find the best solution, this subject needs to combine the example of freezing and blockage of the cold box of a liquefaction plant in Sichuan, and the collected raw gas data through raw gas and operation analyze the causes of freezing and blockage based on the operating procedures of the operators and provide guidance for the design of the Inner Mongolia LNG plant.

3.2.1 Device introduction

The liquefaction capacity of Kunlun Energy's Guang'an LNG plant is $100 \times 10^4 \text{ Nm}^3/\text{d}$. The liquefaction technology uses the PRICO process of American Black & Veatch Company. The process flow is shown in Figure 3.1. Developed and continuously improved in 1950, the liquefaction process adopts a single-cycle hybrid refrigeration process, a centrifugal compressor, and a plate-fin heat exchanger for the cold box.

In this process, the mixed refrigerant is composed of methane, ethylene, propane, nitrogen, and isopentane. The mixed

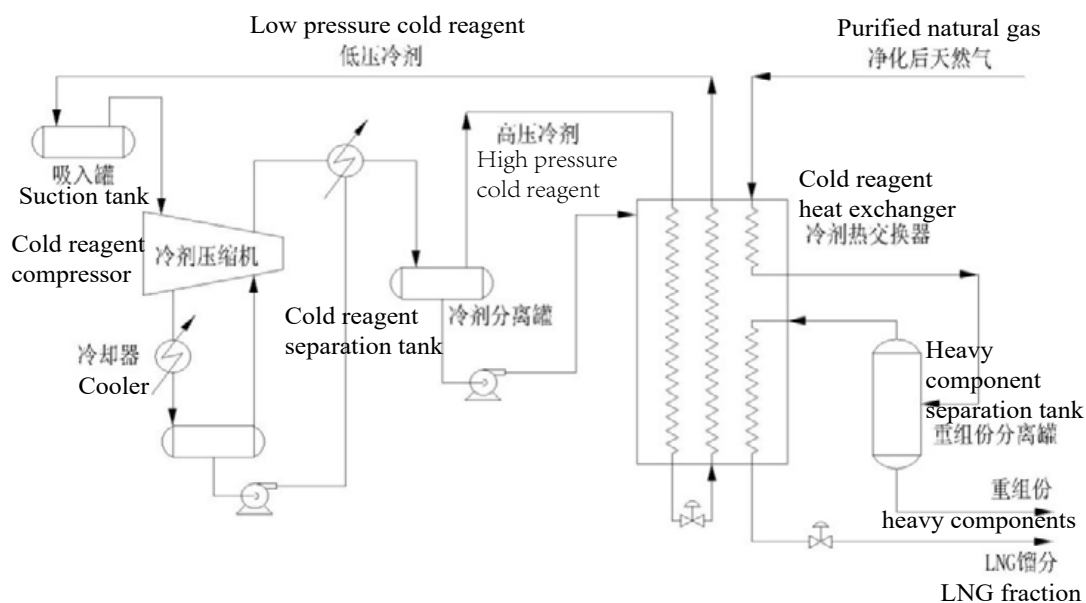


Figure 3.1 PRICO process flow chart

refrigerant is compressed and pressurized by the compressor, and after cooling, it is divided into two phases, but there is only one pressure level. The gas-phase mixed refrigerant and the liquefied mixed refrigerant are mixed through the mixer before entering the cold box, and then enter the plate-fin heat exchanger in the cold box. The equipment flows from top to bottom in the equipment, when it reaches -160°C with LNG at the same time, draw out the cold box. After being depressurized by the refrigerant JT valve, it returns to the plate-fin heat exchanger. The throttled mixed refrigerant becomes a gas-liquid two-phase. The gas phase provides cooling capacity for the mixed refrigerant and natural gas through sensible heat, and the liquid-phase mixed refrigerant the latent heat provides cooling capacity for the mixed refrigerant and natural gas. The natural gas after providing the cooling capacity is then returned to the compression section to complete the closed loop cycle.

Main features of the process:

- (1) Adopt single-cycle single-stage throttling liquefaction technology;
- (2) C2 in the mixed refrigerant is ethylene;
- (3) Using J-T valve to reduce pressure and temperature;
- (4) Due to the single-cycle single-stage throttling liquefaction technology, there is only one refrigeration J-T valve, which is easy to operate;
- (5) Due to the single-cycle single-stage throttling liquefaction technology process, the refrigeration has only one J-T valve, which deviates from the enthalpy curve of the single-cycle multi-stage throttling liquefaction technology process, and the unit liquefaction energy consumption is slightly higher;

3.2.2 Device operation and freezing conditions

Kunlun Energy Huaqi Guang'an Liquefaction Plant was put into operation in April 2012. After one month of commissioning, it reached the full design capacity. After four months of continuous operation, the liquefaction plant was blocked by heavy hydrocarbons in the natural gas channel of the plate-fin heat exchanger. The suspension of production not only brings economic losses to the enterprise but also brings safety hazards

to the installation.

The blockage of the cold box occurs at two places a and b of the natural gas channel of the plate-fin heat exchanger, and the blockage is most likely to occur at b. The actual operation adopted by the plant is shown in Figure 3.2, Figure 3.3 and Figure 3.4 DCS screenshots and Figure 3.5 schematic diagram of freezing blockage.

Through the analysis of the above DCS data, the following conclusions are obtained:

- 1) Temperature range blocked at a.

The phenomenon of blockage at a is manifested by an increase in the resistance drop of the passage of the plate-fin heat exchanger from the weather into the plate-fin heat exchanger and the low-temperature separator, and the natural gas flow into the cold box suddenly decreases, but the mixed refrigerant and the cold outlet. The LNG temperature of the box is within the design temperature range, and the pressure drop at the bottom of the plate-fin heat exchanger has no obvious change. Due to the reduction of natural quantity, the cold and heat balance in the cold box changes with the change of time. Due to the large change in the load of the hot end, the temperature of the mixed refrigerant outlet cold plate-fin heat exchanger will drop, and the temperature of the LNG product at the cold outlet plate-fin heat exchanger will also drop. When the pressure drop processed by a reaches the full scale, it will return to the initial value. At this time, the pressure drop of the lower plate type b will increase. It can be concluded from the DCS that the temperature at this point is $-70^{\circ}\text{C} \sim -74^{\circ}\text{C}$.

- 2) The flow channel of the heat exchanger at b is blocked.

The phenomenon of pressure blockage at b is mainly manifested in the increase of force drop at this place. With the change of time, the temperature in the middle of the plate-fin heat exchanger decreases, and the liquefaction of the low-temperature mixed refrigerant channel of the plate-fin heat exchanger increases. The temperature of the hot and cold ends at the bottom of the box rises while the temperature difference increases significantly. The flow rate of the natural gas cold box becomes smaller, and the flow rate of the product JT into the cold box does not change. From the internal temperature of

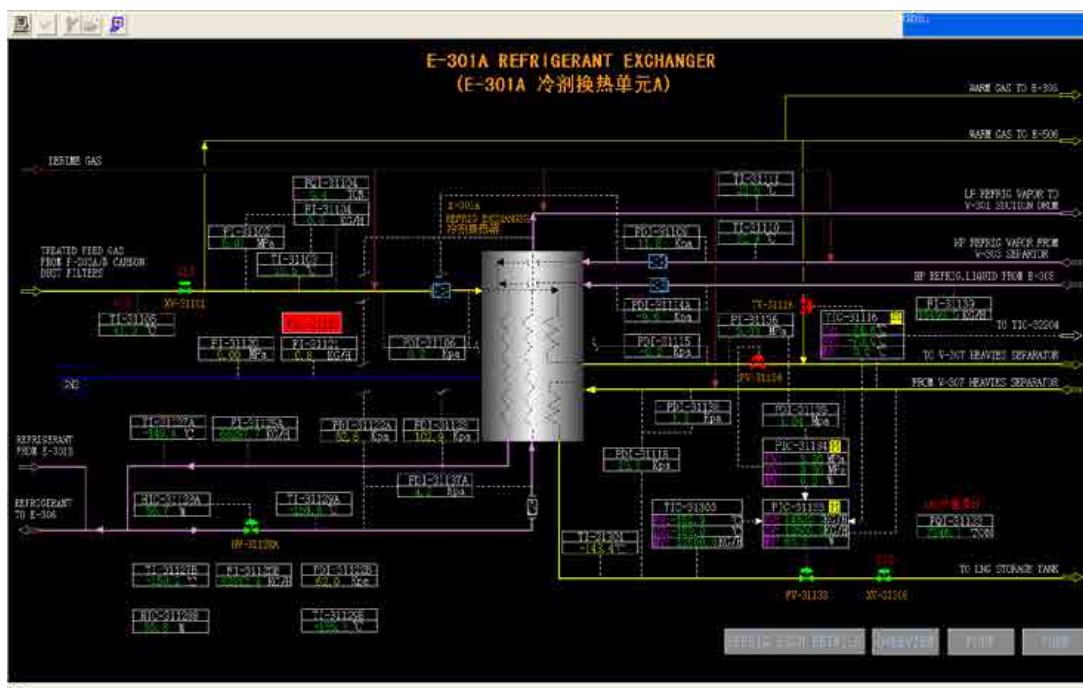


Figure 3.2 Cold box heat transfer unit

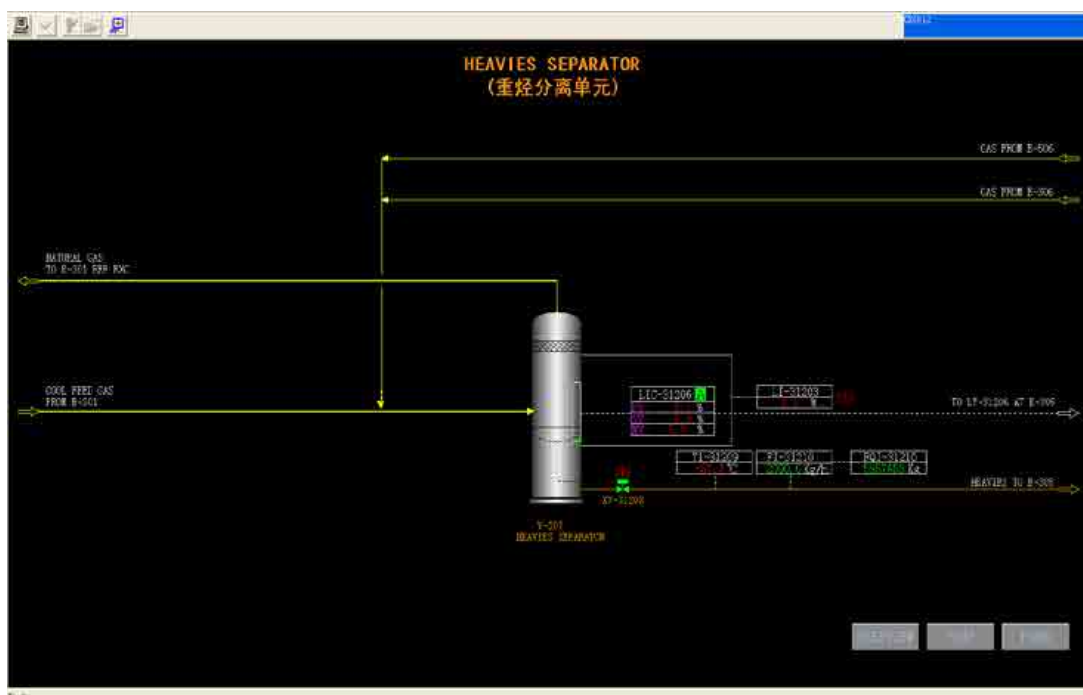


Figure 3.3 Heavy hydrocarbon separation device

the cold box, it can be known that the temperature of b freeze blockage is $-93^{\circ}\text{C}\sim-125^{\circ}\text{C}$.

3.3 The reason for freezing and blocking of the cold box

3.3.1 Blockage of liquid phase refrigerant in refrigerant channel

The cold box plate-fin heat exchanger has a narrow flow path, and sometimes liquid accumulation in the cold box may occur during improper operation. The normal cycle of the cold box is that the high-pressure mixed refrigerant enters the cold box and flows downwards, through throttling to reduce the pressure

and temperature, the gas-liquid separation in the refrigerant separation tank in the cold box, the liquid refrigerant vaporizes, and the natural gas stream and high-pressure mixed cold The agent provides cooling, and the gas phase pushes the liquid phase to flow upward and out of the cold box. When the liquid refrigerant is too much, it cannot be effectively vaporized, and the gas refrigerant cannot take the liquid refrigerant out of the cold box in time, causing the liquid to accumulate in the refrigerant channel so that the gas phase refrigerant cannot pass through the cold box smoothly. If it is not controlled in time, the vicious circle will cause more and more liquid to accumulate, and eventually, the circle will be destroyed.

In the liquefaction process, the low-pressure mixed refrigerant

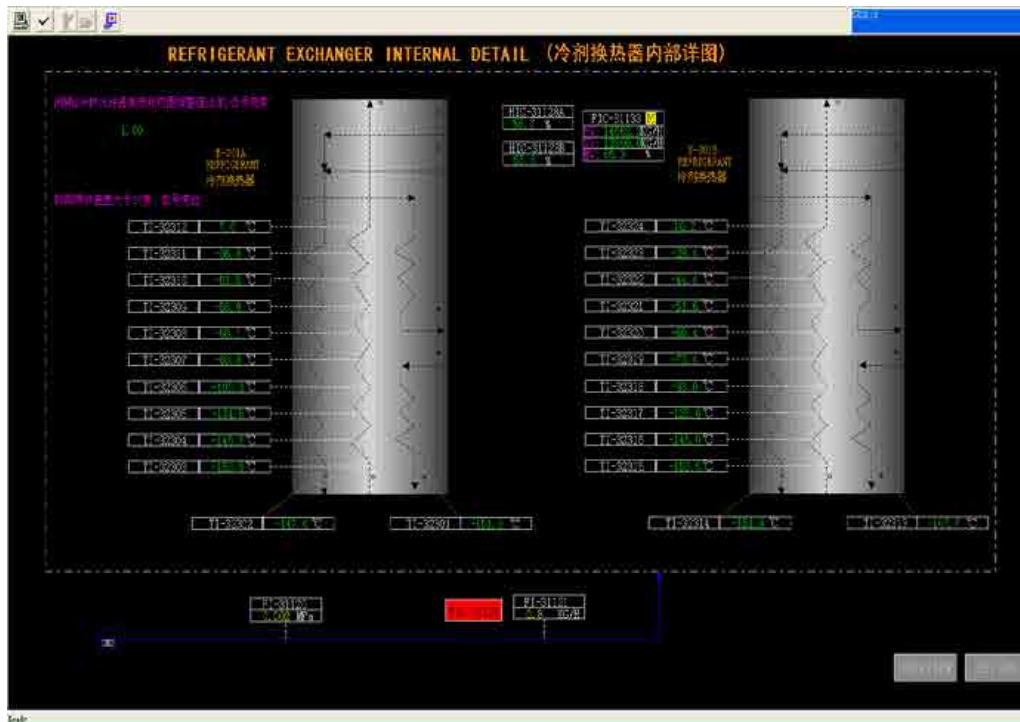


Figure 3.4 Cold box inner temperature

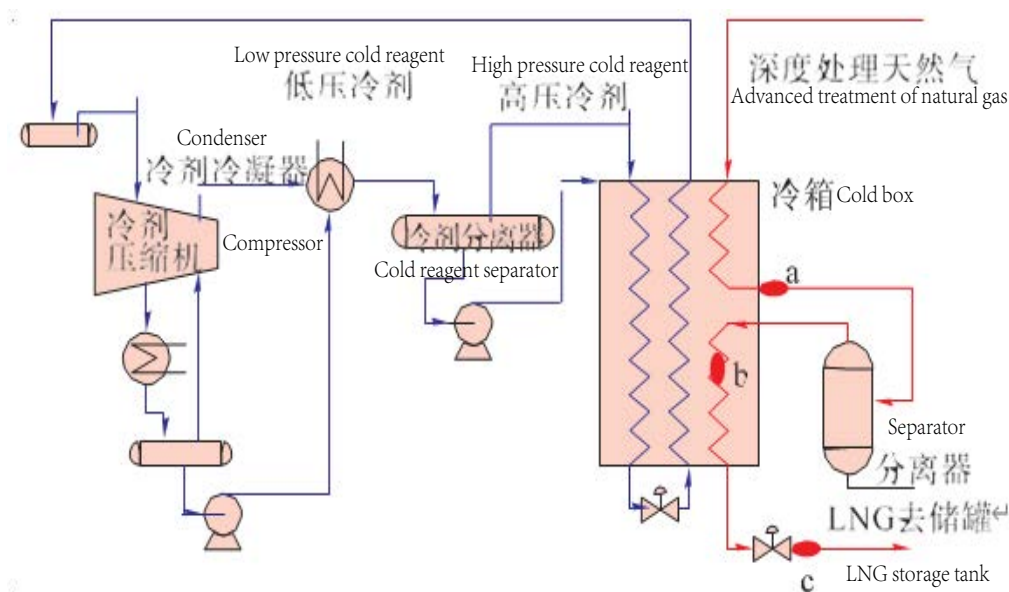


Figure 3.5 Cold box stoppage diagram

flowing out of the cold box is separated by a separator, then enters the compressor in gaseous form to be compressed to high pressure, and then cooled to room temperature with a cooler, and the high-pressure refrigerant returns to the cold box to complete circulation loop. However, when the cold box accumulates liquid, as the liquid refrigerant accumulates in the cold box too much, the liquid will gradually block the refrigerant passage, causing the gas phase refrigerant to fail to pass through the cold box smoothly. The gaseous refrigerant cannot circulate and accumulates at the outlet of the compressor, causing the outlet pressure to rise. The reduction of the refrigerant flowing out of the cold box reduces the suction volume of the refrigerant compressor, and the temperature of the refrigerant flowing out of the cold box is lower due to the accumulation of liquid, which causes compression. The suction pressure at the inlet of

the machine drops. Due to the blockage of the cold box channel, the flow between the compressor sections is insufficient. When the refrigerant compressor speed remains unchanged, the anti-surge valve will automatically open to maintain the stable flow operation of the compressor and increase the production energy consumption.

Besides, the propane and isopentane components in the mixed refrigerant have a high boiling point and are difficult to vaporize, and they act as refrigerants and refrigerant carriers during operation. The role of the refrigerant carrier is to bring the low-temperature cold energy produced by nitrogen and methane at the bottom of the cold box to the upper part of the cold box when the temperature of the heavy refrigerant is lower than the boiling point, and the refrigerant starts vaporization absorbs heat. When the cold box accumulates too much, the gaseous refrigerant

cannot pass the J-T1 and J-T2 valves to produce low-temperature cooling capacity. The liquid refrigerant continuously flows into the cold box to absorb the cooling capacity, and the natural gas also continuously flows through the cold box to absorb the cooling capacity. , Which makes the temperature at the bottom of the cold box rise rapidly. The temperature difference of J-T valve is reduced, and the temperature before and after the valve rises rapidly. In addition, due to the large accumulation of heavy refrigerant and the large energy storage, the cooling capacity is continuously transferred upwards. Because of its high boiling point, it is difficult to vaporize in the upper part of the cold box, resulting in excess cold capacity in the upper part of the cold box, lower temperature, and small temperature change in the middle. The overall view is that the temperature of each point of the cold box converges to the middle.

When liquid accumulation occurs in the cold box, the pressure difference in the low-pressure refrigerant flow path of the cold box rises. The main reason is that the liquid accumulation in the flow channel increases the pressure of the static liquid column, which causes the pressure difference detected by the differential pressure gauge to rise. Low-pressure refrigerant has a low flow rate at low temperatures, but the flow direction of low-pressure refrigerant in plate-fin heat exchange is from bottom to top. In the low-temperature state, the degree of subcooling of the refrigerant is greater, and the liquid is more difficult to overcome the gravity to flow upwards, and the amount of liquid entrainment of the gas phase in the flow is reduced. Cold box liquid accumulation has many hazards. One is that when the cold box liquid is accumulated, the throttle effect of the refrigerant throttle valve is reduced. A large amount of gas-phase refrigerant flows to the anti-surge pipeline of the refrigerant compressor and cannot circulate through the cold box, thereby increasing compression. The second reason is that when the cold box accumulates too much, the temperature of the mixed refrigerant out of the cold box will decrease. When the temperature drops below the refrigerant compressor inlet temperature interlock value, it will trigger an emergency stop of the compressor, resulting in device production Interruption; Thirdly, the liquid refrigerant continues to enter the cold box, which prevents the cold box from establishing a reasonable temperature drop gradient, which will cause local overcooling, and the cold box cannot achieve the purpose of cooling and liquefying natural gas, and it cannot produce qualified LNG product.

Elimination method of cold box liquid accumulation: reduce the amount of high boiling point refrigerant and increase the heat load. When cold box liquid accumulation, gradually reduce or even stop the delivery of liquid refrigerant to the cold box, reduce the accumulation of liquid refrigerant in the cold box, and increase at the same time. The flow of natural gas increases the heat load of the cold box, speeds up the vaporization of liquid refrigerant and gradually flows out of the cold box; increases the gas refrigerant to open a large refrigerant throttle or when the device has a bypass, use the bypass to cool more high-pressure gas The high-pressure refrigerant flows into the cold box, and the high-pressure refrigerant can effectively overcome the influence of the gravity of the liquid refrigerant and push the liquid refrigerant out of the cold box; turn on the heating line and use the high-temperature heating line in the refrigerant compressor to vaporize the excess liquid, and re-compress it through circulation.

As the temperature in the middle of the cold box will be very low when the cold box accumulates liquid, while solving the excessive liquid accumulation in the cold box, the amount of re-refrigerant will be reduced, and the temperature in the middle part will rise, with large transient fluctuations. At this time, pay close attention to the pressure difference of the natural gas passage in the cold box and the heavy hydrocarbon content displayed by online or chromatographic analysis to prevent heavy hydrocarbons from entering the lower part of the cold box and blocking the natural gas passage in the cold box. The cold box effusion needs to be handled carefully to avoid secondary failures such as ice blockage on the natural gas side of the cold box, layered vortex of the large tank, and compressor liquid hammer. The refrigerant effusion caused by accidental shutdown, emergency power failure in Plant A will be recovered or discharged, and the cold box will be insulated through replacement and insulation, which will cause the cold box to freeze and block.

3.3.2 Heavy hydrocarbon freeze blockage of natural gas channel

The natural gas liquefaction process will be deeply deacidified and dehydrated in the pretreatment section. The pretreated purified gas enters the cold box. The content of trace H₂O and CO₂ will generally not cause the cold box to freeze up. Therefore, the cold box natural gas channel is mainly heavy hydrocarbon freeze up. Generally, the pressure drop from the natural gas flow channel after the heavy hydrocarbon separation tank V-3 to the natural gas liquefaction cold box channel has a significant increasing trend, the refrigeration temperature of the pre-coolant and the cold end temperature of the product LNG increase significantly, and the LNG in the product section the flow of the storage tank is reduced.

The freezing of heavy hydrocarbons is caused by liquefaction of heavy hydrocarbons before the natural gas enters the subcooling section, because the high-boiling heavy components contained in the natural gas are liquefied before methane, and the natural gas flow path is frozen and blocked. There are three main reasons for the freezing and blocking of heavy hydrocarbons in the cold box: one is that the change in the quality of the feed gas increases the content of the heavy component; the other is that the designed dewweighting treatment device is too small to meet the treatment requirements; in addition, due to unreasonable operation make the temperature gradient of the cold box fluctuate greatly, or freeze the cold box caused by human factors.

a. Change in composition of raw gas.

The change in raw natural gas composition has a significant impact on the natural gas liquefaction unit. The raw material natural gas purification device of LNG plant has included natural gas acid gas treatment (CO₂, H₂S) and deep dehydration, mercury removal, and other measures, but for the liquefaction device, its function is in addition to refrigeration liquefaction, but also continuous production. At the same time, other impurities in natural gas should be removed according to the requirements of the LNG standard. Retain methane and ethane in natural gas.

Table 3.1 lists the condensation temperatures of different heavy components in natural gas. It can be seen that common heavy hydrocarbon components that cause low-temperature

Table 3.1 The condensation temperature of heavy component in natural gas

component	Molecular weight	Boiling point °C	Freezing point °C	LNG content requirements
n-C5	72.151	27.85	-159.9	-
i-C5	72.151	36.07	-129.72	<0.1%
Neopentane	72.151	26.07	-15.351	5×10^{-6}
Neo-C5	86.178	68.74	-95.35	<0.5%
Methyl ring	84.162	71.81	-142.46	-
benzene	78.151	80.1	5.53	$(1 \sim 10) \times 10^{-6}$
Cyclohexane	84.162	80.74	6.55	$(1 \sim 10) \times 10^{-6}$
Toluene	92.141	110.63	-94.91	-
Ethylbenzene	106.169	136.19	-94.98	-
P-xylene	106.169	138.85	13.26	-
M-xylene	106.169	139.1	-47.87	-
O-xylene	106.169	144.41	-25.18	-
n-C7	100.206	98.43	-90.61	-
n-C8	114.233	125.67	-56.8	-
n-C9	128.26	150.79	-53.52	-
H ₂ O	18.01	100	0	$<0.5 \times 10^{-6}$

blockage include benzene, cyclic aromatic hydrocarbons, neopentane, and benzene derivatives.

According to the calculation method of GPA, the crystallization temperature of different benzene content is predicted

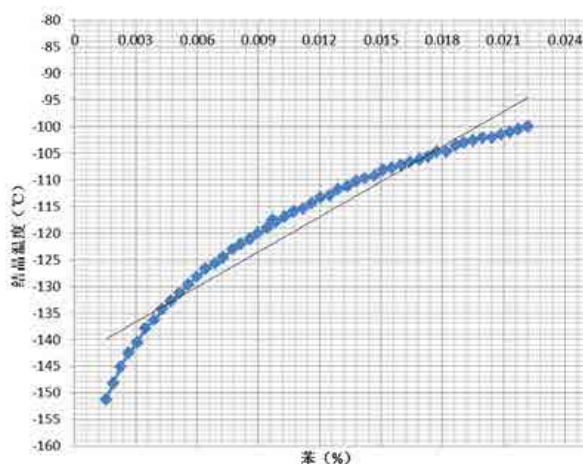


Figure 3.6 Crystallization temperature of different benzene content in LNG

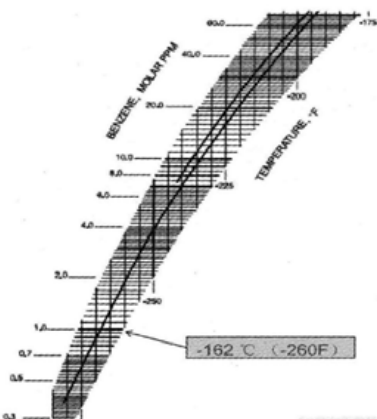


Figure 3.7 The dissolution curve of benzene in methane

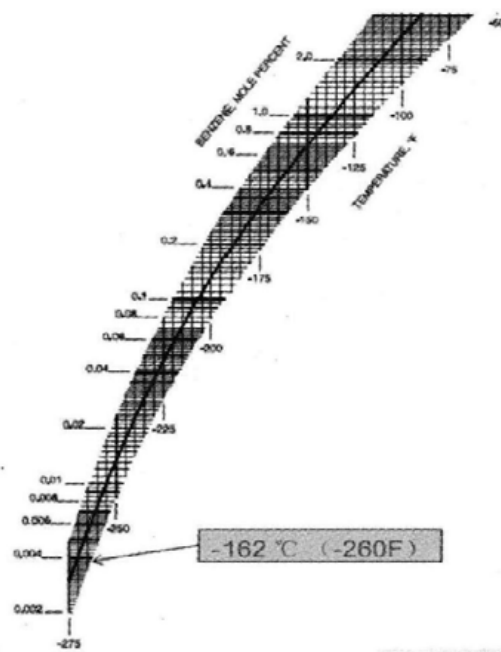


Figure 3.8 The dissolution curve of benzene in ethane

according to the composition of feed natural gas of Huaqi Guang'an LNG plant of Kunlun energy, as shown in Figure 3.6.

From the analysis of Figure 3.6, Figure 3.6 and Figure 3.8, it can be seen that a very small amount of benzene will also crystallize in LNG, and the increase in benzene content will immediately cause a change in the crystallization temperature. In order to avoid low-temperature blockage of natural gas in the liquefaction process, the benzene content in natural gas should generally be controlled below $(1 \sim 10) \times 10^{-6}$.

In the past operation of LNG plants, the indicators of other heavy hydrocarbons in the natural gas liquefaction process are as follows: isobutane is less than 2%, neopentane is less than 5×10^{-6} , isopentane is less than 0.1%, and n-hexane is less than 0.5%, cyclohexane $(1 \sim 10) \times 10^{-6}$. The concentration of heavy hydrocarbon freezing: C₆: 250ppm; C₇: 70ppm; C₈: 0.5ppm.

During the operation of Kunlun Energy Huaqi Guang'an LNG Plant, there are deviations in the composition of the raw gas composition and the design composition. The main deviations are shown in Table 3.2.

It can be seen from Table 3.2 that the upstream feed gas composition changes and the heavy component content increases. Due to the limitation of the ability to process heavy hydrocarbons during the design, when the heavy hydrocarbon content of the upstream natural gas exceeds the design, the unfinished heavy hydrocarbons will directly enter the lower plate heat exchanger in the cold box, slowing down at low temperatures. Therefore, the above-mentioned heavy hydrocarbons are the direct cause of freezing and blocking of the cold box. The composition analysis of the feed gas when the cold box is blocked by A shows that the content of heavy hydrocarbons generally exceeds the designed 70ppm. In addition, the analysis of the raw gas data after drying in Plant A shows that although the amount of components above C₆ is small, it contains relatively more neopentane components, and neopentane generally condenses at -19.5°C. In this case, when the load is increased, it will inevitably cause the heavy hydrocarbons in the cold box to be unclear and freeze up.

b. The natural gas liquefaction plant has insufficient capacity to treat heavy hydrocarbons.

Table 3.2 The component deviation of raw material gas to the natural gas liquefaction device

component	Feed gas composition during design (mol/%)	Actual operating component (mol/%)
hydrogen	0	0
Nitrogen	1.0349	2.076
carbon dioxide	0.3853	0.7174
Methane	93.6928	93.6987
Ethane	3.7078	2.8671
Propane	0.6997	0.4276
i-C4	0.1556	0.0519
n-C4	0.1245	0.0811
i-C5	0.0116	0.0177
n-C5	0.024	0.017
Neo-C5	0.0028	0.0058
N-hexane	0.0015	0.0076
Cyclohexane	0.0097	0.0036
2,2-Dimethylbutane	0.0007	0.005
2,3-Dimethylbutane	0.0008	0.0015
2-methylpentane	0	0.0004
3-methylpentane	0.0001	0.0003
2,2-Dimethylpentane	0.0001	0.0009
Methylcyclopentane	0.0001	0.0013
benzene	0.0015	0.0081
3,3 Dimethylpentane	0	0.0008
2-methylhexane	0.0002	0.0012
3-methylhexane	0.0005	0.0011
N-heptane	0.0004	0.0027
Methylcyclohexane	0.0009	0.0029
2,2,2-Trimethylpentane	0.0002	0.0019
N-octane	0	0.0006
oxygen	0	0
Hydrogen sulfide	0.0003	0.0003

According to the raw gas composition provided by the owner at the time, BV company designed a separator to meet the treatment of heavy hydrocarbons in natural gas liquefaction. Natural gas is extracted underground, and the extracted natural gas will change in composition over time. When the components in the feed gas exceed the designed value, a heavy hydrocarbon separator is installed outside the cold box, and the heavy hydrocarbons in the feed gas natural gas cannot be completely separated, resulting in insufficient processing capacity of the heavy hydrocarbon separator tank.

When the composition of natural gas changes, the nature of natural gas also changes. Natural dew point changes during the liquefaction process and the previously designed separation temperature will not separate the heavy hydrocarbons in the natural gas in time, which may cause solidification when the natural gas processing cold box enters the cryogenic separator. If you adjust the composition of the mixed refrigerant to adjust the temperature of the cold box separation. It will affect the cold distribution of the cold box, and thus affect the processing capacity of natural gas.

Therefore, a cryogenic separator is installed in the natural gas liquefaction process to treat heavy hydrocarbons. The method is too simple. The heavy hydrocarbons in the natural gas cannot be removed to reach the heavy hydrocarbon content index of the LNG, which leads to freezing and blocking of the cold box.

If the resistance drop of the natural gas passage in the plate-fin heat exchanger increases, and there are signs of freezing, adjust the mixed refrigerant composition to reduce the separation temperature and pressure of the cryogenic separator, reduce the flow of natural gas into the cold box, and increase the cryogenic separator. The bottom discharge volume allows the heavier components in the natural gas to be discharged from the bottom of the cryogenic separator to the liquefaction system. At the same time, the cold box distribution is adjusted and the cold box is manually controlled. This method can temporarily alleviate the clogging problem, but the energy consumption of the device is greatly increased, such as after a long-term operation, the device cannot produce at full capacity and the factory cannot be profitable. Therefore, this method is not recommended.

c. Operation causes freezing

It is mainly to control the temperature field and pressure difference of the cold box, and use two sets of mixed refrigerant ratios and cooling capacity to control the midpoint dewpointing diameter temperature and the temperature of the liquefied product. For the freezing and blocking of the cold box caused by pure temperament component changes or human error, the possibility of freezing and blocking of the cold box can be minimized under the same load processing capacity by optimizing the process parameters; but if the raw gas has heavy component content. When increasing, the frozen blockage caused by the insufficient design of heavy hydrocarbon processing capacity can only be solved by adding heavy hydrocarbon removal devices.

Generally, based on the composition of the feed gas, the reasonable design of the process equipment and the reasonable operation in the production can meet the requirements for the heavy hydrocarbon content of natural gas liquefaction. However, when the quality of the feedstock gas changes and heavy hydrocarbons increase, or the designed heavy hydrocarbon separation capacity is insufficient, the excess heavy hydrocarbons that are not removed can freeze the cold box during the liquefaction process. In addition, due to differences in the experience and abilities of plant operators, some operators are unable to determine the trend of freezing blockage in the cold box in time and take effective measures in time, and freezing blockage of the cold box may also occur. For the latter caused by subjective reasons, the cold box can be adjusted in time by reasonable parameter adjustments to make the cold box run normally, while for the first two types of heavy hydrocarbons caused by objective reasons, the removal of heavy hydrocarbons is not complete. Compare economic advantages and disadvantages to improve or increase heavy hydrocarbon removal equipment.

3.4 Summary of this chapter

In the production process of liquefied natural gas, various freezing and blocking situations often occur, and LNG cold box is an important equipment for natural gas production. When analyzing the freezing and blocking situation of LNG cold box, it is necessary to analyze the possible freezing and blocking situation in combination with the specific process of LNG production, so as to make a reasonable judgment. Based on the analysis of LNG production process, this paper explores the freezing blocking position and main causes of LNG cold box,

3.4.1 Reasons

LNG cold box is an important core equipment in the production of liquefied natural gas (LNG). When the temperature in the cold box is reduced to $-162\text{ }^{\circ}\text{C}$, liquefied natural gas (LNG) will be formed. Due to the unique low-temperature characteristics of natural gas, the cleanliness of raw gas is required to be very high. It is necessary to wash and remove various types of gas in the raw gas, so as to prevent freezing and blocking at low temperature in the production process. Damage caused by cold box or other equipment affects the production of liquefied natural gas.

Through the LNG, it is found that the main freezing blocking position of the cold box is in the lower plate fin heat exchanger, and when the temperature of the raw gas is reduced to $-120\text{ }^{\circ}\text{C}$, some of the freezing blockage can be eliminated by opening the commissioning recovery pipeline for purging. It shows that the cause of freezing blockage is not mechanical impurities, but heavy hydrocarbon, mercury and other impurity gases or gases in the raw gas. The reasons are as follows:

(1) the channel port of LNG cold box is frozen and blocked

When the channel port of LNG cold box works normally, the pressure difference that needs to pass through should be kept in the range of 0-15kpa. When the feed gas contains heavy hydrocarbon substances after solidification, it will be frozen and blocked. In this way, the pressure difference at the channel port of the cold box will rise to 25-250kpa, and the pressure difference on the inner wall will reach 2500-4500pa when the cold box is working continuously. In this case, the LNG channel port will be seriously frozen and blocked, resulting in the blockage of the whole LNG cold box, and the system can not work normally.

(2) fv0801 series valves are frozen and blocked

Valve is an important part of liquefied natural gas (LNG) passing through, and it is an important control component connecting each channel. In fv0801 valve, it is easy to freeze and block, which affects the normal operation of LNG system. Because when fv0801 is frozen and blocked, the flow of natural gas in the channel will be reduced. Even if the valve is set at the maximum working degree to improve the gas flow in the pipeline during the working process, the flow of natural gas will slowly decrease due to the existence of freezing blockage.

(3) the natural gas plant does not meet the requirements for removing impurities

In the process of natural gas production, there are often a large number of impurity gases. It is necessary to remove the water, carbon dioxide, heavy metals, mercury and heavy hydrocarbons in the natural gas. In this way, when the temperature of natural gas reaches $-162\text{ }^{\circ}\text{C}$, these impurities will be frozen in the channel in advance, affecting the flow of natural gas. In the process of LNG production, it is necessary to use LNG purification system equipment to remove and purify water, carbon dioxide and other impurity gases in the raw gas. Through

the purification system, the impurities in the raw gas can be controlled within a certain concentration range, and the channel will not be frozen and blocked, and the LNG gas can not exceed the standard to meet the requirements.

(4) it is analyzed that benzene and neooctane are not removed clean from the raw gas

In the process of processing the raw gas of natural gas, there are often a lot of heavy hydrocarbons such as benzene and neoxane, which exceed the standard seriously. In production, it is necessary to use high-precision separator to separate them. If the separation accuracy is not enough, the heavy hydrocarbon and other substances in the gas can not be specifically removed, which leads to the overall removal effect of the equipment is not very ideal, so these gases can not be effectively removed, causing great safety factors and instability, which also leads to freezing of the cold box. One of the important reasons for blockage.

3.4.2 Reforms

When dealing with the freezing and blocking of LNG cold box, it is necessary to analyze the specific situation in combination with the specific process of LNG production, so as to improve the treatment effect effectively by taking specific measures to deal with the freezing blockage. Treatment and transformation strategy of LNG cold box freeze blockage:

(1) strengthen the monitoring and treatment of raw gas

The raw gas often contains a variety of gas components and moisture. In the process of LNG gas production, it is necessary to strengthen the control of the composition of the raw gas, and monitor the impurity composition of the raw gas to check whether there are new components. The raw gas enters the gas supply network to judge whether the purification equipment of the raw gas can meet the requirements. If it is found that the components seriously deviate from the design, it is necessary to redesign the heavy hydrocarbon purification unit of the raw gas to ensure that the new component gas can be removed and all components in the raw gas can be removed to meet the requirements of raw gas purification.

(2) check the working condition of the compressor to ensure its stable working condition

To investigate the upstream booster station, it is necessary to analyze in detail whether the working conditions of the compressor in the LNG system meet the requirements, whether the lubricating oil gas of the compressor leaks into the feed gas, and whether the heavy hydrocarbon composition of the feed gas increases due to the leakage. In the purification process of raw gas, active carbon is mainly added into the composite bed of drying tower, which can not effectively remove the heavy components of lubricating oil gas mixed into the raw gas, which is also an important reason for freezing and blocking of cold box. Therefore, it is necessary to check the working condition of the compressor. It is necessary to actively coordinate with the upstream gas supply unit, strengthen the equipment maintenance

and repair, especially strengthen the inspection of the compressor to prevent the mixing of lubricating oil gas, or use the oil-free lubricating pressure equipment to prevent the lubricating oil gas from entering into the raw gas, so as to provide convenience for improving the later LNG production. If it is confirmed that it is the upstream compressor oil and gas pollution source, targeted measures can also be adopted to reform the purification system, strengthen the adsorption of the lubricating oil gas, improve the gas adsorption effect, and reduce the content of heavy hydrocarbon entering the cold box.

(3) optimize the purification equipment of raw gas

According to the inspection of raw gas, the parameters of raw gas purification equipment are redesigned and optimized to improve the purification effect of raw gas, and ensure that the purity of raw gas can be improved after purification equipment, so as to meet the requirements of LNG gas production. For example, the pressure of feed gas in the purification system can be increased to remove some heavy hydrocarbon gas, and then the moisture and carbon dioxide in the raw gas can be reduced by increasing the flow rate and regeneration temperature of the drying regeneration gas. Finally, the cooling temperature of the regeneration gas cooler can be reduced to remove the gas impurities in the raw gas, so as to improve the effect of heavy hydrocarbon removal by activated carbon adsorption as much as possible. The purification effect of raw gas is improved to delay the freezing and blocking cycle of LNG freezer.

(4) reduce the circulation amount of light refrigerant in the cold box

In view of the freezing and blocking situation of LNG cold box, in order to improve the production efficiency, temporary solutions can be adopted to remove impurities in raw gas. When the lower plate fin heat exchanger of the cold box is obviously frozen and blocked, it is necessary to combine with the specific situation, according to the production demand, to reduce the light refrigerant circulation of the lower plate fin in a planned way, so as to ensure that the lower plate fin temperature can return to -100 without affecting the heat exchange and production of the cold box when the system is working. When the temperature is about $^{\circ}\text{C}$, the plate fin heat exchanger under the cold box will run for a period of time, and then the freezing and blocking conditions of the system will be removed, and the frozen blocking materials in the feed gas channel of the cold box plate fin heat exchanger will be melted and blown out to ensure the smooth channel of the raw gas. Then, the freezing blockage of the cold box can be eliminated, and the heat exchange effect of the cold box can be improved, and the production goal can be achieved. With this method, because the frozen material is still in the gas channel, it will still solidify in the subsequent low-temperature pipeline and system, affecting the gas flow. Therefore, in order to improve the effect of LNG production, it is necessary to thoroughly purge the accumulated heavy hydrocarbon in the pipeline after the system has been running for a long time.

(5) revamp LNG cold box system

The cold box system can be reformed. According to the specific

working conditions, a low-temperature separator for heavy hydrocarbon is added outside the cold box. When the heavy hydrocarbon passes through the pipeline, it can be separated to achieve the goal of purifying the raw gas. In this way, the feed gas can be condensed after passing through the upper plate fin of the cold box, so that the temperature of the raw gas can be reduced to below -60°C . Then the gas is led out to the cold box and then enters into the low-temperature separator for treatment of the low-temperature raw gas. After the separation of heavy hydrocarbon substances, it enters the lower plate fin of the cold box for liquefaction, so as to achieve the purpose of heavy hydrocarbon treatment to a certain extent. The corresponding purification equipment can also be added to the pipeline in front of fv0801 valve at the outlet of lower plate fin or in front of fv0803 valve to add a group of LNG in series. The low temperature blowdown valve can achieve the goal of removing heavy hydrocarbon, and then connect it to the water bath heater or residual liquid separator, so as to remove the heavy hydrocarbon in the raw gas. When the frozen plugging material is re temperature blown and the pipeline blockage is reduced, the valve can also be opened to discharge the frozen plugging material out of the cold box system, so as to improve the working efficiency of the system.

In the process of LNG production, the freezing and blocking of feed gas channel of LNG cold box has an important impact on the production of the whole system. It is also one of the common faults in the production process of LNG. Due to the different situations, the failures of LNG cold box are also different. In the process of LNG production, the specific situation should be combined with LNG. According to the specific situation of the frozen plugging material, the appropriate strategy is adopted to remove the frozen plugging material, which can slow down or eliminate the freezing blockage, reduce the freezing blocking situation in the production process, and reduce the impurity content in the raw gas, which can not only improve LNG The gas production efficiency and product quality can also ensure the safe and stable operation of the system.

3.4.3 Summary

The removal of heavy hydrocarbons in Plant A is separated and removed by a cryogenic separator outside the cold box at low temperature. There are fewer blockages caused by the liquid accumulation in the cold box. The main reasons for the blockage are as follows:

(1) When the quality of the feed gas changes or the production load increases, the content of heavy components in the feed gas in the cold box exceeds the 70 ppm heavy hydrocarbon content required by LNG; in addition, the analysis of the raw gas data after drying in Plant A shows that it is above C6. The components are small but contain relatively more neopentane components, neopentane generally can condense at -19.5°C ;

(2) Before the construction of the project, due to poor consideration of the change in the content of heavy components in the feed gas, the design capacity for heavy hydrocarbon removal was insufficient, resulting in the low heavy hydrocarbon processing capacity of the heavy hydrocarbon cryogenic separator used in the cold box;

(3) Through DCS analysis, the freezing block temperature range of the LNG plant is $-70^{\circ}\text{C}\sim 125^{\circ}\text{C}$.

and puts forward the transformation strategy of LNG cold box to blocking

4 LNG plant cold box freezing solution

In most LNG plants that have been in operation, only one low-temperature heavy hydrocarbon separator is designed in the cold box of the natural gas liquefaction plant. This scheme is too simple. When the feed gas composition of the plant deviates from the design composition during the operation of the plant. At this time, the dew point of natural gas changes accordingly, but the separation temperature of natural gas in the cold box is based on the separation temperature of the original design component design. When the heavy component in natural gas is less than the heavy hydrocarbon component in the design, the dew point of natural gas will be lowered, resulting in the separation temperature of the original component design in the low-temperature heavy hydrocarbon separation. The heavy hydrocarbons are not completely separated, and the heavy hydrocarbons will enter the lower temperature heat exchanger, which will cause the plate-fin heat exchanger to pass. The blockage of the natural gas channel causes the cold box to freeze and block the plate-fin heat exchanger without continuous full-load operation. In order to make the LNG plant capable of low energy consumption and continuous production, it is necessary to study and design a set of heavy hydrocarbon solutions to ensure the continuous low power consumption operation of the plant. According to the feed gas conditions of the factories in Inner Mongolia, several design schemes for heavy hydrocarbon removal were proposed and the different schemes were compared.

4.1 Feed gas conditions

4.1.1 Raw gas collection and analysis

Use a gas chromatograph to sample the incoming raw gas for full component analysis. Chromatography is also called chromatography, which is a physical separation technique. Its separation principle is to distribute the components in the mixture between two phases. One of the phases is immobile, called the stationary phase, and the other phase is the fluid that pushes the mixture through the stationary phase, called the mobile phase. When the mixture contained in the mobile phase passes through the stationary phase, it will interact with the stationary phase. Due to the different properties and structures of each component, the magnitude of the interaction is also different. Therefore, under the same driving force, the residence time of different components in the stationary phase is long or short, and they flow out from the stationary phase in sequence. This way, the components in the mixture are separated by the principle of two-phase distribution. The technology is called chromatographic separation technology or chromatography. When the liquid is used as the mobile phase, it is called liquid chromatography, and when gas is used as the mobile phase, it is called gas chromatography. The gas chromatograph is composed of five main parts: sampling system, carrier gas system, separation system, detection system, and recording system. After decompression, purification, and measurement, the gas in the cylinder reaches the sampling system, where it is mixed with the sample, and the sample is carried into the separation system for separation. The separated components flow out sequentially

and are carried by the carrier gas into the detector. The detector converts the concentration (or mass) of the components into electrical signals, which are recorded by the recorder to obtain gas chromatograms and data tables.

4.1.2 Sample collection

Firstly, prepare two professional sampling steel cylinders for natural gas sampling at the sub-ying sub-transmission station and Saihan terminal station. The sampling port should be replaced and purged before sampling. Then replace the nitrogen with natural gas, the replacement time is about 5 minutes and then inflate the cylinder. When the pressure in the cylinder reaches a certain pressure, close the sampling valve, press to seal, and take out the cylinder, that is, sampling is complete.

4.1.3 Chromatographic analysis

Using the method of International Standard Organization ISO 6974-2:2001e, this method uses gas chromatography to analyze the composition of natural gas under a certain degree of uncertainty. It is stipulated that helium is used as the carrier gas. ISO 6974:2001 stipulates the chromatogram for analysis. The column length is 3m, the inner diameter is 2mm, and the stationary phase is Pora Pak R with a particle diameter of 150-180m (80-100 mesh). The detection system requires thermal conductivity detector (TCD) and hydrogen flame ionization detector (FID). TCD detects methane, ethane, propane, carbon dioxide, nitrogen and, other components, while FID is mainly used to detect small or trace amounts of octane after butane components.

The sample enters the chromatograph through the sampler. The gas sample passes through the six-way valve with the carrier gas to reach the first chromatographic column. The TCD detection system detects light components, carbon dioxide, and nitrogen within 40 minutes, and then passes through a ten-way valve. The valve uses the FID detection system to detect the heavy components of butane on the second chromatographic column until 90 minutes to complete the entire sampling process.

4.1.4 Component analysis results (Figure 4.1)

4.1.5 Phase envelope diagram(Figure 4.2)

4.2 Solution for freezing blockage of cold box

4.2.1 Scheme 1: Solid adsorption heavy hydrocarbon device + regeneration gas cooling scheme

1) This plan is to install a set of silica gel adsorption heavy hydrocarbon removal device after the molecular sieve dehydration and mercury removal device. The natural gas dried by the molecular sieve is sent to this device, and the natural gas is sent to the downstream device after the adsorption is completed.

Removal of heavy hydrocarbons from raw natural gas. The solid temperature swing adsorption process is used to deeply remove heavy hydrocarbons in raw natural gas. The natural gas from the molecular sieve dehydration unit passes through the ice machine system and then the temperature drops to about 20°C, and then passes through the mercury removal tower to remove the mercury in the natural gas. After content removal reaches the

		旗下营	赛罕末站
氢气	Hydrogen	0.04	0.04
氦气	Helium	0.050	0.056
氮气	Nitrogen	1.28	1.87
氧气	Oxygen	0.000	0.000
硫化氢	H ₂ S	0.000	0.000
氩气	Argon	0.000	0.000
二氧化碳	CO ₂	1.48	1.43
二氧化硫	SO ₂	0.000	0.000
甲烷	Methane	91.09	90.58
乙烷	Ethane	4.37	4.36
乙烯	Ethene	0.000	0.000
丙烷	Propane	0.96	0.94
异丁烷	i-C ₄	0.21	0.21
正丁烷	n-C ₄	0.23	0.23
新戊烷	Neo-C ₅	0.0087	0.0086
异戊烷	i-C ₅	0.099	0.10
正戊烷	n-C ₅	0.050	0.048
己烷	C ₆	0.062	0.060
庚烷	C ₇	0.025	0.023
辛烷	C ₈	0.0069	0.0070
壬烷	C ₉	0.0018	0.0009
癸烷及以上	C ₁₀ ⁺	0.0003	0.000
甲基环戊烷	Mecyclopentane	0.015	0.014
苯	Benzene	0.0028	0.0035
环己烷	Cyclohexane	0.0094	0.0089
甲基环己烷	Mecyclohexane	0.014	0.013
甲苯	Toluene	0.0015	0.0019
乙苯	E-Benzene	0.000	0.000
对二甲苯	p-Xylene	0.000	0.000
间二甲苯	m-Xylene	0.000	0.000
邻二甲苯	o-Xylene	0.000	0.000

说明：如未特别说明，表中数据为体积百分含量。

Note: If not specified, the data in the table are volume percentage.

Figure 4.1 Raw material gas component of a LNG factory in Inner Mongolia

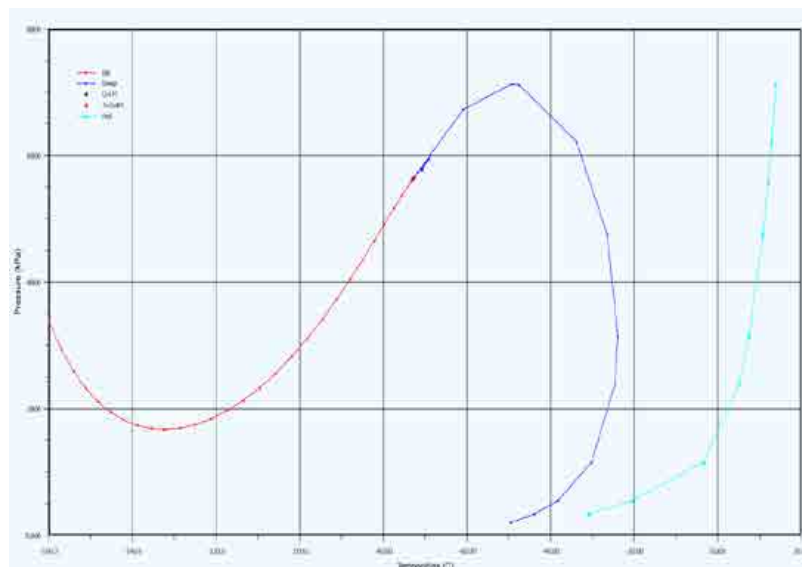
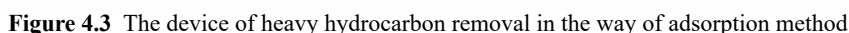


Figure 4.2 Phase envelop diagram of the raw material gas



After dehydrocarbon tower A completes the adsorption, switch to dehydrocarbon tower C, that is, dehydrocarbon tower C adsorption, dehydrocarbon tower A regeneration process heating stage, dehydrocarbon tower B regeneration process blowing cooling stage, and so on.

Symbol Description:

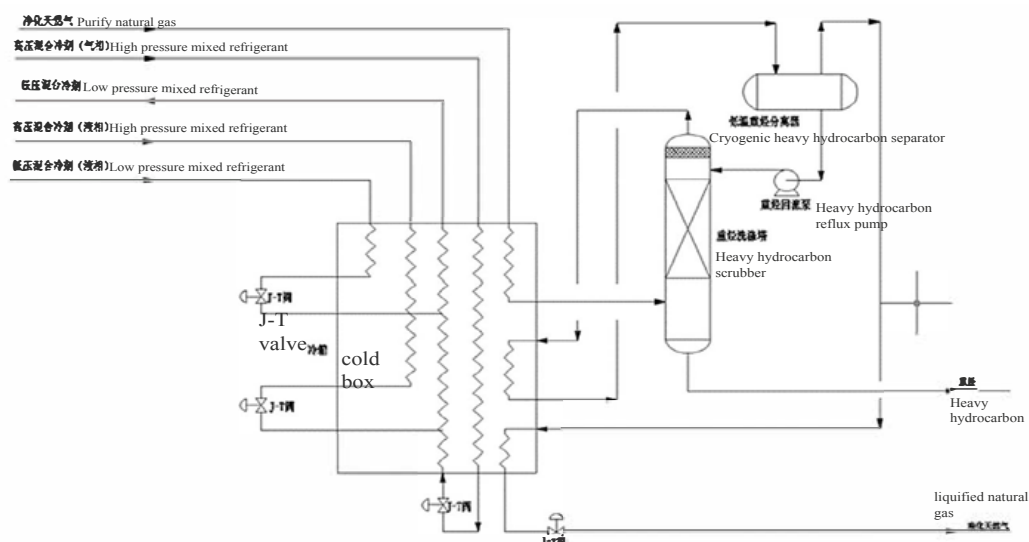


Figure 4.4 The device of heavy hydrocarbon washing

The implementation of the entire heavy hydrocarbon removal process is completely controlled by the program valve without manual operation. The operator can adjust the program time to control the process of heavy hydrocarbon removal by actually adjusting the program time.

4.2.2 Scheme 2: Heavy hydrocarbon washing method

A heavy hydrocarbon scrubber is installed outside the cold box. Using the principle of similar compatibility, the heavy hydrocarbons contained in the natural gas are separated in the heavy hydrocarbon scrubber according to the difference between the boiling points of heavy hydrocarbons and natural gas. As shown in Figure 4.4 below, after purified natural gas is pre-cooled to a certain temperature in the cold box, it first enters the scrubber. After the heavy hydrocarbons are removed, the natural gas is returned to the cold box and cooled to a lower temperature, and then the cold box is extracted again and then gas-liquid separation, the separated natural gas enters the cold

box again for liquefaction, and the separated heavy hydrocarbons are pumped to the top of the heavy hydrocarbon scrubber, and contact the first pre-cooled natural gas in the heavy hydrocarbon scrubber to remove the natural gas.

(1) Process simulation

From the raw gas group, it can be seen that the raw material gas neopentane, aromatic hydrocarbons and, aromatic hydrocarbon derivatives. In the natural gas liquefaction simulation process, a scrubber is used to remove neopentane, aromatic hydrocarbons, and aromatic hydrocarbons. According to the previous low-temperature simulation calculation experience and the comparison of on-site operating data, the Peng-Robinson equation of state is selected for the gas phase physical properties when simulating the natural gas liquefaction process, and the LK equation is selected for the liquid state equation. The combined equation is widely used in the field of natural gas processing. There are other impurities such as CO₂, N₂, in natural gas, and the calculated and actual values are between 0.5% and 2%. The specific simulation process is shown

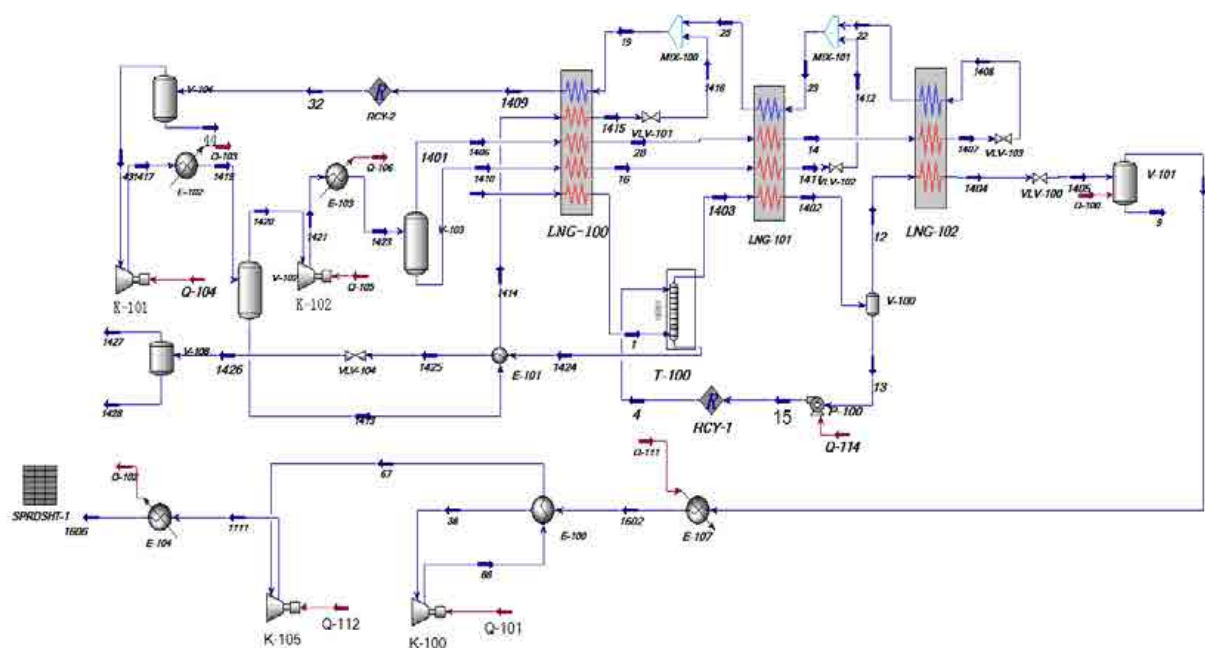


Figure 4.5 The HYSYS simulation of heavy hydrocarbon washing

in Figure 4.5.

(2) Process description

1) Natural gas liquefaction part

After acid gas removal and dehydration, the natural gas enters the main low-temperature plate-fin heat exchanger and is first cooled to -25°C , and then is extracted from the cold box into the heavy hydrocarbon scrubber to remove heavy hydrocarbon components above C_5+ in the natural gas. After the heavy hydrocarbon is removed the natural gas is returned to the plate-fin heat exchanger at about -47°C to continue cooling, condensed to about -71°C , and then enters the heavy hydrocarbon reflux tank for gas-liquid separation, and the gas phase is returned to the plate-fin heat exchanger and is supercooled to about -160°C , the product is throttled down to about 180kPa.g by the product JT valve to obtain -161.2°C LNG, and part of the flash gas (BOG, about 2.95%), which enters the LNG tank area. The liquid phase is used as the reflux liquid at the top of the heavy hydrocarbon scrubber and is in countercurrent contact with the natural gas at the bottom of the heavy hydrocarbon scrubber for absorption.

The heavy hydrocarbons removed from the heavy hydrocarbon scrubber at about -29°C enter the heavy hydrocarbon heater and the low-pressure liquid mixed refrigerant from the separator tank between the refrigerant compressor sections for heat exchange. After the regulating valve, the pressure drops to 1.6MPa.g. Then heated to 20°C and then enters the heavy hydrocarbon separation tank, the flash vapor enters the fuel gas system or the feed gas pressurization device, and the liquid phase enters the refrigerant and the heavy hydrocarbon storage tank in the heavy hydrocarbon storage device.

2) Refrigerant circulation part

The hybrid refrigeration system adopts a closed-cycle refrigeration process. The mixed refrigerant undergoes four processes (compression, cooling, condensation, and throttling) to convert electrical energy into cold energy to provide cold energy for natural gas liquefaction. The refrigerant is composed of methane, nitrogen, propane, ethylene, and isopentane.

The mixed refrigerant from the main low-temperature plate-fin heat exchanger first enters the inlet buffer tank of the refrigerant compressor for gas-liquid separation to prevent liquid droplets from entering the refrigerant compressor and causing liquid shock to the refrigerant compressor. The separated low-pressure gaseous refrigerant enters the first-stage inlet of the refrigerant compressor, pressurized to 1.5MPa.g, and then exits the first-stage compressor through the air cooler between refrigerant compressor sections, and then through the refrigerant compressor section. The intermediate water cooler is cooled to 38°C , and then enters the inter-stage separator tank of the refrigerant compressor for gas-liquid separation, and the gaseous refrigerant enters the secondary inlet of the compressor. The separated liquid refrigerant enters and exchanges heat with low-temperature heavy hydrocarbons, and then enters the refrigerant heat exchanger for cooling.

The gas phase refrigerant from the separator tank between the refrigerant compressor sections enters the secondary inlet of the refrigerant compressor and is compressed to 4.05MPa.g. The compressed mixed refrigerant is first cooled to 50% by the refrigerant compressor outlet air cooler, and then cooled to 38°C by the refrigerant compressor outlet water cooler, enter

the refrigerant compressor outlet liquid separation tank for gas-liquid separation, the gas phase refrigerant and the liquid phase enter the refrigerant heat exchanger respectively.

The high-pressure gaseous refrigerant from the cold box enters the cold box and passes through the plate-fin heat exchanger from top to bottom. After being pre-cooled, liquefied, and subcooled to about -160°C in the plate-fin heat exchanger, it is throttled down by the gas phase JT valve. After being compressed, the low-pressure and low-temperature refrigerant re-enters the bottom to provide cooling capacity for natural gas, high-pressure refrigerant, and low-pressure refrigerant from bottom to top. The liquid phase undergoes subcooling and then throttling. Finally, the low-pressure and low-temperature refrigerant re-enters, and after reheating, the temperature rises to 35.3°C and comes out from the top of the plate-fin heat exchanger, and the pressure is 0.195MPa.g.

The mixed refrigerant from the low-pressure liquid phase is cooled by low-temperature heavy hydrocarbons and then passes through the plate-fin heat exchanger from top to bottom. After being cooled to -25°C , it is extracted from the plate-fin heat exchanger, and then throttled and reduced by the JT valve. The latter low-pressure and low-temperature refrigerant re-enters, mixes with the low-pressure refrigerant from the bottom of the plate-fin heat exchanger, and flows upward to provide cold energy to the high-temperature section of the raw gas, high-pressure refrigerant, and medium-pressure refrigerant.

The high-pressure liquid phase mixed refrigerant from top to bottom is cooled to -60°C through the plate-fin heat exchanger, and then exits the main-fin heat exchanger, and is throttled down to 0.220MPa.g by the J-T valve. The low-pressure refrigerant after throttling re-enters the plate-fin heat exchanger, mixes with the low-pressure refrigerant from the bottom of the heat exchanger, and flows upward to provide cold energy to the high-temperature section of the raw gas, high-pressure refrigerant, and medium-pressure refrigerant.

The low-pressure refrigerant from the plate-fin heat exchanger is generally above the dew point, there is no liquid. When a fault occurs or there is liquid during operation, the liquid refrigerant will be separated. At this time, the hot blowing line from the first stage outlet to the bottom can be opened to blow the liquid inside, and the liquid refrigerant is vaporized by heating, and the refrigerant is renewed. Enter the system loop.

(3) Simulation results

Since the freezing point of neopentane is -20°C , in order to prevent neopentane from clogging the cold box, natural gas is selected to enter the heavy hydrocarbon scrubber at -25°C , and the reflux liquid is calculated at 4.6MPa, -71°C , -65°C , and -60°C . Under the working condition of -55°C , the low-temperature separator inlet and outlet conditions, the specific results are shown in Table 4.2 to Table 4.5: TOWERINFLOW represents the inlet low-temperature scrubber stream, TOWERGAS represents the gas stream at the top of the scrubber, and TOWERLIQUIN represents the scrubber inlet Logistics. SPEIN represents the stream entering the cryogenic separator, and SEPGAS represents the stream of the cryogenic separator.

(4) The effect of reflux temperature on the removal of heavy hydrocarbons from the scrubber.

Under the above-mentioned various working conditions (-71°C , -65°C , -60°C , -55°C), the molar percentages of

Table 4.2 The component simulation result of heavy hydrocarbon washing the gas into and out of the low temperature separator under the condition of 4.6 MPa & -71°C

Substance	Gas In Abs	Liquid In Abs	Gas out Abs	C5 out Abs	Gas in Spe	Gas out Spe
Methane	0.948541	0.787019	0.925684	0.347913	0.925684	0.951242
Ethane	0.026753	0.110324	0.039599	0.065800	0.039599	0.026572
Propane	0.005491	0.071414	0.015535	0.060042	0.015535	0.005243
i-Butane	0.000999	0.021301	0.003918	0.064147	0.003918	0.000684
n-Butane	0.001098	0.004740	0.000814	0.227484	0.000814	0.000107
i-Pentane	0.000448	0.000000	0.000000	0.101192	0.000000	0.000000
n-Pentane	0.000216	0.000000	0.000000	0.048895	0.000000	0.000000
n-Hexane	0.000131	0.000000	0.000000	0.029550	0.000000	0.000000
n-Decane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
n-Heptane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
22-Mpropane	0.000053	0.000023	0.000004	0.011730	0.000004	0.000000
n-Octane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
n-Nonane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
CO ₂	0.000019	0.000038	0.000022	0.000020	0.000022	0.000019
Nitrogen	0.016067	0.005141	0.014422	0.001657	0.014422	0.016134
H ₂ O	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
H ₂ S	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Mecyclohexane	0.000055	0.000000	0.000000	0.012468	0.000000	0.000000
Cyclohexane	0.000046	0.000000	0.000000	0.010331	0.000000	0.000000
Mecyclopentan	0.000064	0.000000	0.000000	0.014493	0.000000	0.000000
Benzene	0.000019	0.000000	0.000000	0.004280	0.000000	0.000000
Toluene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
o-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
m-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
p-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
E-Benzene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Helium	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Hydrogen	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

Table 4.3 The component simulation result of heavy hydrocarbon washing the gas into and out of the low temperature separator under the condition of 4.6 MPa & -65°C

Substance	Gas In Abs	Liquid In Abs	Gas out Abs	C5 out Abs	Gas in Spe	Gas out Spe
Methane	0.948541	0.662164	0.930207	0.323385	0.930207	0.949721
Ethane	0.026753	0.121399	0.033130	0.061127	0.033130	0.026719
Propane	0.005491	0.096748	0.011616	0.051238	0.011616	0.005443
i-Butane	0.000999	0.043228	0.003825	0.026951	0.003825	0.000952
n-Butane	0.001098	0.066448	0.005455	0.049887	0.005455	0.000993
i-Pentane	0.000448	0.002562	0.000201	0.212275	0.000201	0.000016
n-Pentane	0.000216	0.000087	0.000004	0.110499	0.000004	0.000000
n-Hexane	0.000131	0.000000	0.000000	0.066293	0.000000	0.000000
n-Decane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
n-Heptane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
22-Mpropane	0.000053	0.003810	0.000302	0.003573	0.000302	0.000045
n-Octane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
n-Nonane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
CO ₂	0.000019	0.000037	0.000020	0.000019	0.000020	0.000019
Nitrogen	0.016067	0.003517	0.015240	0.001486	0.015240	0.016093
H ₂ O	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
H ₂ S	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Mecyclohexane	0.000055	0.000000	0.000000	0.027971	0.000000	0.000000
Cyclohexane	0.000046	0.000000	0.000000	0.023177	0.000000	0.000000
Mecyclopentan	0.000064	0.000000	0.000000	0.032515	0.000000	0.000000
Benzene	0.000019	0.000000	0.000000	0.009603	0.000000	0.000000
Toluene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
o-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
m-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
p-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
E-Benzene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Helium	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Hydrogen	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

Table 4.4 The component simulation result of heavy hydrocarbon washing the gas into and out of the low temperature separator under the condition of 4.6 MPa & -60°C

Substance	Gas In Abs	Liquid In Abs	Gas out Abs	C5 out Abs	Gas in Spe	Gas out Spe
Methane	0.948541	0.577294	0.937606	0.307067	0.937606	0.949355
Ethane	0.026753	0.116793	0.029544	0.059167	0.029544	0.026696
Propane	0.005491	0.099190	0.008384	0.049221	0.008384	0.005425
i-Butane	0.000999	0.047097	0.002420	0.024977	0.002420	0.000963
n-Butane	0.001098	0.076684	0.003423	0.044043	0.003423	0.001034
i-Pentane	0.000448	0.065053	0.002376	0.089408	0.002376	0.000336
n-Pentane	0.000216	0.010107	0.000369	0.140654	0.000369	0.000037
n-Hexane	0.000131	0.000328	0.000002	0.120261	0.000002	0.000000
n-Decane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
n-Heptane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
22-Mpropane	0.000053	0.004520	0.000190	0.002715	0.000190	0.000048
n-Octane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
n-Nonane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
CO ₂	0.000019	0.000035	0.000019	0.000019	0.000019	0.000019
Nitrogen	0.016067	0.002790	0.015667	0.001349	0.015667	0.016087
H ₂ O	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
H ₂ S	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Mecyclohexane	0.000055	0.000000	0.000000	0.047573	0.000000	0.000000
Cyclohexane	0.000046	0.000009	0.000000	0.039644	0.000000	0.000000
Mecyclopentan	0.000064	0.000085	0.000000	0.057268	0.000000	0.000000
Benzene	0.000019	0.000013	0.000000	0.016634	0.000000	0.000000
Toluene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
o-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
m-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
p-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
E-Benzene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Helium	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Hydrogen	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

Table 4.5 The component simulation result of heavy hydrocarbon washing the gas into and out of the low temperature separator under the condition of 4.6 MPa & -55°C

Substance	Gas In Abs	Liquid In Abs	Gas out Abs	C5 out Abs	Gas in Spe	Gas out Spe
Methane	0.948541	0.511815	0.941750	0.286999	0.941750	0.948889
Ethane	0.026753	0.108131	0.028076	0.056441	0.028076	0.026748
Propane	0.005491	0.094906	0.006940	0.046487	0.006940	0.005480
i-Butane	0.000999	0.046760	0.001740	0.022881	0.001740	0.000993
n-Butane	0.001098	0.078548	0.002351	0.039125	0.002351	0.001087
i-Pentane	0.000448	0.083609	0.001793	0.042789	0.001793	0.000437
n-Pentane	0.000216	0.060177	0.001186	0.031171	0.001186	0.000213
n-Hexane	0.000131	0.007275	0.000137	0.181376	0.000137	0.000008
n-Decane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
n-Heptane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
22-Mpropane	0.000053	0.004734	0.000128	0.002256	0.000128	0.000052
n-Octane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
n-Nonane	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
CO ₂	0.000019	0.000032	0.000019	0.000019	0.000019	0.000019
Nitrogen	0.016067	0.002348	0.015850	0.001196	0.015850	0.016074
H ₂ O	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
H ₂ S	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Mecyclohexane	0.000055	0.000000	0.000000	0.088305	0.000000	0.000000
Cyclohexane	0.000046	0.000149	0.000002	0.073439	0.000002	0.000000
Mecyclopentan	0.000064	0.001310	0.000024	0.097932	0.000024	0.000001
Benzene	0.000019	0.000207	0.000004	0.029585	0.000004	0.000000
Toluene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
o-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
m-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
p-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
E-Benzene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Helium	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Hydrogen	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

components above C_5 in the gas phase of the heavy hydrocarbon scrubber are 4ppm, 528ppm, 2937ppm, 3244ppm. Use mole percentage as the ordinate and temperature as the abscissa to make a graph, as shown in Figure 4.6:

Under the above-mentioned various working conditions (-71°C, -65°C, -60°C, -55°C), the molar percentages of components above C_5 in the gas phase out of the cryogenic separator are respectively: 0, 61, 422 ppm, 711 ppm. Use mole percentage as the ordinate and temperature as the abscissa to

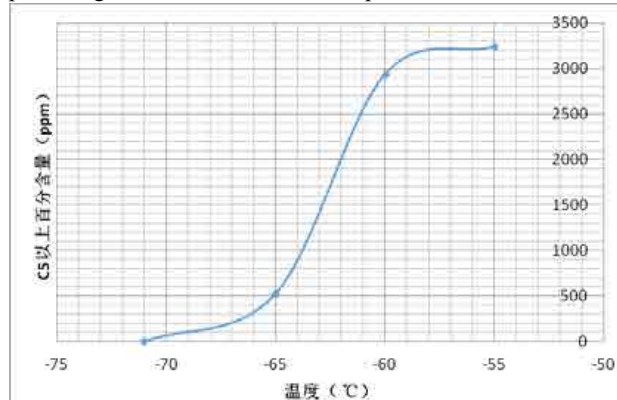


Figure 4.6 The gas phase of heavy hydrocarbon out of washing tower with the temperature change

make a graph, as shown in Figure 4.7:

When the content of heavy hydrocarbons in natural gas is constant, the lower the reflux temperature is required to process the natural heavy hydrocarbon content to the heavy hydrocarbon content in liquefaction. When the content of heavy hydrocarbons in natural gas increases, the lower the reflux temperature will be. The reason is that there are more heavy hydrocarbons need to be

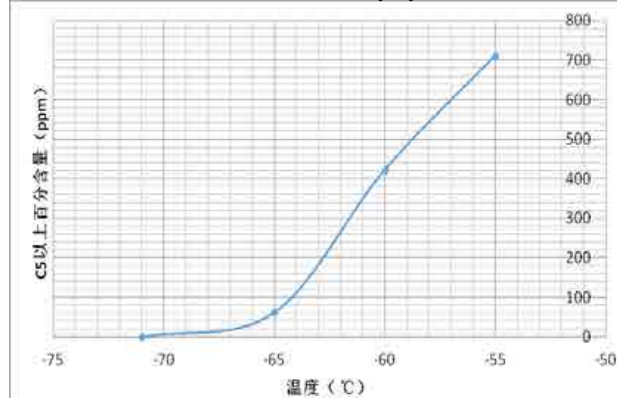


Figure 4.7 The gas phase of heavy hydrocarbon out of low temperature separator with the temperature change

Figures 4.6 and Figure 4.7 show that above -65 ~ -60°C, the content of heavy hydrocarbons above C_5 increases rapidly. When the slope of temperature change increases, the content of heavy hydrocarbons above C_5 in the purified gas increases faster. In the natural gas liquefaction process, the content of neopentane in the gas phase component at the outlet of the scrubber should be controlled below 20ppm, and the total content of heavy hydrocarbon components above C_5 in the gas phase component at the outlet of the low-temperature heavy hydrocarbon separator should be controlled at 10ppm, according to Figure 4.6 and Figure 4.7. It can be judged that the critical value is when the reflux temperature is around -71°C. The simulation calculation of the gas at -71°C, the outlet of the scrubber, and cryogenic separator, the calculation results are shown in Table 4.2.

The results show that the volume percentage of neopentane component in the scrubber is 4ppm, and the scrubber pentane content of the low-temperature heavy hydrocarbon separator is 0ppm. Therefore, under 4.6MPa working conditions, the reflux temperature of -71°C can be selected. Ensure the effect of heavy hydrocarbon removal and save energy consumption.

(5) Influence of reflux temperature on energy consumption per unit of liquefaction

Under the above-mentioned different working conditions (-71°C, -65°C, -60°C, -55°C), the influence on unit liquefaction energy consumption is shown in Figure 4.8

According to Figure 4.8, when the reflux temperature is between -60 and -65, the energy consumption per unit of liquefaction does not change much as the reflux temperature decreases. When the reflux temperature is below -60, the energy consumption per unit of liquefaction increases as the reflux temperature decreases.

(6) After the simulation, the heat transfer curve of Scheme 2 is

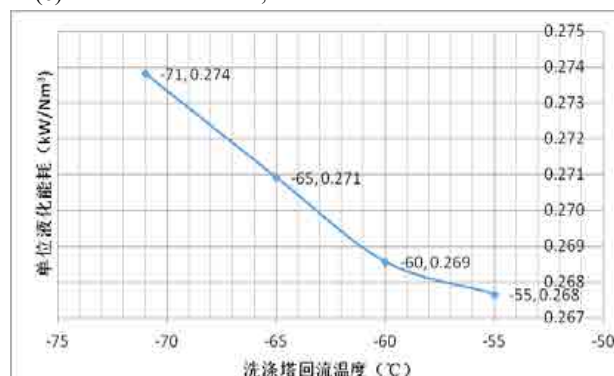


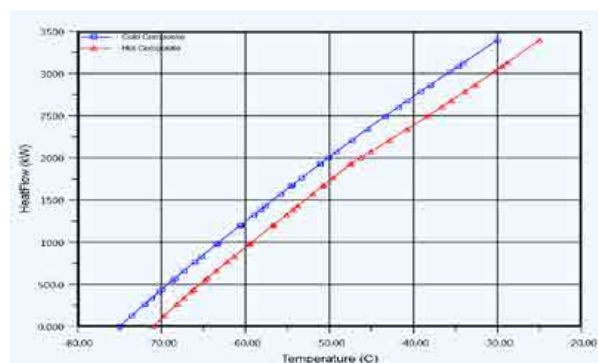
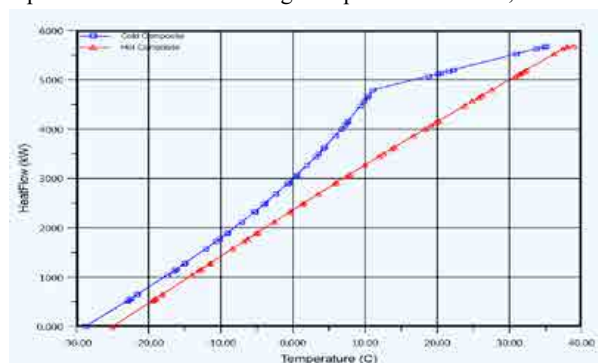
Figure 4.8 The effect of separation temperature on the energy consumption

as follows

(7) Main equipment

(8) Research conclusion:

1) When the content of C_5 and above components in natural gas is constant, heavy hydrocarbons in natural gas need to be processed to the natural gas liquefaction index, the lower



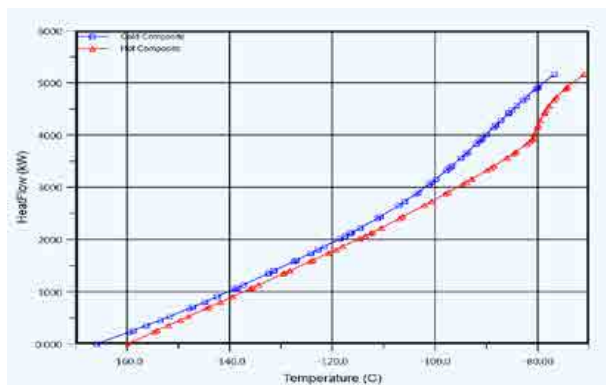


Figure 4.9 The heat transfer curve of Proposal 2

the reflux temperature needs to be, and the higher the unit

Serial number	Device name	Model specification	Number
1	Heavy hydrocarbon scrubber	DN700×5000	1
2	Cryogenic heavy hydrocarbon separator	DN1100×3600	1
3	Low temperature heavy hydrocarbon reflux pump	Head: 50m, power: 2kW	2
4	Cold box	Heat load: 13898kW	1

liquefaction energy consumption.

2) When the low-temperature scrubbing method is used in the Inner Mongolia LNG plant, the temperature is selected as -71°C to ensure the effect of heavy hydrocarbon removal, and the unit energy consumption for liquefaction is $0.274\text{Kw}/\text{Nm}^3$.

3) This method is suitable for raw gas whose C_5 content above does not exceed 8000ppm in natural gas. The reason is that the higher the heavy hydrocarbon content, the lower the required reflux temperature. As a result, the loss of raw gas will increase, and the energy consumption of liquefaction will increase

accordingly.

4.2.2 Scheme 3: Gas stripping + heavy hydrocarbon reflux scrubbing method

A heavy hydrocarbon scrubber is installed outside the cold box, a hot gas is introduced at the bottom of the tower as the stripping gas of the scrubber. The process flow diagram is shown in Figure 4.10. After purification, the natural gas is divided into two routes. One route of natural gas is pre-cooled in the cold box to a certain temperature and then extracted from the cold box to the scrubbing tower. After the temperature is lower, the cold box is drawn out again and then the gas-liquid separation is carried out. The separated natural gas enters the cold box again for liquefaction. The separated heavy hydrocarbons are pumped to the top of the heavy hydrocarbon scrubber and are in heavy weight with the natural gas after the first pre-cooling. Reverse contact in the hydrocarbon scrubber to remove heavy hydrocarbons from natural gas. The other way of natural gas directly enters the bottom of the tower, and the light components entrained in the heavy hydrocarbons are evaporated by heat. Thereby reducing the loss of light components.

(1) Process simulation

From the raw gas group, it can be seen that the raw gas neopentane, aromatic hydrocarbons, and aromatic hydrocarbon derivatives, in the natural gas liquefaction simulation process, the neopentane, aromatic hydrocarbons, and aromatic hydrocarbons are removed by the scrubber. According to the previous low-temperature simulation calculation experience and the comparison of on-site operating data, the Peng-Robinson equation of state is selected for the gas phase physical properties when simulating the natural gas liquefaction process, and the LK equation is selected for the liquid state equation. The combined

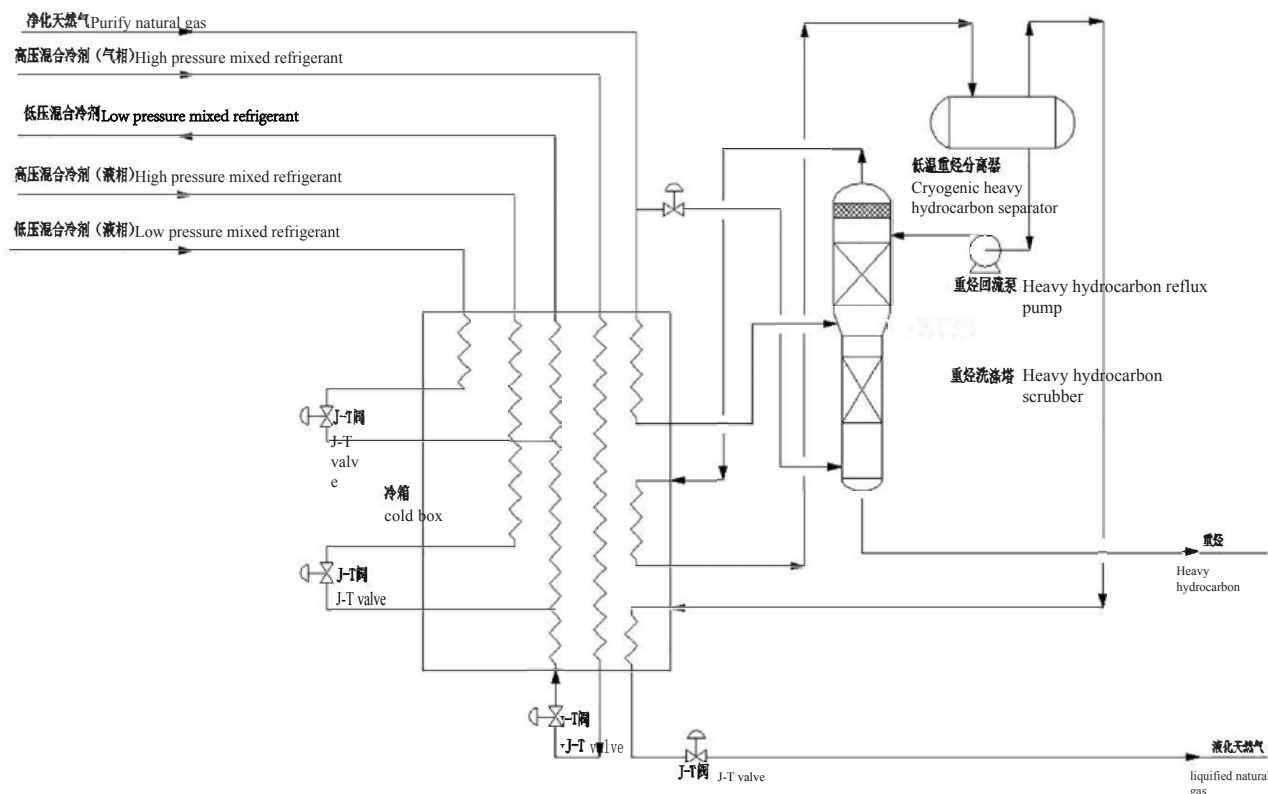


Figure 4.10 The device of heavy hydrocarbon backflow add gas stripping

liquefaction were studied respectively. In this study, the gas stripping amount was selected as 0.05, 0.10 and 0.15

From Figure 4.12, it can be known that when the percentage of stripping gas to the total gas volume is less than 10%, the percentage content of C_5 or more in the gas phase from the heavy hydrocarbon scrubber does not change significantly, and when the percentage of stripping gas to the total gas volume is 10%

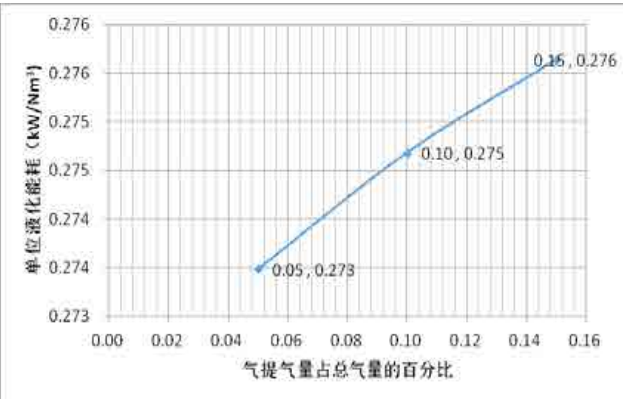


Figure 4.13 The effect of gas stripping amount on the energy consumption

At ~15%, the percentage of C_5 or more in the gas phase from the heavy hydrocarbon scrubber drops significantly.

(5) The influence of gas stripping volume on unit liquefaction energy consumption

From Figure 4.13, we can know that when the percentage of

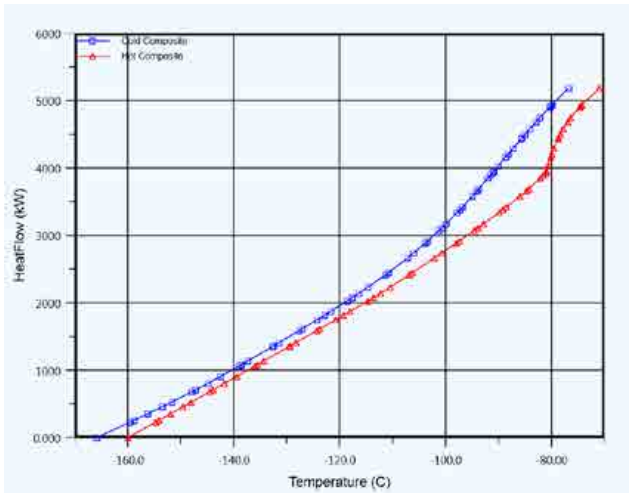
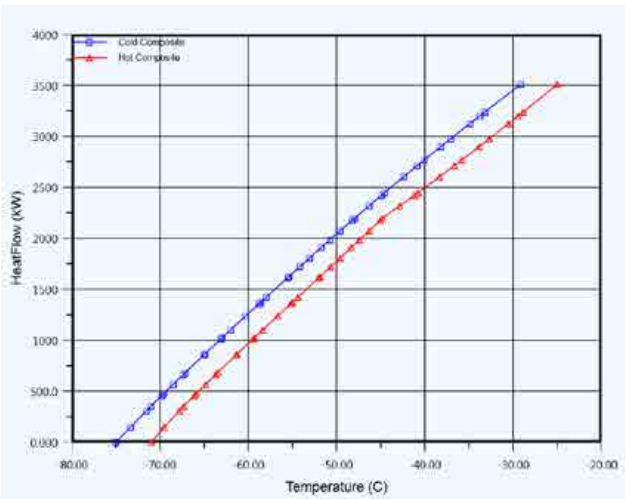
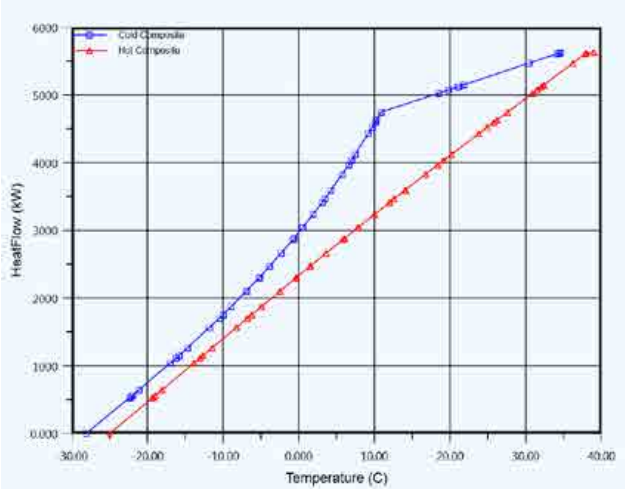


Figure 4.14 The heat transfer curve of Proposal 3

air stripping gas to the total gas volume increases, the energy

Serial number	Device name	Model specification	Number
1	Heavy hydrocarbon scrubber	DN700×DN350×6000	1
2	Cryogenic heavy hydrocarbon separator	DN1100×3600	1
3	Low temperature heavy hydrocarbon reflux pump	Head: 50m, power: 2.5kW	2
4	Cold box	Heat load: 14318kW	1

consumption per unit of liquefaction increases.

(6) After the simulation, the heat transfer curve of Scheme 3 is as follows

(7) Main equipment

(8) Research conclusion

1) According to Figure 4.12 and Figure 4.13, when the gas scheme is adopted, the percentage of stripping gas to the total gas volume is 15%, the total content of aromatic hydrocarbons above C_5 and benzene in the gas phase out of the heavy hydrocarbon scrubber is about 2PPM. The energy consumption per unit of liquefaction is 0.276kW/Nm³.

2) The gas stripping scheme is suitable for the liquefaction of feed gas with a small content of neopentane.

3) This technical solution is not applicable to liquefaction plants with a large content of heavy hydrocarbons in the feed gas.

4.2.3 Scheme 4: Removal of heavy hydrocarbons by distillation

A set of low-temperature rectification towers are installed in the natural gas liquefaction unit to remove heavy hydrocarbons and benzene. The process flow is shown in Figure 4.15. The principle of the process uses the principle that light components are volatile and heavy components are easy to condense. After decarburization, dehydration, and mercury removal, the natural gas first enters the plate-fin heat exchanger for pre-cooling. When it is cooled to a certain temperature in the plate-fin heat exchanger, it is extracted from the equipment and enters the rectification tower to remove heavy hydrocarbons and benzene. The natural gas is returned to the plate-fin heat exchanger again for cooling, and when it is cooled to a lower temperature, the plate-fin heat exchanger is extracted into the heavy hydrocarbon separator to further separate the heavy hydrocarbons in the natural gas, and the separated natural gas is returned to the cold box for liquefaction manufacturing Into LNG. The heavy hydrocarbons from the cryogenic heavy hydrocarbon separator are sent to the top of the rectification tower by cryogenic pumps as the reflux liquid of the rectification tower. The cryogenic

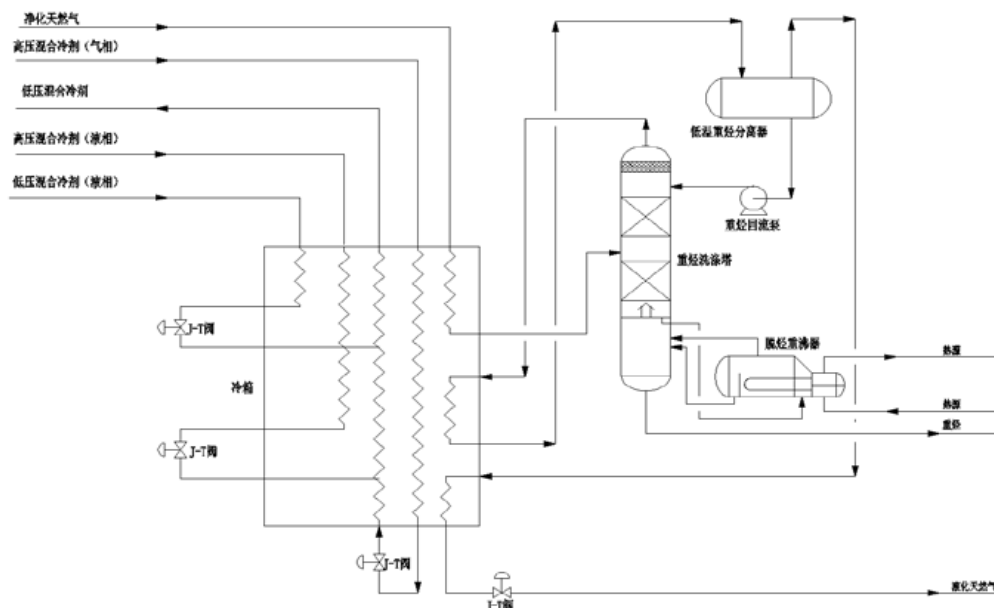


Figure 4.15 The device of heavy hydrocarbon removal by distillation

liquid is in reverse contact with rising natural gas to wash out the heavier heavy hydrocarbons and benzene in the natural gas, and then flows downward along the packing in the tower into the reboiler at the bottom of the tower. By controlling the temperature of the reboiler, the lighter volatile components escape from heavy hydrocarbons. Thus, the lighter components in natural gas are not easily lost.

(1) Process simulation

From the raw gas group, it can be seen that the raw gas neopentane, aromatic hydrocarbons, and aromatic hydrocarbon derivatives, in the natural gas liquefaction simulation process, the neopentane, aromatic hydrocarbons, and aromatic hydrocarbons are removed by the scrubber. According to the previous low-temperature simulation calculation experience and the comparison of on-site operating data, the Peng-Robinson equation of state is selected for the gas phase physical properties when simulating the natural gas liquefaction process, and the LK equation is selected for the liquid state equation. The

combined equation is widely used in the field of natural gas processing. There are other impurities such as CO_2 , N_2 , etc, and the calculated and actual value is between 0.5% and 2%. The specific simulation process is shown in Figure 4.16.

(2) Description of process flow

After being purified, the plate-fin heat exchanger is pre-cooled to -25°C , and then the cold box is drawn out from the middle of the rectification tower and enters the rectification tower. The natural gas is removed from the rectification tower and C_5 and above heavy hydrocarbon components are removed. After hydrocarbons, the natural gas is returned to the plate-fin heat exchanger at about -47°C to continue cooling and condenses to about -75°C , and then enters the heavy hydrocarbon reflux tank for gas-liquid separation, and the gas phase is returned to the plate-fin heat exchanger and is supercooled to the temperature is about -160°C , and the pressure is reduced to about 180kPa.g through the product JT valve to obtain -161.2°C LNG and part of the flash gas (BOG, about 2.95%), which enters the LNG

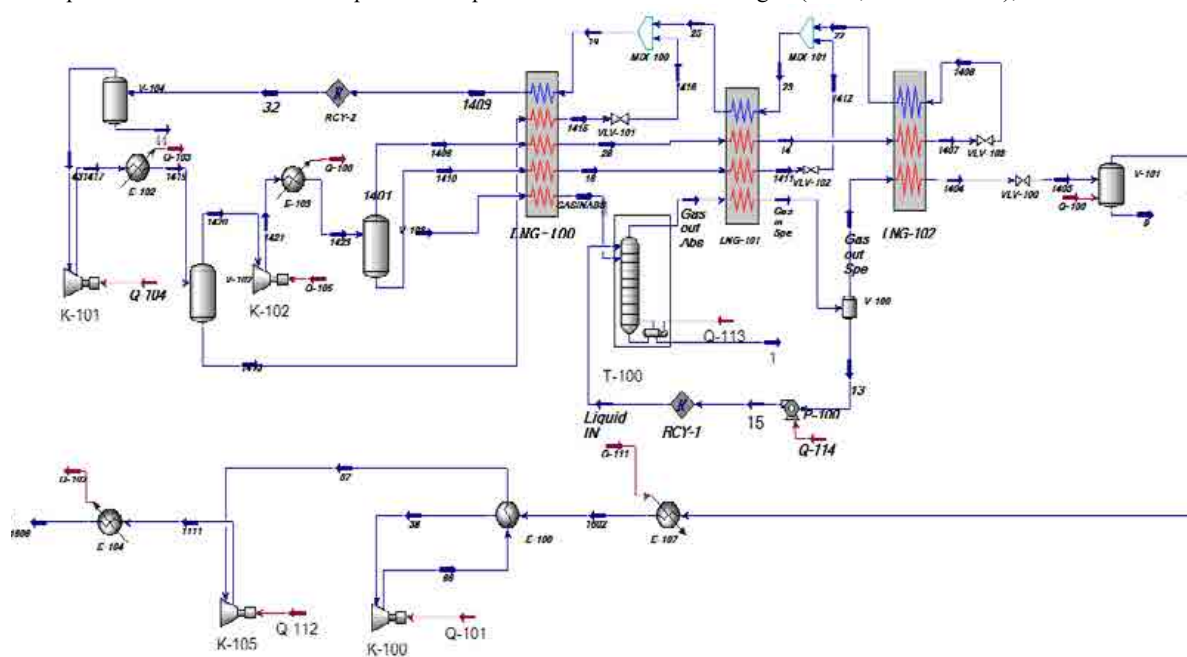


Table 4.7 The component simulation result of heavy hydrocarbon distillation under different temperatures

Substance	The reflux temperature is -71℃	The reflux temperature is -72℃	The reflux temperature is -73℃	The reflux temperature is -74℃	The reflux temperature is -75℃
22-Mpropane	0.000033	0.000032	0.000018	0.000009	0.000004
i-Pentane	0.000066	0.000040	0.000021	0.000010	0.000005
n-Pentane	0.000012	0.000007	0.000004	0.000002	0.000001
n-Hexane	0.000000	0.000000	0.000000	0.000000	0.000000
n-Heptane	0.000000	0.000000	0.000000	0.000000	0.000000
n-Octane	0.000000	0.000000	0.000000	0.000000	0.000000
n-Nonane	0.000000	0.000000	0.000000	0.000000	0.000000
n-Decane	0.000000	0.000000	0.000000	0.000000	0.000000
Mcyclopentan	0.000000	0.000000	0.000000	0.000000	0.000000
Benzene	0.000000	0.000000	0.000000	0.000000	0.000000
Cyclohexane	0.000000	0.000000	0.000000	0.000000	0.000000
Mcyclohexane	0.000000	0.000000	0.000000	0.000000	0.000000
Toluene	0.000000	0.000000	0.000000	0.000000	0.000000
E-Benzene	0.000000	0.000000	0.000000	0.000000	0.000000
p-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000
m-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000
o-Xylene	0.000000	0.000000	0.000000	0.000000	0.000000
H ₂ O	0.000000	0.000000	0.000000	0.000000	0.000000

tank area. The liquid phase is used as the reflux liquid at the top of the rectification tower, and is in countercurrent contact with the natural gas entering the bottom of the rectification tower for absorption.

(3) Simulation results

This project observes the effect of heavy hydrocarbon removal by adjusting the reflux temperature. This project selects -71℃, -72℃, -73℃, -74℃, -75℃ for simulation, and the simulation results are shown in Table 4.7.

Table 4.7 Distillation simulation results at different reflux temperatures

(4) Influence of reflux temperature on heavy hydrocarbon removal

This topic selects -71℃, -72℃, -73℃, -74℃, -75℃ for

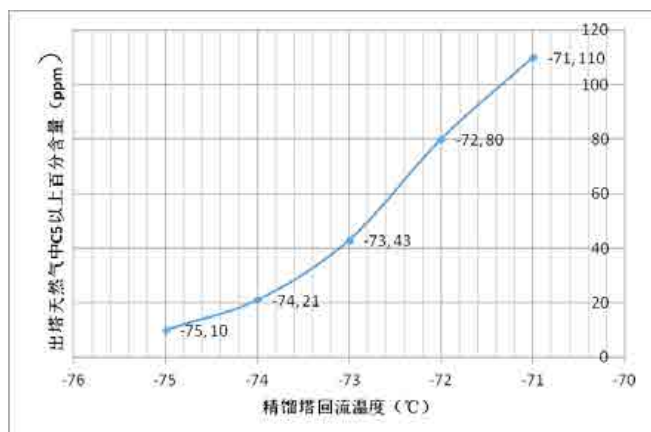


Figure 4.17 The effect of reflow temperature on hydrocarbon removal

simulation, and the reboiler temperature is selected as 100℃. The relationship between the reflux temperature and the heavy hydrocarbon content in the gas phase at the outlet of the distillation tower is shown in Figure 4.17.

(5) Influence of reflux temperature on energy consumption per

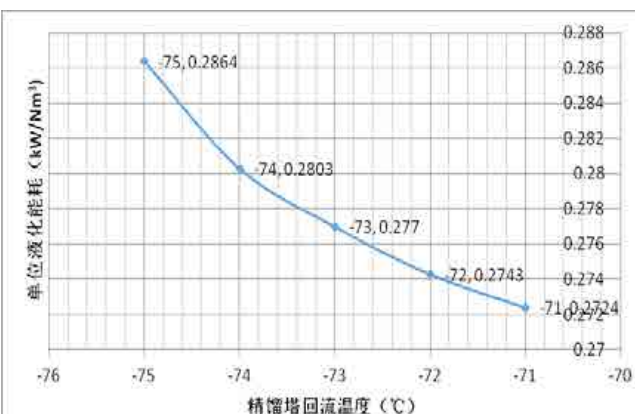
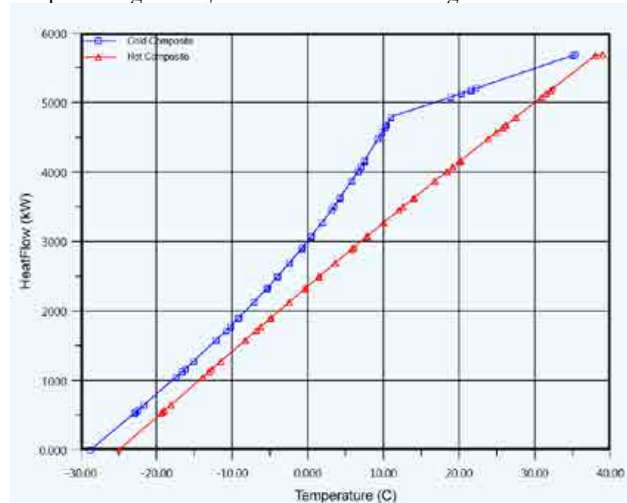


Figure 4.18 The effect of reflow temperature on the energy consumption

unit of liquefaction

From Figure 4.17 and Figure 4.18, it can be known that when the temperature of the gold distillation tower decreases, the percentage of C₅ or more in the natural gas from the tower



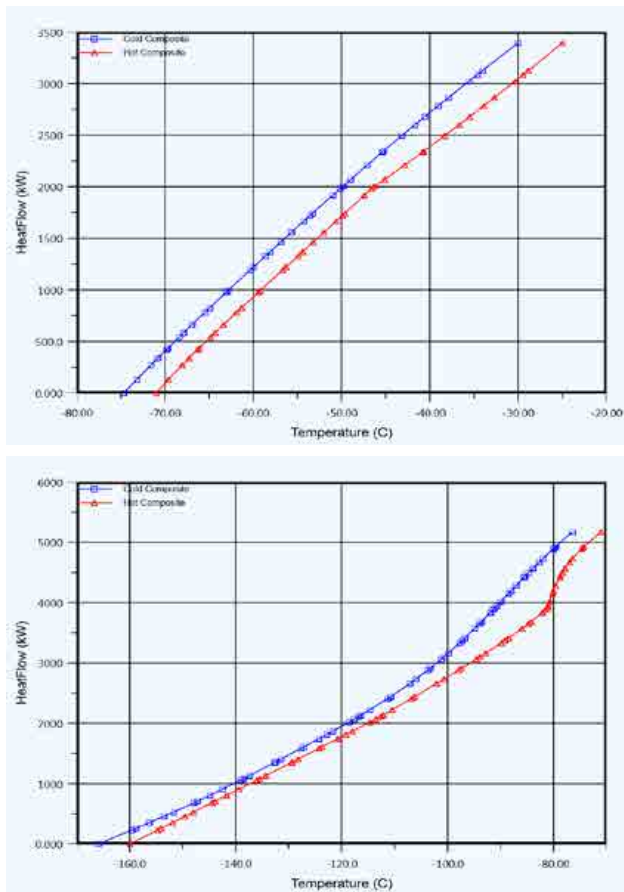


Figure 4.19 The heat transfer curve of Proposal 4

decreases, and the energy consumption per unit of liquefaction

Serial number	Device name	Model specification	number
1	Distillation tower	DN800×6000	1
2	Cryogenic heavy hydrocarbon separator	DN1100×3600	1
3	Low temperature heavy hydrocarbon reflux pump	Head: 50m, power: 2.5kW	2
4	cold box	Heat load: 14662kW	1
5	Reboiler	Heat load: 30kW	1

increases.

(6) After simulation, the heat transfer curve of Scheme 4 is as follows.

(7) Main equipment

(8) Research conclusion

1) From Figure 4.17, it can be known that when the reflux temperature reaches -75°C , the C_5 content in the rectification tower can be below 10ppm. From Figure 4.18, it can be known that the unit liquefaction energy consumption at this time is $0.2864\text{kW}/\text{Nm}^3$.

2) The rectification method for removing heavy hydrocarbons is suitable for feed gas with large heavy hydrocarbon content. This method is widely used in lightly combined production projects.

4.3 Comparative analysis of cold box freezing and blocking solutions

4.3.1 Advantages and disadvantages of each scheme

The scheme 1 adsorption and adsorption of heavy hydrocarbons is a method of separating heavy hydrocarbons in the feed gas using the principle of different adsorption capacities of adsorbents at different temperatures and using porous structured adsorbents to separate the hydrocarbon components in natural gas with different adsorption capacities. Its characteristic is to

use the difference in the adsorption capacity of hydrocarbon components to separate natural gas components, which is suitable for working conditions where the content of heavy hydrocarbon components in natural gas is not high and the design is not large. The disadvantages of this process are high energy consumption and high operating costs. At present, the use of temperature swing adsorption to remove heavy hydrocarbons from natural gas is a relatively mature process. This process utilizes the characteristic that the equilibrium adsorption capacity of the mixed gas by the solid adsorbent decreases with the increase of temperature. The characteristic of this process is adsorption at room temperature and the process of using heated adsorbent to separate heavy hydrocarbons from the adsorbent and enter the regeneration gas. At the same time, an ice machine is introduced in Option One to cool the regeneration gas and separate heavy hydrocarbons. So that the regeneration gas can be recycled.

The scheme 1: silica gel for heavy hydrocarbon removal. After the design of the general adsorber is completed, when the content of heavy hydrocarbons in the feed gas becomes rich, it may be unqualified for heavy hydrocarbon removal. Therefore, the method of adsorbing and removing heavy hydrocarbons has poor adaptability. The first option has higher investment and a small operating flexibility range. The device should not be installed separately. If the device needs to be used, it must be used in combination with the second option.

The scheme 2 is to set up a set of low-temperature washing and removing heavy hydrocarbons in the liquefaction unit. The advantage of this scheme is that heavy hydrocarbons are removed cleanly and the operation flexibility is large. However, the energy consumption of compression and cooling is higher than that of low-temperature separation alone. The heat load of the cold box is relatively small. After the heavy hydrocarbons from the bottom of the tower are flashed, the volatile part can be used as fuel gas for the whole plant without entering the tower for circulation, thereby reducing the scrubbing load of the tower. After being added to the low-temperature heavy hydrocarbon separation tank, the remaining heavy hydrocarbons can be further removed. When the quality of the raw material changes, the isopentane in the refrigerant storage and distribution needs to be used to wash and remove the heavy hydrocarbons, which increases the refrigerant consumption.

In the scheme 3, a gas is introduced at the bottom of the heavy hydrocarbon removal tower as the gas stripping gas for the heavy hydrocarbon scrubber. The advantage of this scheme is that the cold capacity of heavy hydrocarbons can be directly used. After the heat exchange between the heavy hydrocarbons and the stripping gas at the bottom of the tower, the volatile light components in the heavy hydrocarbons at the bottom of the tower will enter the gas phase at the top of the tower, reducing the loss of natural gas. The disadvantage of this method is that heavy hydrocarbons in natural gas cannot be removed when the amount of gas stripped is too small.

The scheme 4: When the rectification tower removes heavy hydrocarbons, although it can effectively remove heavy hydrocarbons, the bottom of the general rectification tower needs to be heated and flashed by a heat source, and the top of the tower needs to be cooled and separated by a cold source, a distillation tower bottom heating system is required. And the cooling system at the top of the tower, energy consumption is relatively large; when the bottom of the tower is heated,

neopentane is easy to volatilize into the gas phase at the top of the tower, it is necessary to increase the reflux at the top of the tower. Therefore, the second separation requires a lower temperature than the second and third options.

4.3.2 Comparison of energy consumption per unit of liquefaction

When the heavy hydrocarbon content in the raw materials is liquefied in schemes 2, 3 and 4, the unit liquefaction energy consumption of scheme 2 is $0.274\text{kw}/\text{Nm}^3$, the unit liquefaction energy consumption of scheme 3 is $0.276\text{kw}/\text{Nm}^3$, and the unit liquefaction energy of scheme 4. The consumption is $0.286\text{kw}/\text{Nm}^3$, so the second scheme is the least energy consumption for liquefaction.

4.3.3 Investment analysis

Please refer to the main equipment table in each chapter for the equipment size and specifications in the second, third, and fourth project of this project. By comparison, the heat load of the cold box in Scheme 2 is the smallest, and the heat load in Scheme 4 is the largest. The second option has the least equipment investment, and the fourth option has the largest equipment investment.

The conclusion of the study is based on the above comparison: the second option for the cold box freeze blocking solution of the Inner Mongolia LNG plant.

4.4 The actual operation and operation precautions of the heavy hydrocarbon removal tower

4.4.1 Problems encountered in actual driving

The first train of the Inner Mongolia LNG plant was commissioned with the air intake on December 30, 2015. During the trial production, there were several blockages of the natural gas flow passage in the plate-fin heat exchanger, and the main cause of the natural gas was the JT on the cold box. The blockage is more serious. When opening the JT valve, it will be found that there are solidified heavy hydrocarbons in the valve core.

From the field point of view, the LNG product valve is opened wide, the flow of natural gas entering the cold box remains unchanged, and the differential pressure before and after the valve of the LNG product J-T increases. When the bypass of the LNG product J-T valve is manually opened, the natural gas flow increases, the differential pressure after the front valve of the LNG product J-T valve returns to normal.

According to on-site online analysis and testing data, when natural gas enters the liquefaction unit, the H_2O in the purified gas is $\leq 0.1\text{ppm}$ and $\text{CO}_2 \leq 50\text{ppm}$. The natural gas after the deep purification treatment before entering the cold box and the natural gas after the heavy hydrocarbon tower are sampled and analyzed. The detection found that the content of benzene and benzene derivatives in the feed gas exceeded the standard, which means that the poor removal of heavy hydrocarbons is the main cause of freezing.

The reasons for the above blockage were analyzed. The raw material gas of the Inner Mongolia LNG plant comes from the Changqing Gas Field, which is at the peak of gas consumption in winter. The upstream gas volume is too large to be fully processed by the purification plant, so it directly enters the

pipeline network. The benzene and cyclohexane in the purified natural gas entering the cold box seriously exceed the standard. Even after the heavy hydrocarbon scrubber, the content of benzene and cyclohexane in the natural gas still cannot meet the content requirements of the natural gas liquefaction index, and further liquefaction leads to a plate-fin type. The natural gas channel is blocked. When the liquefaction unit is in the pre-cooling stage, the heavy hydrocarbon scrubber cannot be washed, and the cryogenic separator needs to establish a liquid level. During this period when the liquid level is established, heavy hydrocarbons cannot be separated. Therefore, it is easy to block the cold box.

In response to emergencies such as partial blockage of the cold box and freezing of the outlet valve, the following measures are summarized based on the factory's production and operating experience:

(1) Increase the flow rate of the high-pressure gas phase refrigerant, lower the temperature of the natural gas entering the heavy hydrocarbon scrubber, and lower the pressure into the tower to achieve a better effect of heavy hydrocarbon removal.

(2) If the cold box and outlet valve are frozen and blocked, the air intake can be manually controlled. Increase the flow of natural gas into the cold box to flush the cold box heat exchanger. When increasing the flow of natural gas, you must also pay attention to adjusting the refrigerant flow and always pay attention to the change of the pressure difference between the two ends of the heat exchanger. If the situation improves, adjustments should be made in time. If the outlet valve is frozen and blocked, it is necessary to switch the bypass to open the discharge space and perform partial reheating of the valve. In short, we should observe more, find out early, and try to avoid the situation that the freezing block is serious and the situation that must be stopped occurs.

4.4.2 Matters needing attention in production operation

(1) In actual production, it is important to strictly monitor the liquid level, pressure and flow rate of the heavy hydrocarbon scrubber. When the cold box is pre-cooled, the pre-cooling pipeline of the low-temperature heavy hydrocarbon pump should be opened to allow the pump and the cold box to pre-cool together. When the cryogenic separator has a certain liquid level and the temperature of the low-temperature heavy hydrocarbon reflux pump is at -70°C , the low-temperature heavy hydrocarbon reflux pump should be used immediately. In short, pre-cooling is very important during the start-up phase. The operation should be slow and the liquid level should be established. Stable, in the beginning, the outlet of the low-temperature heavy hydrocarbon pump should not be automatically controlled, and then it will be automatically switched on after the parameter temperature.

(2) The camp under Inner Mongolia is an area with a large temperature difference between day and night. The ambient temperature directly affects the separation of the mixed refrigerant. Changes in the composition of the mixed refrigerant will cause the temperature in the middle of the cold box to change. Therefore, it is very important to control the refrigerant compressor stage and outlet temperature during operation.

(3) When the content of heavy hydrocarbons in the feed gas is found to increase, the components of the mixed refrigerant should be adjusted immediately, and ethylene should be added

to the refrigerant to lower the temperature in the middle of the cold box, thereby adjusting the separation temperature of heavy hydrocarbons. At the same time, open the flow control valve of the low-temperature heavy hydrocarbon reflux pump. When a heavy hydrocarbon pump cannot meet the requirements, the standby pump should be turned on to adjust the effect of heavy hydrocarbon removal.

4.4.3 Summary of Inner Mongolia LNG Removal of Heavy Hydrocarbon Design

After the LNG plant in Inner Mongolia was put into production, the changes in the composition of the feed gas were continuously observed. Through continuous correction of the reflux temperature for heavy hydrocarbon removal. The device has been running continuously for one year without freezing and blocking of heavy hydrocarbons. HYSYS is used to analyze the simulation of heavy hydrocarbon removal and field data sampling. The error is 0.1%. Therefore, the heavy hydrocarbon removal design in Inner Mongolia is very successful.

4.5 Summary and recommendations

(1) In the initial stage of design and construction of LNG plant, the impact of raw material gas changes on the process and equipment should be fully considered, especially the introduction of foreign process package technology or engineering projects involving foreign engineering companies, such as raw gas quality, raw gas source, water source, etc. In order to fully consider its changing characteristics, to improve the operational adaptability of LNG plant processes and equipment to changes in different factors, and to avoid reduced load operation due to device problems. Before the general project is put into production, the heavy hydrocarbon removal device should be designed according to the feed gas composition, processing load and processing volume requirements.

(2) According to the principle of heavy hydrocarbon removal from natural gas, basic methods such as absorption method, cryogenic separation method and washing method are used to remove heavy hydrocarbons. In actual production, according to different process packages and liquefaction processes, different heavy hydrocarbon removal methods can be selected. According to the content of heavy hydrocarbons in the feed gas, several methods can be combined for removal. Because of the design of the Inner Mongolia LNG plant, for several heavy hydrocarbon removal schemes, the best scheme can be selected through comparative economic advantages, and it is more reasonable to compare scheme two. As long as the heavy hydrocarbon components in the feed gas are selected, the appropriate heavy hydrocarbon removal process can be selected to ensure the accuracy of heavy hydrocarbon removal, solve the problem of freezing and blockage of the cold box, ensure the normal operation of the liquefaction process, and promote the long-term stable operation of the device. Increase the liquefaction rate, increase LNG production, and reduce the specific power consumption of the device.

(3) Scheme 2 heavy hydrocarbon removal is suitable for feed gas with heavy hydrocarbon content of less than 8000ppm in natural gas, and liquefaction plants with a liquefaction scale of less than $100 \times 10^4 \text{ Nm}^3/\text{d}$. Scheme 3 heavy hydrocarbon removal is suitable for natural gas with heavy hydrocarbon content lower

than 8000ppm. The following feed gas is a liquefaction plant with a liquefaction scale greater than $100 \times 10^4 \text{ Nm}^3/\text{d}$. Option 3 is suitable for LNG plants that co-produce LNG and light hydrocarbons, or LNG plants that produce ethane.

5 Conclusion

Natural gas is one of the most clean energy, and its application is more and more in today's increasingly serious environmental problems. In view of the excessive heavy hydrocarbon components, it is easy to cause freezing and blocking in LNG production. We should choose the appropriate heavy hydrocarbon removal process according to the actual production needs, not only to ensure the removal efficiency, but also to ensure the economic benefits of the enterprise, but also to pay attention to the cost savings in production. At present, the natural gas industry is still in the development stage, and there is no perfect natural gas pipeline network. The pit gas is often directly used as the feed gas, and the composition of the gas is relatively fixed. The cryogenic separation process is a good choice. In the process of application of this method, the extraction point is mainly taken from the cold box, which not only reduces the pressure of the cold box, but also reduces the temperature of natural gas to below 50°C . The heavy components in the feed gas will condense. Since the natural gas is still a gas at this time, the impurity components can be effectively separated out by using the gas-liquid separation device, so as to avoid the phenomenon of freezing and blocking in the cold box. In the actual application process, the operation of this method is the most simple. If the component content in the feed gas exceeds 1000 mg/kg , the temperature at the extraction point of the cold box will be lower, and many effective components will be liquefied in advance, which will cause LNG. If there are many aromatic hydrocarbon components such as toluene and benzene in the feed gas, but the content is low, this method can effectively remove the heavy hydrocarbon in the feed gas and avoid the occurrence of freezing and blocking phenomenon. This method has low cost and simple operation in practical application, so it has the widest application range. However, if the content of medium component in feed gas exceeds 1000 mg/kg . If there are more toluene and benzene in the raw material, it will greatly increase the difficulty of heavy hydrocarbon removal, and it is easy to freeze and block.

The freezing and blocking parts of LNG cold box are mainly in the channel of plate heat exchanger, and the frozen plugging materials mainly include water, CO_2 , heavy hydrocarbon which are not removed to normal process indexes in the purification process.

(1) Impact on liquefaction capacity and energy consumption

After the cold box is frozen and blocked, due to the existence of frozen materials in the inner wall of the feed gas channel, heat transfer is seriously affected, and the heat transfer effect of the lower plate heat exchanger becomes worse. After the refrigerant is added, the feed gas treatment capacity cannot be effectively improved, and the refrigeration energy consumption is increased.

(2) Affect system security and stability

When the cold box is frozen and blocked, the refrigerant can't

(3) Affect the safety of equipment operation

5.1 Main conclusion

(1) The freezing and blocking of the cold box of Plant A is mainly because the heavy hydrocarbon components were not fully considered in the project design. Only a heavy hydrocarbon removal tank was installed in the middle of the cold box, and the treatment scale was small. After the equipment was put into production, due to the change in the quality of the raw gas, the cold box heavy hydrocarbons were frozen and blocked when the device was continuously operating at full load. The raw gas components during the freezing and blocking were analyzed, and it was found that the heavy hydrocarbons above C_6 exceeded 70 ppm of natural gas liquefaction requirements.

(3) Heavy hydrocarbon washing and heavy hydrocarbon removal are suitable for feed gas with heavy hydrocarbon content less than 8000ppm in natural gas, liquefaction scale is less than 100×10^4 Nm/d, gas + heavy hydrocarbon washing and heavy hydrocarbon removal is suitable for heavy hydrocarbons in natural gas. For liquefaction plants with a content of less than 8000ppm of the feed gas, the liquefaction scale is greater than 100×10^4 Nm/d, rectification and de-heavy hydrocarbons are suitable for LNG plants that produce LNG and light hydrocarbons, or LNG plants that produce ethane.

(5) When the gas stripping + heavy hydrocarbon scrubbing scheme is adopted, when the gas stripping volume accounts for 15% of the total gas volume, the total content of aromatic hydrocarbons above C₅ and benzene in the gas phase from

(6) When the rectification method is used, when the reflux temperature reaches -75°C , the C_5 content in the rectification tower can be below 10ppm. Energy consumption per unit of liquefaction $0.2864\text{kw}/\text{Nm}^3$.

In recent years, with the rapid development of China's LNG industry, the problems exposed in the production of LNG plants have become increasingly prominent, one of which is freezing and blocking. In the initial stage of design and construction, the influence of feed gas change on process and equipment shall be fully considered, especially for the engineering projects in which foreign process package technology or foreign engineering companies are involved, and the change characteristics shall be fully considered from the input conditions of original data, such as feed gas quality, meteorological data, water source, etc., so as to improve the quality of feed gas, the quality of raw gas, the quality of raw gas, the quality of raw gas, the quality of raw gas, the quality of raw gas, the quality Climate conditions and other factors change the operation adaptability, to avoid the occurrence of plant load reduction operation, repeated plant start-up and shutdown, and even safety production and other issues. At the initial stage of construction, the construction unit, Design Institute, PMC and other participating units shall fully consider the difference of engineering design at home and abroad, and fully demonstrate the possibility of changes in the original data provided, so as to enhance the adaptability of the device process and equipment.

For the deep removal of heavy hydrocarbons in the natural gas liquefaction process, due to the differences in actual projects and liquefaction processes used, there is no general data or sometimes even reference for the operation of low-temperature separation and removal of heavy hydrocarbons. Therefore, for different processes, it is necessary to establish a small skid-mounted module to analyze the heavy hydrocarbon removal process in different situations.

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