Refrigeration Cycles in Low-Temperature Distillation Processes for the Purification of Natural Gas

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Abstract

The increasing energy demand has made low-quality natural gas reserves worthy of consideration for exploitation. As a consequence, industries have developed new process solutions in order to exploit these gas reservoirs in a profitable way. Most of these solutions are natural gas purification processes by distillation at low-temperature, involving or not solid CO_2 formation. Due to the low-temperatures reached in this type of processes, the choice of the appropriate refrigeration cycle becomes of paramount importance for limiting their energy consumptions and, thus, their operating costs. The aim of this work is to compare the performances of different types of refrigeration cycles using the coefficient of performance (COP) as discriminating factor. Several compounds (such as nitrogen, light hydrocarbons and ethylene) and their mixtures have been considered as working fluids and both non-cascade and cascade systems have been taken into account. Simulations by means of Aspen Hysys® V7.3 have led to conclude that the propane-ethylene cascade refrigeration cycle allows to attain the best performances.

Keywords: Refrigeration Cycles, Low-Temperature Processes, Purification, Natural Gas, Coefficient of Performance, Distillation.

1. Introduction

Projections on global energy trends show that the energy demand is expected to grow rapidly in the next twenty years. In this scenario, primary energy consumption is predicted to rise by 41% within 2035, with a great contribution coming from growing emerging economies. Among fossil fuels, natural gas is expected to have the most rapid growth (BP, 2014).

Data reported in open literature prove the existence of many gas resources which are contaminated with significant amounts of hydrogen sulfide and carbon dioxide (Northrop and Valencia, 2009). Therefore, industries have to find technologies that allow the exploitation of these fields in a profitable way.

Low-temperature processes are preferred to traditional chemical or physical absorption for gas purification when the carbon dioxide concentration in natural gas streams is high. Examples of applications of low-temperature gas purification by distillation to the natural gas industry (Fig. 1 a, b, c) are the CFZ^{TM} process (Haut et al., 1989; Parker et al., 2011; Northrop and Valencia, 2009; Valencia and Denton, 1985; Valencia and Victory, 1990; Valencia and Victory, 1993), the Ryan-Holmes process (Holmes et al., 1983; Holmes et al. 1982a,b) and, more recently, a new process based on dual pressure distillation (Pellegrini, 2014; Pellegrini et al., 2015; Langè et al., 2015). Such low-temperature technology can be also applied to biogas upgrading (Pellegrini, 2014) and syngas purification (Berstad et al., 2011; Berstad et al., 2013). In recent years, the interest in low-temperature processes for carbon dioxide removal has increased.

“INSERT FIGURE 1”

In this kind of processes, the refrigeration section is fundamental and attention must be devoted to its design. The system is held at the low temperatures which are characteristic of these processes by means of refrigeration cycles. These cyclical processes employed for refrigeration are typically operated by consuming mechanical or electric power for driving compressor refrigerating machines (Haaf and Henrici, 2003). The performances of a chilling cycle are evaluated in terms of the coefficient of performance (COP), which gives the ratio between the refrigerating effect and the net electrical or mechanical power supplied. Therefore, optimal solutions with high coefficients of performance are mandatory to save energy and reduce operating costs.

Several technologies are available to produce cooling duties and several compounds can be employed as working fluids in refrigeration cycles, either as pure or as mixed refrigerants.

Refrigerants can be either natural (e.g., hydrocarbons, ammonia, carbon dioxide, etc.) or synthetic (e.g., chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons). However, the Montreal Protocol on Substances that Deplete the Ozone Layer has limited the use of synthetic refrigerants for environmental reasons. As a result, natural refrigerants have received a greater attention in the refrigeration industry. The choice of the most appropriate refrigerant is based on the operating conditions. Ethylene, methane, propane and ethane are used as pure fluids in several low-temperature applications, such as LNG production (Zhang and Xu, 2011; Kanoğlu, 2002; Lee et al., 2002) or the cold box section of hydrocarbons steam cracking plants (Fabrega et al., 2010). The most common application of refrigeration cycle for natural gas liquefaction is the *Phillips optimized cascade LNG process*, which consists of a three-loop cascade system that employs three pure refrigerants (typically propane, ethane or ethylene and methane) with different boiling temperatures in each loop. Also, mixed refrigerant can be used for low-temperature applications: mixtures of nitrogen and light hydrocarbons have been studied, for instance, for olefin separation (Mafi et al., 2009) and in several processes for LNG production (Wang et al., 2009).

In this work, different solutions to generate cold at temperatures around 173.15 K have been studied with the aim of defining a good solution for low-temperature upgrading processes of natural gas streams with high CO_2 content. In the open literature, no other works on the assessment of refrigeration technologies for low-temperature distillation, applied to the purification of natural gas, have been found. The work has been focused on the study of different configurations industrially used to generate cold in low-temperature processes, considering working fluids that are typically used in industrial applications for LNG production or air separation units. The studied technologies are mainly the Claude cycle (Barron, 2003), the vapor compression cycle and the cascade refrigeration cycle (Haaf and Henrici, 2003). Cascade refrigeration systems are particularly suitable for industrial applications when the evaporating temperatures are very low. For their application to low-temperature distillation processes, two different systems have been studied. The first one, which integrates the cold product of the distillation column, involves propane in the high-temperature loop and a mixture of methane and ethane, or a mixture of nitrogen, methane and ethane, or pure ethylene in the low-temperature loop. In the second one, propane and ethylene are used in the two circuits with different configurations for both the high and the low temperature loops.

The structure of classical vapor compression and cascade refrigeration cycles has been modified to maximize the COP, which has been chosen as the key parameter for comparing the performances of the analyzed solutions. Nitrogen, methane, ethane, propane and ethylene have been employed as refrigerants, both as single and as mixture fluids. Mixtures of nitrogen and methane, nitrogen and ethane, nitrogen and methane and ethane, methane and ethane have been considered in vapor compression cycles in comparison with propane - ethylene, propane - methane + ethane and propane - nitrogen + methane + ethane cascade cycles. In this work, the chilling cycles have been simulated with Aspen Hysys® V7.3, using the SRK (Soave, 1972) equation of state.

2. Non-cascade refrigeration cycles

The first cycle taken into account in this work is shown in Fig. 2. It is similar to the basic Claude's cycle. Stream *8*, which consists of pure nitrogen, of pure ethylene or of mixtures containing nitrogen + methane, nitrogen + ethane, nitrogen + methane + ethane, methane + ethane, enters the first stage of compression (*K-100*) at a pressure which depends on that of the stream leaving the turbo-expander (which is set to a value equal to that of the stream leaving the condenser) and on the pressure drop in the heat exchanger (0.1 bar). It leaves the compression train at 50 bar. Before entering *Heat Exchanger-1*, the stream is cooled down to 303.15 K. In the heat exchanger stream *1* heats stream *7* up before it enters *K-100*. Stream *2*, whose temperature is adjusted to obtain a minimum approach of 5 K in *Heat Exchanger-1*, is split into two streams which are sent to the turbo-expander (*2a*) and to a second heat exchanger (*2b*). Stream *3* then enters the *JT-valve*, in which it is expanded to 148.15 K. Stream *4* is heated up to 173.15 K (T_5) in the *Column Condenser*. Stream *5* is then mixed with the one which has been expanded in the turbo-expander and the resulting stream is later heated up in two heat-exchangers, before entering the compressor *K-100*. Since the refrigeration cycle is adopted to provide the cooling duty at the condenser of low-temperature distillation processes for natural gas purification, the minimum temperature of stream *4* (148.15 K) has been chosen so that CO_2 freezing conditions are not reached on the process side. By using the CO_2 Freeze-Out utility available in Aspen Hysys® V7.3, with the SRK equation of state as thermodynamic package, it is possible to calculate the freezing conditions for carbon dioxide in mixture with methane. Considering a molar fraction of methane in the range from 0.98 (2 mol% of CO_2 as pipeline quality gas) to 0.9999 (nearly pure methane as for LNG production), the freezing point of CO_2 decreases from 161.77 K to 107.42 K. A reasonable average value, obtained varying the methane molar fraction, is about 143.15 K and, considering 5 K of temperature difference between the two fluids, 148.15 K has been chosen as the temperature of the stream (stream *4*) entering the *Column Condenser*.

"INSERT FIGURE 2"

The coefficient of performance for the refrigeration cycle is usually defined as the ratio of the refrigeration capacity (heat removed from the cold reservoir) to the energy input and it is calculated as (Eq. (1)):

$$COP = \frac{\dot{Q}_c}{\dot{W}_{NET}} = \frac{\dot{Q}_c}{\sum_{i=1}^{n} \dot{W}_{C,i} - \dot{W}_T} \tag{1}$$

where $\dot{Q}_c$ is the thermal power removed from the process (cooling duty), $\dot{W}_T$ is the power output from the turbo-expander, $\dot{W}_C$ is the power required for each compression stage, *i* is referred to the compression stage and *n* is the total number of compressor stages. Each compression stage has an intercooler, where the working fluid is cooled down to 303.15 K.

The outlet pressure, P_n, for the *n*-th compression stage is calculated according to the following expression (Eq. (2)):

$$P_n = P_{n-1} \left(\frac{P_{out}}{P_{in}}\right)^{\frac{1}{n}} + \Delta P_{HE} \tag{2}$$

where $\frac{P_{out}}{P_{in}}$ is the global compression ratio between the inlet and outlet pressure of the fluid in the total compression train and ΔP_{HE} is the pressure drop in the stage intercooler.

The working fluids used for the Claude-type refrigeration cycle have been also employed in the refrigeration cycle shown in Fig. 3. Stream *5* enters the compression train at a pressure which depends on that of the stream leaving the turbo-expander and on the pressure drop the fluid experiences in the heat exchangers (0.1 bar in each heat exchanger). The working fluid is compressed in three intercooled stages, where the pressure after each stage is calculated according to Eq. (2) and the temperature of the working fluid after each cooler of the compression train is 303.15 K. The working fluid is further cooled in the *Regenerator* before being expanded in the turbo-expander to the minimum temperature of the cycle (148.15 K), chosen as previously explained. Hence, it is heated up to 173.15 K in order to provide cold to low-temperature distillation processes. Before being compressed, the working fluid is further heated up in the *Regenerator*.

“INSERT FIGURE 3”

3. The cascade refrigeration cycle integrating the top product from the distillation column

In the first cascade refrigeration cycle, propane is the refrigerant circulating in the high-temperature loop while for, the low-temperature loop, pure ethylene and mixtures containing methane + ethane and nitrogen + methane + ethane have been tested. The composition of the ternary mixture is the one of the mixed refrigerant used in the propane pre-cooled mixed refrigerant (C3MR) process for natural gas liquefaction (Wang et al., 2009) and it is made by 8 mol% nitrogen, 46 mol% methane and 46 mol% ethane.

As shown in Fig. 4, the cold product stream coming from the reflux drum of the low-temperature distillation unit (that can be any of the low-temperature distillation processes quoted in the introduction section) is integrated in the low-temperature loop. In this way, a part of the cooling duty is supplied by the cold product itself and this allows to partially reduce the energy consumptions of the cycle. It has to be pointed out that, in this way, the gas fed to the distillation process cannot be pre-cooled by the distillate top product as it is usually done in accordance with common engineering practices.

The heat exchanger called "*Column Condenser*" is fed with pure methane at 40 bar (which is at about 186.15 K) and a vapor fraction is specified for the outlet stream (*L-V Mixture*) to obtain the desired reflux ratio (the ratio between the molar flows of the streams "*Reflux*" and "*Top Column Vapor*") in the process. The vapor stream leaving the reflux drum is at about 186.15 K (pressure drop in the hot side of *Column Condenser* has been neglected) and can be heated-up in two heat exchangers, *LNG-101* and *LNG-100*, to 298.15 K (temperature of the stream *Hot Distillate*) by the working fluid which is at a higher temperature. When a methane + ethane mixture is used in the low-temperature loop, the ethane content of such mixture is equal to 72 mol%: it has been chosen since it corresponds to the maximum amount of ethane that leads to a pressure equal to the atmospheric one for stream *4* (P_4=1.021 bar). The working fluid is evaporated in the *Column Condenser* and is then heated-up in *LNG-101* by the warmer stream *12* which has previously made propane evaporate in the cascade cooler (*LNG cascade*) and which also heats-up the stream *Cold Distillate* to 233.15 K.

Stream *2* is further heated-up in *LNG-100*, before entering the three-stage compression system from which it exits (stream *10*) at about 27.80 bar. This value is determined by the pressure of stream *10* (provided that a pressure drop of 0.1 bar is specified in the heat exchanger *E-102*), which is calculated so that the temperature of stream *3* is equal to 232.15 K with the mixture of methane and ethane as working fluid, 206.52 K with ethylene and 231 K with the ternary mixture. These temperatures allow to maximize heat recovery in *LNG-101* provided that ΔT_{min} is 5 K. After being compressed, the working fluid is pre-cooled by heating stream *2* and stream *3*, the latter one reaching the desired temperature of 298.15 K as *Hot Distillate*. Afterwards, the working fluid (stream *11*) enters the *LNG cascade*, in which it is further liquefied (stream *12*). It is completely liquefied and cooled down in *LNG-101*, before entering the expansion valve *VLV-100* and then the *Column Condenser*. The temperature of stream *13* is fixed at 188.15 K, which is the minimum compatible with a value of 5 K for the minimum temperature approach in *LNG-101*.

The high-temperature loop is less complex than the low-temperature one: propane is compressed in three stages, it is condensed in the heat exchanger *E-105* and subcooled to 265.71 K in *LNG-102*, where it heats-up the vapor stream leaving the heat exchanger *LNG cascade* before it enters compressor *K-103*. After leaving the heat exchanger *LNG-102*, propane is expanded in valve *VLV-101*.

The molar flow of propane to be used in the high-temperature loop is calculated so that ΔT_{min} in *LNG-100* is 5 K.

“INSERT FIGURE 4”

4. The propane – ethylene cascade refrigeration cycle

To assess the effect of the cold recovery between the process and the refrigeration cycle, the same configuration as the one shown in Fig. 4 has been tested avoiding the recovery of the cold of the product stream *Cold Distillate*. In both the high and low temperature loops, the compression has been performed using three stages and intercoolers. The compressor discharge pressures have been calculated according to Eq. (2), while the temperature of the working fluid at the outlet of each intercooler has been set to 303.15 K.

The cascade system uses propane in the high-temperature loop to cool the ethylene stream down to 243.15 K while ethylene provides the cooling duty at temperatures of 173.15 K in the low-temperature loop.

This choice is due to the better performances obtained with these working fluids when studying the scheme shown in Fig. 4.

The cycle has been simulated using five different configurations. In all of them pressure drops of 0.1 bar have been considered on each side of heat exchangers and the value of the minimum temperature approach for heat exchangers has been fixed to 5 K. The minimum pressure on both the two circuits of the cascade cycle has been set to 1 atm, to avoid vacuum conditions that can cause air intake into the process and can, consequently, bring about safety hazards due to flammability of hydrocarbons-air mixtures. The inlet temperature to the first compressor of each compression train has been fixed to 298.15 K, and the outlet temperature from intercoolers is 303.15 K. The choice of 298.15 K at compression train intake has been made to maximize the cold recovery inside each side of the cycle and to avoid the use of cryogenic compressors. In this way, part of the heat requirements at the condensers (particularly at the ethylene one) are supplied internally by a pre-cooling of the high pressure fluids at 303.15 K at the outlet of compression trains.

The process flow diagram of the first configuration, which is the classical scheme of a cascade refrigeration cycle, is reported in Fig. 5. On the ethylene side, internal heat recovery is present to reduce the dependence on the cooling duty coming from the propane side. *LNG-100* is used to subcool the ethylene stream from its bubble point (stream *11*, 243.15 K at 19.61 bar) to 216.96 K, by using stream *1*, the ethylene vapor at its dew point (173.15 K at 125.2 bar). Moreover, *LNG-101* is used to heat ethylene stream *2* from 238.15 K to 298.15 K before entering the compression train and to pre-cool the high pressure ethylene stream *9* from 303.15 K to 254.38 K. In this way, stream *10* is closer to its dew point and lower duties from the propane side are required. *LNG-103* is the cascade heat exchanger. The propane side is similar to the ethylene one, with the exception that no subcooling is provided to the high pressure liquid propane stream *24* at its bubble point (298.15 K, 9.62 bar). In this way, propane is expanded in the Joule-Thomson valve *VLV-101* as saturated liquid. The highest pressure on the ethylene side is 19.71 bar, while on the propane side it is 9.72 bar, this latter value chosen to have a bubble point sufficiently close to temperature levels where air or service water coming from cooling towers can be used. The compression is performed by means of three intercooled stages to reduce the compression work. The outlet pressure for each compression stage is calculated according to Eq. (2).

“INSERT FIGURE 5”

In the second configuration studied for the propane - ethylene refrigeration system (Fig. 6), the subcooling of liquid propane before expansion has been introduced, by means of a heat exchanger (*LNG-104*) which uses the cold of propane vapor (stream *16*) after the heat exchanger *LNG-102*, in which the liquefaction of the high pressure ethylene stream takes place. In this case, the configurations of both the ethylene and the propane sides are the same (Fig. 6). The assumptions adopted for the simulation are the same as for the first process configuration.

By adding a subcooling of the propane stream before the JT valve, the vapor fraction is decreased from 0.3660 (first process solution) to 0.1545. This allows a better use of the total heat of vaporization of propane at the lower pressure of the cycle. In this way, the total compression work for the propane side decreases and the COP of the cycle increases.

“INSERT FIGURE 6”

In the third scheme (Fig. 7), the configuration of the propane cycle has been modified to improve the performances. The expansion is performed in two stages, with an intermediate flash tank. The liquid is then subcooled and expanded again to the lower pressure, while the vapor produced during the first expansion step is used to cool the propane coming from the condenser and to pre-cool the compressed propane vapor before the condenser. At this point, this stream is mixed with the remaining part of the propane vapor, coming from the propane cycle evaporator, which is preliminary compressed at the same pressure. The entire gas stream is then compressed back.

In this solution, the positive effect on the COP is given by the split of the total propane flow and the subcooling of only the liquid coming from the first expansion valve. The vapor fraction of propane stream after expansion is 0.0642 and so the compression work is reduced.

“INSERT FIGURE 7”

In the fourth scheme, the double expansion solution with an intermediate flash tank has been adopted also for the ethylene side of the cascade (Fig. 8). The effect on the ethylene side is the same observed for the propane side in the third process solution presented in Fig. 7: the COP is increased since the vapor fraction of the ethylene stream after expansion is decreased to 0.0733. The subcooling of the refrigerant before the JT valve is enhanced, and the temperature of the fluid before the expansion valve passes from 217.67 K (third process solution) to 190.36 K.
This effect on both propane and ethylene sides allows to increase the COP of the cycle, with respect to that of the first, second and third process solutions.

“INSERT FIGURE 8”

In the last configuration adopted for the propane - ethylene cascade refrigeration cycle (Fig. 9), the double expansion has been applied only to the ethylene side to determine if the use of a double expansion cycle has a more evident positive effect when adopted in the ethylene circuit rather than in the propane one. Therefore, the propane side is practically the same as that in the second configuration shown in Fig. 6, while the ethylene side is the same as that in the fourth configuration (Fig. 8).

“INSERT FIGURE 9”

5. The propane – ethylene cascade refrigeration cycle

In this section, the results obtained for each of the refrigeration cycles previously described are reported.

5.1 Claude-type refrigeration cycle

As for the Claude-type refrigeration cycle with nitrogen shown in Fig. 2, the value of the coefficient of performance has been determined by varying the split fraction of stream *2a*. Results are reported in Table 1 and Fig. 10. Temperature of streams *2* and *3* have been varied to satisfy the constraint of having 5 K as the minimum temperature approach simultaneously in *Heat Exchanger-1* ($\Delta T_{min,HX1}$) and *Heat Exchanger-2* ($\Delta T_{min,HX2}$). The optimum split fraction is 0.7, which yields to a COP of 0.1699.

“INSERT TABLE 1”

“INSERT FIGURE 10”

When adopting a mixture of nitrogen and methane as refrigerant, the change of the COP has been investigated by varying the split fraction for each composition of the mixture, using the optimum value of the split fraction obtained for the previous considered case as the starting point. The addition of methane enhances the value of the coefficient of performance which results to be maximum when the content of nitrogen is 10 mol% and the split fraction is 0.78. In these conditions the COP is 0.3384. Results are reported in Table 2.

“INSERT TABLE 2”

The trend of the optimal value of COP obtained for the different mixture compositions is shown in Fig. 11.

“INSERT FIGURE 11”

When methane is replaced by ethane in the mixture with nitrogen, attention should be paid to avoid that the inlet stream to the turbine has a fraction of liquid phase. Thus, in this case, the vapor fraction of stream *2* (Fig. 2) is specified (it is set equal to 1) instead of its temperature. Moreover, it should be also checked that stream *4* is obtained at pressures higher or equal to 1 atm at 148.15 K, in order to avoid vacuum conditions in the system. To accomplish that, only the temperature of stream *3* can be varied to have a minimum approach of 5 K in *Heat Exchanger-2*, while the split fraction has been varied to obtain a minimum approach of 5 K in *Heat Exchanger-1*. The COP of the cycle, in this case, is lower than the one obtained when considering nitrogen + methane as working fluid. In order to avoid vacuum conditions in *Column Condenser*, the limit is given by a mixture composed by 50 mol% nitrogen and 50 mol% ethane. The variation of the COP with the composition of the mixture has been studied and is reported in Table 3 and Fig. 12.

“INSERT TABLE 3”

“INSERT FIGURE 12”

When applying the ternary mixture of nitrogen + methane + ethane reported by Wang et al. (2009), the pressure at 148.15 K of stream *4* is under vacuum. The composition has been changed to 10 mol% nitrogen, 80 mol% methane, 10 mol% ethane and 5 mol% nitrogen, 90 mol% methane and 5 mol% ethane, in order to reduce the effect due to the presence of ethane, avoiding the formation of a liquid phase at the inlet of the expander and to operate in the region close to the one corresponding to the optimal value for the COP obtained when using a nitrogen + methane mixture.

An optimal split fraction has been found to be around 0.73 for the ternary mixture having 5 mol% nitrogen, 90 mol% methane and 5 mol% ethane. Results are reported in Table 4.

“INSERT TABLE 4”

The cycle has been also tested by simply considering a binary mixture of methane and ethane, paying attention to the limitations related to the formation of a liquid phase at the expander inlet. For instance, two mixtures have been tested, which contain 90 mol% and 80 mol% methane, respectively. It has been observed that the further addition of ethane decreases the COP of the cycle and favors the formation of the liquid phase in stream *2*. The maximum value of the COP is 0.3517 and is obtained for the mixture having 90 mol% methane. Results are shown in Table 5.

“INSERT TABLE 5”

For the case having 20 mol% ethane, decreasing the split fraction of stream *2a* under 0.65 leads to the formation of a liquid phase at the turbine inlet. With 0.64 as split fraction, the liquid fraction of stream *2* is 0.90 and the COP 0.3099.

When trying to use pure ethylene as working fluid, it is not possible to satisfy the constraints for this cycle since at 148.15 K, the gas phase exists under vacuum conditions.

5.2 Refrigeration cycle with internal regenerator

As far as the vapor refrigeration cycle in Fig. 3 is concerned, the turbo-expander outlet pressure has been changed to understand its effect on the COP, which is calculated according to Eq. (1). The value of the pressure for the outlet stream from the compressor has been adjusted so that the minimum temperature approach in the *Regenerator* is 5 K. As the temperatures across the heat exchanger *E-101* (Fig. 3) have been fixed (148.15 K – 173.15 K), it is possible to notice that, for all the considered refrigerants and their mixtures, the value of the COP increases as the discharge pressure from the compression train increases.

Results obtained for pure nitrogen are reported in Table 6 and shown in Fig. 13.

“INSERT TABLE 6”

“INSERT FIGURE 13”

Results show that the value of the COP increases with the compression ratio and the variation between the first point and the last point is about 5 %. Moreover, the levels of upper and lower pressures of the cycle remain high.

When methane is added to nitrogen in the vapor refrigeration cycle shown in Fig. 3, the composition of the mixture in terms of percentage of methane has been changed to understand its effect on the COP. For each percentage of methane, the pressure of the outlet stream from the expander has been changed and the discharge pressure of the compression train has been adjusted to obtain a minimum approach in the *Regenerator* equal to 5 K. Table 7 summarizes the COP obtained for each composition of the nitrogen-methane mixture that has been taken into account. Results are also reported in Fig. 14.

“INSERT TABLE 7”

“INSERT FIGURE 14”

The mole fraction of methane which maximizes the COP of the refrigeration cycle in Fig. 3 is 30%. The COP (0.3730) is slightly higher than the one obtained with pure nitrogen as the circulating refrigerant, however the compression ratio remains too high. The highest pressure for simulations is the limit condition at which the cycle can work: beyond those values of pressure, the simulator failed to numerically close calculations.

The same vapor refrigeration cycle (Fig. 3) has been studied with a mixture of nitrogen and ethane. Unlike the previous cases, with pure nitrogen and the nitrogen + methane mixture used as refrigerants, here the vapor fraction (equal to 1) instead of the temperature of stream *3* has been specified in order to avoid the presence of a liquid phase into the stream entering the turbo-expander. As in the case of the nitrogen + methane mixture, for each percentage of ethane the pressure of the expander outlet stream (P_4) has been changed, while the pressure at the outlet of the compression train (P_{10}) has been adjusted in order to guarantee that the minimum approach in the *Regenerator* is equal to 5 K. The variation of the value of the COP has been studied and results are reported in Table 8.

“INSERT TABLE 8”

Contrary to the previous considered cycle, the COP increases as the ethane molar fraction increases, however its value remains lower than the one obtained when the nitrogen + methane is used as refrigerant in the cycle shown in Fig. 3. The variation of the COP with the turbine discharge pressure is better illustrated in Fig. 15.

“INSERT FIGURE 15”

It is possible to notice that the trend of the COP variation with pressure is strongly dependent on the composition. This can be due to the fact that, in comparison with the previous cases, when adding ethane to nitrogen the vapor fraction equal to 1 has been assigned to the turbine inlet, and the minimum temperature of the cycle has not been fixed (148.15 K). In this case, the minimum

temperature changes after expansion and remains at acceptable values for the heat exchange in *E-101* (Fig. 3).
Ternary mixtures containing nitrogen + methane + ethane have been adopted also for the cycle configuration reported in Fig. 3. Since the cycle does not work for mixture compositions rich in methane, in this case higher values of the nitrogen molar fraction in the mixture have been used. Particularly, two mixtures have been considered keeping the ratio between methane and ethane constant. Also in this case the vapor fraction of the inlet stream to the turbo-expander has been fixed to 1 to avoid the formation of a liquid phase at turbine inlet. Results are shown in Table 9.

"INSERT TABLE 9"

Mixtures richer in nitrogen allow to obtain higher values of the COP. The maximum value for the COP is 0.3691 and its value remains lower than the ones obtained with the nitrogen + methane mixture. Temperatures at turbine outlet remain acceptable and higher than the minimum considered. An increase of the hydrocarbon fraction in the ternary mixture leads to a decrease of the COP, but it allows to reduce the maximum pressure of the cycle.
For the same configuration, mixtures of methane + ethane have been considered. In order to simulate the cycle using this mixture, it has been necessary to specify both the vapor fraction equal to 1 and the temperature of 173.15 K for stream *4* in order to assure that the turbine inlet is in the gas phase. The minimum temperature of the cycle is fixed at 148.15 K. Due to the presence of ethane it is not possible to vary the mixture composition in all the range of molar fractions, because, when the ethane molar fraction is 0.3, the turbine inlet is totally in liquid phase despite the used constraints.
Results for this solution are reported in Table 10.

"INSERT TABLE 10"

The maximum value of the COP is obtained with a mixture containing 25 mol% ethane and its value is 0.3891. This value is comparable with the ones obtained using nitrogen + methane mixtures as working fluids, but, for the case of the methane + ethane mixture, the maximum pressure of the cycle remains lower.
It is not possible to use ethylene as refrigerant in this cycle configuration (Fig. 3), due to its normal boiling point of about 169.5 K, higher than the minimum operating temperature of this cycle.

5.3 Cascade refrigeration system with cold recovery from process product stream

From the simulations performed for the cascade refrigeration system shown in Fig. 4 that uses propane and a mixture of methane and ethane, the COP is 0.8211. As already stated before, the mixture comprising methane and ethane contains 72 mol% ethane, since this is the maximum amount of ethane compatible with a pressure equal to the atmospheric one for stream *4*. Indeed, if the mole fraction of ethane is lowered to 70 mol%, the COP decreases to 0.8097, whereas the pressure for stream *4* increases to 1.053 bar. On the contrary, if the mole fraction of ethane is increased from 72 mol% to 74 mol%, the COP increases to 0.8327 but the pressure for stream 4 becomes lower than the atmospheric one (i.e., 0.991 bar). If the ethane content is decreased to 68 mol%, the COP decreases to 0.7985 and the pressure of stream *4* increases to 1.087 bar. Any further decrease of the ethane content favors the increase of the pressure of stream *4*, since the mixture becomes richer in methane (the lighter compound), but it lowers the COP of the refrigeration cycle, introducing the necessity of strong modifications to the adopted low-temperature loop of the cascade system.

When considering the ternary mixture containing nitrogen, methane and ethane the obtained value of the COP is 0.6171 and is lower than the one obtained using the methane + ethane mixture. When using ethylene in the low-temperature loop, the COP increases to 0.9749. When adopting the ternary mixture or ethylene, the pressure of stream *4* increases to 1.66 bar and 1.78 bar, respectively. The maximum pressure of the low-temperature loop of the cycle increases from 27.8 bar when using the methane + ethane mixture, to 69.6 bar with the ternary mixture of nitrogen + methane + ethane and to 30 bar when using ethylene.

When the cold of the product stream coming from the reflux drum is not used inside the refrigeration cycle, the value of COP reduces to 0.5750 when the working fluid is the methane + ethane mixture, 0.4259 when the ternary mixture of nitrogen + methane + ethane is used and 0.7728 when the working fluid is ethylene. The pressure changes to 36 bar when the working fluid is the methane + ethane, to 90 bar when the ternary mixture of nitrogen + methane + ethane is used in the low-temperature loop and to 18.8 bar when ethylene is the refrigerant for the low-temperature loop of the cascade cycle.

Generally, the integration of the process product stream into the refrigeration cycle gives advantages to the COP, but the feed to cryogenic distillation columns should then be pre-cooled by another refrigeration cycle.

This analysis allows to conclude that the most promising fluid for the low temperature loop seems to be ethylene.

5.4 Propane - ethylene cascade refrigeration cycle

Since from the previous case ethylene has resulted to be the most performing refrigerant for the cascade refrigeration system, it has been employed with different refrigeration cycle configurations.

The comparison of the five process configurations for the propane - ethylene cycle has been performed on the basis of their COP, calculated according to Eq. (1). Results are reported in Table 11.

“INSERT TABLE 11”

The introduction of the subcooling of liquid propane before its expansion in the second solution leads to an effective increase of the COP if compared with the one of the first solution. Moreover, the introduction of the double expansion only on the propane side allows to increase the COP, although not significantly. A better result is obtained when considering the fifth configuration, where the double expansion is adopted on the ethylene side, but an effective improvement is obtained only with the introduction of the double expansion with intermediate flash tank on both the ethylene and the propane sides (fourth process configuration). In terms of COP, the fourth process solution seems to be the most promising one among the five studied configurations for the propane - ethylene cycle. The fifth process solution can be competitive as well, since its COP is similar to the one of the fourth solution and the configuration is simpler. Furthermore, it has to be noticed that the adoption of a double expansion cycle on the ethylene side has a more positive effect on the COP than the adoption of the same solution for the propane side only.

6. Discussion

Different solutions have been studied to provide cooling duty to low-temperature processes for the purification of natural gas by distillation at temperatures of about 173.15 K. Non-cascade refrigeration cycles with nitrogen and mixtures of nitrogen + methane, nitrogen + ethane, nitrogen + methane + ethane and methane + ethane do not reach high performances in terms of COP, with higher values around 0.37 – 0.39 and high pressures required.

Regarding cascade refrigeration systems, the first proposed solution that uses the top cold distillate product has a high COP (around 0.8 – 0.9), but it does not allow to use the cold vapor stream coming from the reflux drum of the distillation column to pre-cool the process gas feed. Moreover, the integration of the refrigeration system with the process can result in difficulties regarding the control and the operability of the process. In this way, the most suitable solution is the propane - ethylene cascade system: it allows to reach a value for the COP that is around 0.67, it is decoupled from process streams and so it is more flexible and can guarantee a better control of the process. Industrially, this solution is used for LNG production (Kanoğlu, 2002).

7. Conclusion

Projections on the growth of the global energy demand show a significant increase in the next twenty years, with a key-role played by natural gas. Many natural gas resources not yet exploited are estimated to be sour and/or with high carbon dioxide contents. In this scenario, industries are developing new process solutions to allow the profitable exploitation of this kind of low-quality gas reserves, in order to meet the market demand while satisfying the requested purity for the produced gas. Low-temperature purification technologies are of interest when CO_2 concentrations in the raw natural gas are high. Refrigeration cycles play a significant role in the development of such a kind of process solutions, since their performances affect the energy costs of these purification processes. In this work, refrigeration cycles like the Claude-type, gas compression/expansion, integrated and non-integrated cascade systems with or without double expansions have been considered for comparison. Nitrogen, methane, ethane and their mixtures have been applied to non-cascade cycles and propane – methane + ethane, propane – nitrogen + methane + ethane or propane - ethylene cascade cycles have been studied for cascade refrigeration systems. Working fluids have been selected based on their possible on-field availability or their potential industrial applications to industrial processes (air separation units and LNG production). The cycles have been studied using a commercial process simulation software and their performances compared on the basis of their COP. Cascade refrigeration cycles have turned out to have higher performances compared to non-cascade systems.

Abbreviations

BP	British Petroleum
C	Column
COP	Coefficient of Performance
CFZ	Controlled Freeze Zone
E	Heat Exchanger
HX	Heat Exchanger when referred to minimum temperature approach
JT	Joule-Thomson
K	Compressor
in	Inlet
LNG	Liquefied Natural Gas or Heat Exchanger (if followed by a number)
n	Compression Stages
out	Outlet
P, P_j	Pressure, pressure of stream j

$\dot{Q}_c$	Cooling Duty
SRK	Soave-Redlich-Kwong
T, T_j	Temperature, temperature of stream j
VLV	Valve
$\dot{W}_{NET}$	Net Power Input
$\dot{W}_C$	Compression Power Input
$\dot{W}_T$	Expander Power Output
ΔT_{min}	Minimum Temperature Approach
ΔP_{HE}	Pressure Drop across a Heat Exchanger
mol%	Molar Composition Percent

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