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Mathematical Method and Thermodynamic Approaches to Design Multi-Component Refrigeration Used in Cryogenic Process
Part I: Optimal Operating Conditions

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Abstract: Minimizing the work consumed in refrigeration system is the most effective measure to reduce the cost of products in sub-ambient chemical processes. The introduction of mixed working fluids into refrigeration system in place of pure working fluids is a recent advancement applied in the field. Due to the lack of systematic design method for Mixed Refrigerant Cycle (MRC), conventional approaches are largely trial-and-error, and therefore, operations might be far away from Optimal operating conditions. In this paper, a novel method for systematic design of MRCs with a given configuration is presented. It combines the benefits of thermodynamics approach and mathematical optimization. An ethylene process was chosen as a typical example of low temperature process. The simulation results show that MRCs can improve the thermodynamic performance of refrigeration system in the case of using Optimal operating conditions and also proper arrangement of the cycle components (cycle configuration).

Keywords: Mixed Refrigerant Cycle, Low Temperature Process, Optimal Operating Conditions

1. Introduction

For many years, cascade refrigeration cycles have been used to cool and liquefy feed streams in sub-ambient processes such as olefin (ethylene recovery) plants. Such cascade cycles have commonly included a plurality of individual refrigerants having decreasing atmospheric boiling points each of which is circulated in a closed cycle to heat exchange with the feed streams. Unfortunately, the use of such individual refrigerants requires a very large number of separate heat exchangers, pumps, compressors and associated piping and valving for the separate closed loops of each state. Even more importantly, the cooling curves of individual refrigerants do not closely match the continuous cooling curve of the feed stream, and this is of particular importance with respect to the low temperature end of the

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cascade system wherein very substantial amount of power are wasted by this inherent inefficieny in such cascade systems (Gaumer Jr & Newton, 1973).

Minimizing the work consumed in the refrigeration cycle is the most effective measure to reduce the cost of products of sub-ambient chemical processes. A recent advancement has been the introduction of mixed working fluids in refrigeration systems in place of pure working fluids. This refrigeration method with multi-component mixture has demonstrated high performance in the low temperature ranges (Maoqiong Gong, Wu, Luo, Qi, & Zhou, 2004).

The concept of using a mixture as refrigerant has been around for a long time. The mixed refrigerant cycle was patented by Podbeilniak (Podbielniak, 1936) that utilizes three stages of throttling and a single compressor in a close cycle. Thereafter, several MRCs have been patented during the past years on gases liquefaction and separation applications (Becdelievre, Kaiser, & Paradowski, 1978; Gaumer Jr & Newton, 1973; Howard & Rowles, 1995; Kleemenko, 1959; Wei, 2001). Also, many investigations are available in the open literatures on the performance of MRCs in different low temperature applications (Alexeev, Thiel, Haberstroh, & Quack, 2000; Cao, Lu, Lin, & Gu, 2006; MQ Gong, Wu, & Luo, 2004; Maoqiong Gong et al., 2004; Remeljej & Hoadley, 2006).

Nowadays, the MRC is widely used in the commercial natural gas liquefaction fields where liquefaction capacities are very large (Cao et al., 2006; Remeljej & Hoadley, 2006). The simplification of the compression and heat exchange processes in such a cycle may offer potential for reduced capital expenditure in comparison with the conventional cascade cycle.

Generally, the MRCs offer many benefits such as a low compression ratio and relatively high volumetric efficiency. However, system chemistry and heat exchangers. are complex, refrigerant compositions are sensitive, and compressor displacement is large.

Usually, a mixture of hydrocarbons and nitrogen is used in sub-ambient chemical process industries to provide desired refrigerant characteristics for specific refrigeration demand. The most common hydrocarbon refrigerants are propane, propylene, ethane, ethylene and methane. They are used in many cases where the process streams involve them as constituents. Therefore, besides the above mentioned benefits for MRCs, one advantage of these cycles is the use of natural fluids which, unlike the CFCs, HFCs and their mixtures, are environment friendly.

In sub-ambient processes, the design of refrigeration systems is the major concern for energy consumption and capital investment. The synthesis and optimization of MRCs for low temperature processes are complex due to the large number of design options. In the design of mixed refrigeration system for chemical processes, the main key issues are composition of mixed refrigerant, operating pressures (suction and discharge pressure of compressors), and heat integration between refrigeration system and process streams to achieve close matching of the hot and cold composite curves.

The previous research works do not concentrate on the MRCs used in complex low temperature chemical processes such as olefin plants. In this paper, the operation of conventional cascade refrigeration system of a typical olefin plant (as an example of low temperature processes) is described first. Then, two sets of low temperature MRCs are developed to replace the pure ethylene cycle of the conventional cascade refrigeration. A methodology with graphical and numerical tools is developed in this study. It makes it possible to analyze and optimize the operating conditions of MRCs with a given configuration.

The objective of this investigation is to provide improvements through mixed working fluids in place of pure working fluid in cryogenic section of low temperature processes with a view of decreasing the power consumption for providing the same refrigeration duty.

2. Low Temperature MultiStage Cascade Refrigeration System of Olefin Plants

In the current paper, we concentrate on MRC design for complex low temperature chemical processes. As a typical example of low temperature process, an ethylene process (olefin plant) was chosen. In an ethylene recovery process, a feed gas comprising hydrogen, methane, ethane, ethylene, propane, propylene, and minor amounts of other light components is compressed, cooled, and partially condensed in single stage condensers or alternatively in one or more dephlegmators which impart several stages of separation during the condensation step. The condensate is separated from lighter gases and is passed to one or more demethanizer columns which recover a light gas overhead comprising chiefly methane and hydrogen, and a bottoms stream rich in C2 and C3 hydrocarbons. This hydrocarbon stream is further fractionated to yield a high purity ethylene product, an ethane-rich byproduct, and a stream of C3 and heavier hydrocarbons.

Essentially, all olefin plants use an ethylene-propylene cascade refrigeration system to provide the major portion of refrigeration required in the olefin plant. Most of the propylene (high level) refrigeration is utilized at several pressure/temperature levels in the initial feed precooling and fractionation sections of the plant to cool the feed from ambient temperature to about -35°C and to condense the ethylene refrigerant at about -30°C. Similarly, the ethylene (low level) refrigeration is utilized at several pressure/temperature levels in the cryogenic section of the plant for two following aims: first, to cool the feed from -35°C to about -100°C in order to condense the bulk of the ethylene in the form of liquid feeds to a demethanizer column and second, to condense the demethanizer column overhead at about -101°C to provide reflux to that column. Refrigeration below -101°C, to condense the remaining ethylene from the feed, is provided primarily by work of expansion or Joule-Thomson expansion of rejected light gases, H2 and methane, and/or by vaporization of methane refrigerant which has been condensed by the ethylene refrigerant. The work of expansion or Joule-Thomson expanded gases are normally used as fuel and consist primarily of the overhead vapor from the demethanizer column, mostly methane, and any uncondensed feed gas, mostly H2 and methane, which is not processed in the H2 recovery section of the olefin plant (Gaumer Jr & Newton, 1973).

The cascade refrigeration system of olefin plant analyzed in this study consists of ambient cooling water at near ambient temperature, closed cycle propylene and ethylene systems. Refrigeration below -101°C is provided by Joule-Thomson expansion of rejected light gases from the demethanizer column overhead vapour and uncondensed feed gas in the H_2 recovery section of the plant. Propylene refrigeration is utilized at several temperature levels (+5, -20 and -35°C) to cool and heat the feed in the initial fractionation sections of the plant. Similarly, the ethylene refrigeration is utilized at several temperature levels (-65 and -101°C) to cool the feed in the cryogenic section of the plant. Detailed description of the ethylene-propylene cascade refrigeration system has been presented in our previous work (Mafi, Naeynian, & Amidpour, 2009).

Figure 1 shows the flow diagram of ethylene refrigeration cycle (Mafi, Amidpour, & Mousavi Naeynian, 2009). Figure 2 shows the refrigeration system matched against the GCC (Grand Composite Curve) of the olefin plant separation process analyzed in this work (Mafi et al., 2009). Table 1 gives the corresponding refrigeration system details including three propylene levels (P1, P2 and P3) and two ethylene levels (E1 and E2) (Mafi et al., 2009). It shall be noted that the values given in Figures 1 and 2 and also Table 1 are extracted from an existing olefin plant (Tabriz Petrochemical Complex).

Sometimes, the refrigeration levels shall be fitted against a nearly flat portion of the GCC (e.g. propylene refrigeration levels in Figure 2). In this case, the pure refrigerants and azeotropic mixtures are the best options because of isothermal vaporization in the evaporators. Sometimes, the refrigerant level needs to be fitted against a sloping of the GCC as ethylene refrigeration levels shown in Figure 2. In this case, there is a degree of freedom to choose the level of the refrigeration (Smith, 2005). For example, the GCC of the separation process analyzed in this work shows that having multiple stage evaporations for ethylene refrigeration cycle makes the average temperature difference between process streams and the refrigerant small. This results in smaller exergy destruction in the E-308 and E-305 evaporators since the greater the temperature difference, the greater the exergy destruction. As the number of evaporation stages increases, the exergy destruction decreases. However, adding more stages means additional equipment cost and more than two stages for ethylene cycle in olefin plants is not justified (Lee, 2001, p. 123).

Table 1. Refrigeration levels details (Mafi et al., 2009)

Refrigeration level	Temperature (°C)	Refrigeration Load (MW)
P1	+5	3.37
P2	-20	1.88
P3	-35	11.20
E1	-65	0.32
E2	-101	0.77

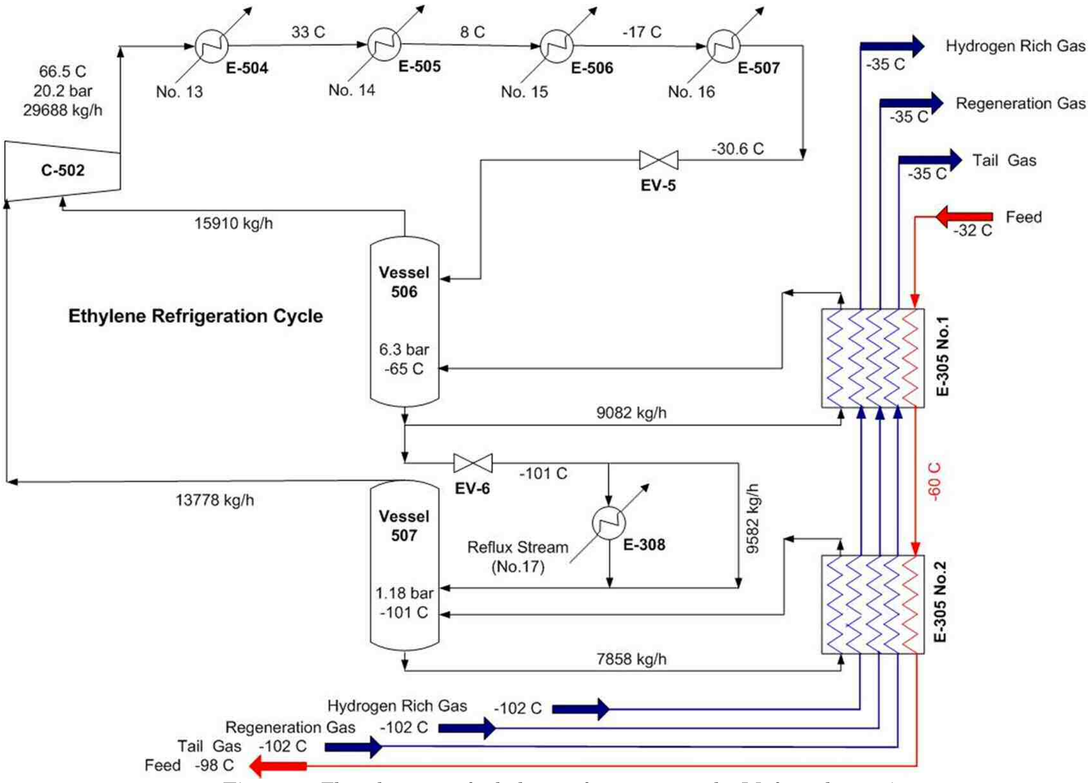

Figure 1. Flow diagram of ethylene refrigeration cycle (Mafi et al., 2009).

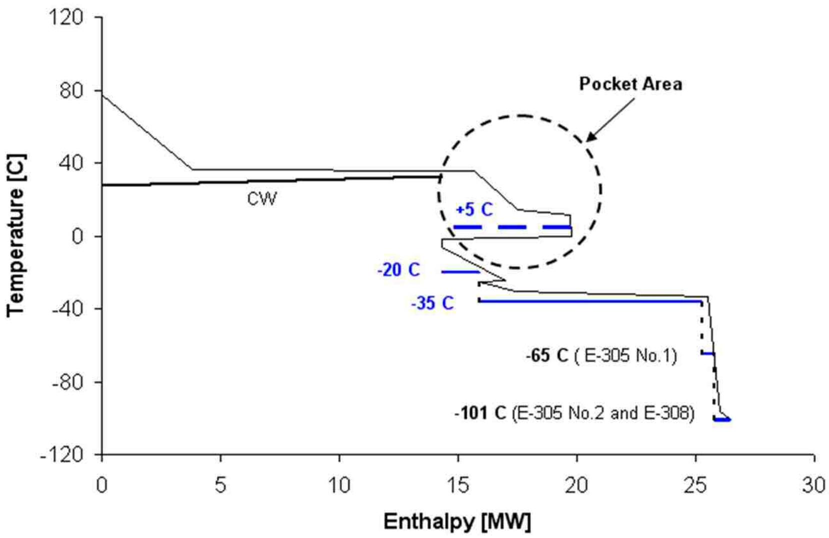

Figure 2. GCC of the refrigeration system analyzed in this work (Mafi et al., 2009).

3. Developing MRCS for Providing Low Level Refrigeration

Going from the two-stage evaporation (including -65°C and -101°C levels) in the ethylene cycle as shown in Figure 2 to a multiple-stage one saves power with additional level of complexity because of the restricted working range over which it can operate. The working range of refrigerant fluids can be extended and modified by using a mixture rather than a pure component.

MRC uses a mixture as refrigerant instead of a pure refrigerant. Unlike pure refrigerants, the temperature and vapour and liquid composition of non-azeotropic mixtures do not remain constant at constant pressure as the refrigerants evaporate or condense. The composition of the mixture can be selected in a way that the liquid refrigerant evaporates over a temperature range similar to that of the process cooling demand to provide the desired refrigerant characteristics (e.g. close matching of the hot and cold composite curves, with small temperature driving forces over the whole temperature range). Small temperature driving force leads to near-reversible operation, thus better thermodynamic efficiency, and lower power requirement. Also, a MRC features a simpler machinery configuration (complexity) in comparison with a pure refrigerant multiple stage cycle (Smith, 2005).

Two MRCs on the basis of the characteristics of olefin plant cryogenic section that is particularly well-suited to provide low level refrigeration (below -35°C) are developed and investigated in this paper. Figure 3 and 4 show two-flow diagrams of MRCs (A and B configurations) developed in this section for providing low level refrigeration in place of pure ethylene refrigeration cycle shown in Figure 2.The flow diagrams for these cycles have been patented in the United States by Becdelievre et al. (1978) and Howard & Rowles (1995). (Becdelievre et al., 1978; Howard & Rowles, 1995) The values given in these flow diagrams have been adjusted based on the existing olefin plant conditions and overall power saving. It shall be noted that there is no change in propylene refrigeration cycle. Thus, it remains the same for both MRCs. Details of these cycles have been presented in our previous work (Mafi et al., 2009).

4. Thermophysical Properties of Mixed Refrigerant

In this paper, a mixture of hydrocarbons (propane, ethane, methane) and nitrogen is used to provide desired refrigerant characteristics for specific refrigeration demand in the MRCs. The difficulties in the design of MRC come mainly from two sources. First, the complex nature of the thermodynamic and physical properties of mixtures makes consumption of MRCs expensive and highly non-linear. Second, the small temperature approach between the hot and cold composite curves in multi-stream heat exchangers (the profiles of evaporation and condensation) and the wide temperature range make MRCs extremely sensetive to the change of operating conditions. These not only increase the difficulty of the modelling for the problem, but also add to the non-linearity when carrying out optimization (Lee, 2001, p. 83). Therefore, the accurate prediction of phase equilibrium for vapour-liquid ratios and values of enthalpy and entropy is essential for the mixtures.

4.1. Vapour-Liquid Equilibrium Calculations

In general, any equation of state which provides reliable volumetric data over the full range of the above integral can be used to describe the fluid phase behaviour. The simplest and highly successful equation is the semi-empirical two-parameter cubic equation such as the Peng-Robinson and Soave-Redlich-Kwong equations (Danesh, 1998). In the present work, the Peng-Robinson equation of state has been used in the calculation of phase equilibrium.

4.2. Thermodynamic Properties Calculation

The Lee-Kesler equation of state is an accurate general method for the prediction of thermodynamic properties of non-polar mixtures ((Reid, Prausnitz, & Poling, 1987). In this work, the mixed refrigerant consists of methane, ethane, propane and nitrogen. Therefore, the Lee-Kesler equation of state has been used in the calculation of the enthalpy and entropy of mixed refrigerant.

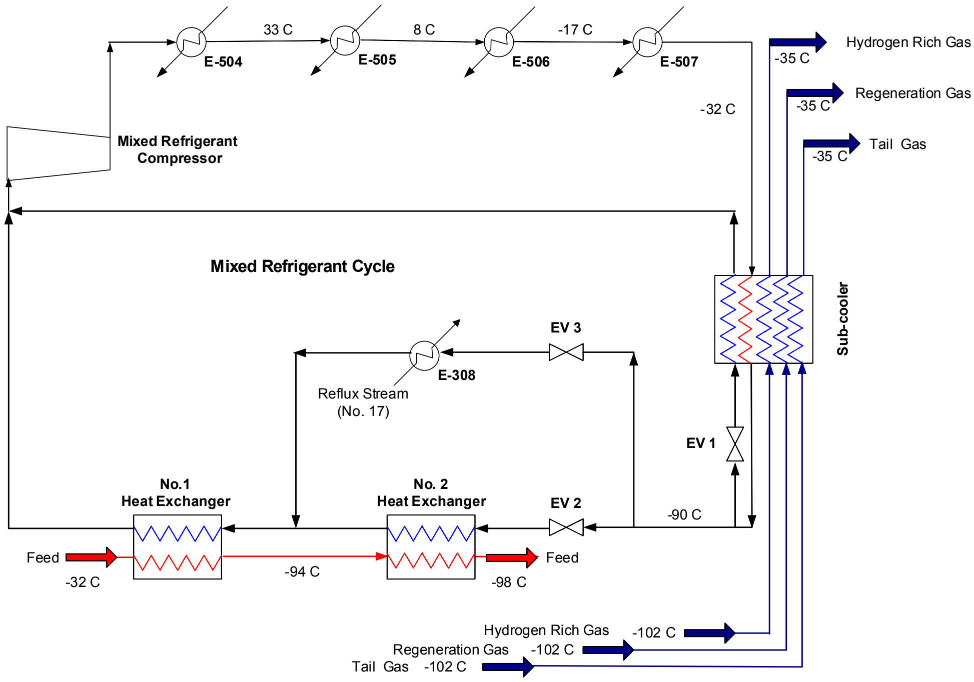

Figure 3. Mixed refrigerant cycle (Configuration A) (Mafi et al., 2009).

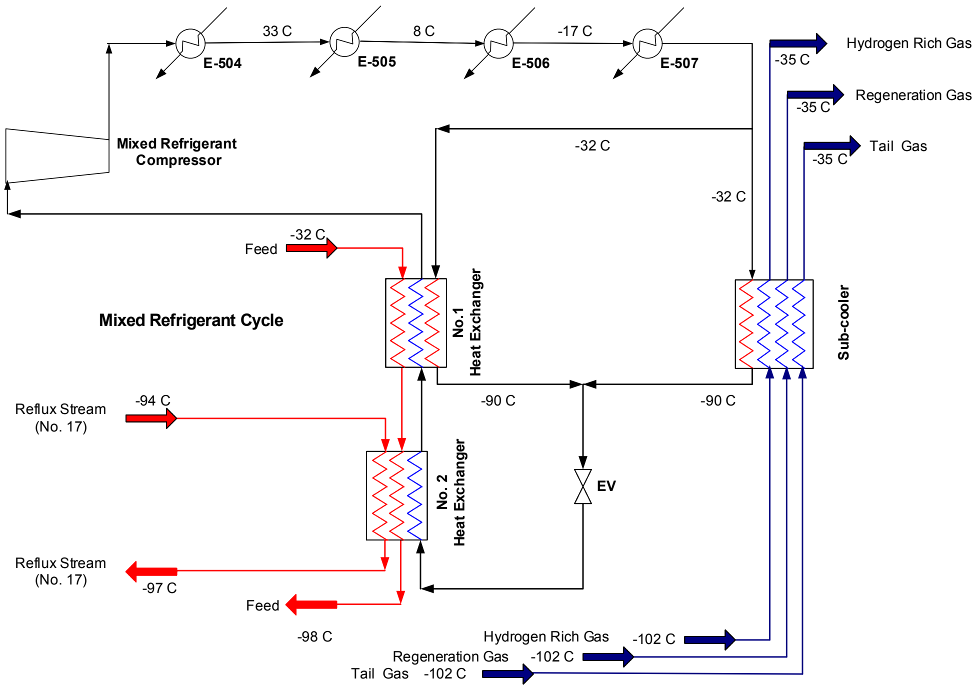

Figure 4. Mixed refrigerant cycle (Configuration B) (Mafi et al., 2009).

5. Optimization Algorithm

Many factors influence the performance of a certain MRC; for instance, operating pressures of the cycle (suction and discharge pressures of cycle compressor), temperature of the refrigerant before expansion, and mole fraction of mixed refrigerant components such as nitrogen, methane, ethane, propane, etc. In this work, the optimization problem lies in the determination of the optimum parameter values that minimize the power consumption. The objective function is:

$$min \quad f(x_1, x_2, \ldots, x_n) = W \qquad (1)$$

where W is the power consumption of mixed refrigerant compressor and xi denotes operating parameters such as composition of refrigerant, suction and discharger pressures of compressor, etc. In fact, it is necessary to take into account all factors such as initial cost, power consumption, plant area, simplicity of the process, etc., but many of these factors are not purely technical. In this paper, only power consumption is considered as the optimization objective. The constraints are as follows:

- The sum of the mole fractions of the mixed refrigerant is 1.
- The temperature of the mixed refrigerant at the compressor inlet is higher than its dew point.
- The temperature difference between the hot and cold streams cannot be negative.

In this section, we have proposed a systematic design method to find the optimum values of operating pressures and refrigerant composition which minimize the power consumption of MRC with a given configuration. The basic idea is to find a set of refrigerant compositions that give the minimum power consumption under given pressure levels (high and low operating pressures of MRCs) and remove all above mentioned constraints. Then, the pressure levels of MRC are changed in limited ranges defined by user and the procedure of finding the best refrigerant composition is repeated iteratively. Figure 5 explains the methodology.

As seen in Figure 5, to arrive at the best solution and avoid being trapped in local optima, a two-phase hybrid method has been developed. The first phase is explorative, employing an Enumerative method to identify promising areas of the search space. The best solution found by the Enumerative method is then refined using a Pattern Search method during a subsequent exploitative phase. We selected hybridization of global and local search algorithms to produce high quality optimal solution, although computational time is relatively expensive.

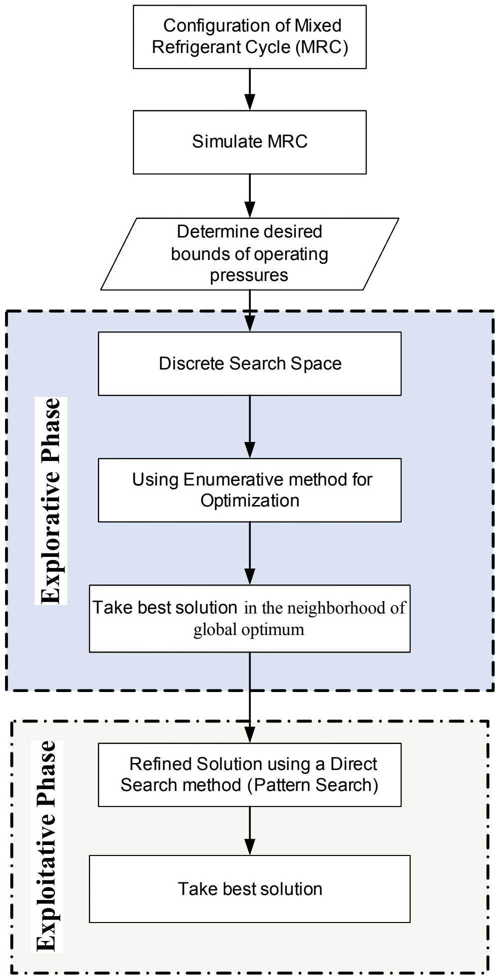

Figure 5. Proposed systematic design method for optimal selection of refrigerant composition and operating pressures of MRC with a given configuration

It should be mentioned that one of important features in the proposed method is to ensure heat integration between refrigeration system and process streams. It is guaranteed by combining the cold process streams (hydrogen rich gas, tail gas and regeneration gas streams in this study) and cold refrigerant streams as a cold composite curve and also combining the hot process streams (feed and reflux streams in this study) and warm refrigerant as a hot composite curve.

6. Simulation Results and Discussions

The mixed refrigerant cycles have been simulated at steady-state condition. Simulation results have been obtained based on 75% isentropic efficiency for the compressors. Error! Reference source not found. obtains the solution found by the enumerative method to arrive at the best solution in the neighborhood of global optimum. Table 3 obtains the refined solution using the direct search method which minimizes the power consumption of MRCs shown in Figure 3 and Figure 4.

As seen in Figure 1, Figure 3 and Figure 4, it is obvious that the condensers of pure ethylene and MRCs are affected by the propylene evaporators including E-505, E-506 and E-507. These evaporators extract towards the outside a major portion of the heat wasted by ethylene cycle and MRC condensers. This leads to the need of providing a large refrigerating circuit working with propylene which requires a large compressor power consumption. Table and 5 present the key parameters of pure-ethylene cycle and two optimized MRCs based on the systematic design method explained in the previous section.

It can be inferred from this table that configuration B behaves in a more thermodynamically favorable manner than pure-ethylene cycle, thereby making it possible to achieve substantial power saving for providing the same refrigeration duty. The shaft work of configuration B is calculated to be 1489 kW which is 175 kW lower than that required by pure ethylene refrigeration cycle.

7. Conclusion

In this paper, a systematic design method for optimal selection of refrigerant composition and operating pressures of MRC with a given configuration was presented. Also, two MRCs were developed and optimized for a typical olefin plant using the systematic design method. The results show that MRCs can improve the thermodynamic performance of refrigeration system in the case of using optimal mixture composition, optimal high and low operating pressure and also proper arrangement of the cycle components (cycle configuration).

Table 2. The best solution of MRCs shown in Figure 3 and Figure 4 using enumerative method

Configuration	Pmin (kPa)	Pmax (kPa)	Propane (mol%)	Ethane (mol%)	Methane (mol%)	Nitrogen (mol%)
A	180	1450	32	35	32	1
B	200	1250	36	34	29	1

Table 3. Optimal operating conditions fo MRCs shown Figure 3 and Figure 4 using pattern search method

Configuration	Pmin (kPa)	Pmax (kPa)	Propane (mol%)	Ethane (mol%)	Methane (mol%)	Nitrogen (mol%)
A	180	1450	32.30	35.19	32.50	0.01
B	200	1250	36.72	33.85	28.77	0.66

Table 4. Comparison between the compressors power consumption of pure ethylene and optimized MRCS

Type of cycle	Power Consumption of cycle compressor(kW)	Power Consumption of Propylene cycle compressor (kW)
Pure ethylene	1664	5299
Configuration A	1843	4089
Configuration B	1489	4118

Table 5. Comparison between the key parameters of pure ethylene and optimized MRCs

Type of cycle	Pmax (kPa)	Pmin (kPa)	Total power Consumption (kW)
Pure ethylene	2020	108	6963
Configuration A	1450	180	5932
Configuration B	1250	200	5607

Nomenclature

MRC	mixed refrigerant cycle
ECC	exergy composite curve
GCC	grand composite curve
Pmin	low operating pressure of refrigeration cycle
Pmax	high operating pressure of refrigeration cycle

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