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Low Temperature Refrigeration Utilizing Zeotropic Mixtures

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LOW TEMPERATURE REFRIGRATION
UTILIZING ZEOTROPIC MIXTURES

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ABSTRACT

The utilization of non-flammable, fluorine substituted mixtures for distributed refrigeration applications is of increasing commercial interest. System designs, which accommodate fluorine-based refrigerants face engineering challenges that are atypical of hydrocarbon based systems. A process has been developed which is tailored to the demands associated with the quick freezing of food and pharmaceutical applications. The refrigeration system has been designed to interface directly with a cryogenic tunnel freezer within the context of a large processing facility.

A design methodology has been employed which focuses upon integrated system development and low cost compression. A dual circuit mixed gas refrigeration system has been developed which sequences the refrigerant dew and bubble point thereby minimizing total cycle power. A methodology for component selection has been developed which averts cold-end freezing and two-phase flow. The process has been shown to be competitive with other low temperature refrigeration alternatives such as direct-cryogen application.

1. INTRODUCTION

Mixed Gas Refrigeration (MGR) technology offers a means for attaining high refrigeration/liquefaction efficiency and cryogenic, cold-end temperatures. These facts have led to the popularity of MGR application for natural gas liquefaction. Unfortunately, the adaptation of large scale MGR technology toward applications other than hydrocarbon liquefaction has been met with significantly more resistance. In natural gas MGR liquefaction processes, hydrocarbon mixtures are utilized as refrigerants (Lee, 2000). Since the fluid to be liquefied is also a hydrocarbon mixture, introducing the MGR system does not substantially alter overall safety considerations. The objective of this work is to address issues pertinent to the development of cost effective MGR systems suitable for applications related to pharmaceuticals and the quick-freezing of food. More particularly, the objective of this study is to develop a MGR system, which relies upon non-flammable (Richard, 1992), environmentally acceptable refrigerants.

There are four major considerations that typically influence MGR system design for non-energy related applications. These considerations include refrigerant-process safety, design operability/reliability, operating expense and installed system cost. The quick-freezing of food and low-temperature pharmaceutical reactions often require temperatures ranging between –70 C and –110 C. Such temperatures are substantially below the temperatures easily accessible through conventional vapor compression cascade systems (e.g. –57 C CO_2/NH_3) (Groll, 2000). Another criterion for operation includes the need to deliver refrigeration at points (evaporator) significantly removed from the primary process equipment (machinery room). These distances can be upwards of several hundred feet. In many instances, workers have to service the process equipment, which requires them to enter the vessel or confined space through which the refrigerant circulates. Therefore, there is a need to remove or evacuate the refrigerant from the use point. These factors provide motivation to use of non-flammable and non-toxic mixtures. In the case of the quick freezing of food, operations are often intermittent. Significant fluctuations in utilization and load can be encountered. In these cases, installed system cost and operational expense must be carefully balanced with the anticipated use profile.

2. REFRIGERATION COMPONENT SELECTION

The US Clean Air Act Amendments of 1990 resulted in a shift away from CFC/HCFC to HFC and natural refrigerants. This shift was motivated by the content of the Montreal Protocol (1987) (Reed, 1993). Unfortunately,

non-toxic natural refrigerants with boiling points in the range of -60 C and –186 C do not exist. For safety reasons, hydrocarbons and flammable HFC based working fluids are not possible options. Freezing point considerations narrow the list of potential compounds even further. These facts result in a short list of potential, component compounds. The compounds shown in Table 1 are relatively non-toxic, non-flammable, chemically inert and present minimal ozone depletion potential.

Table 1 Boiling and Freezing Points of Selected HFC's and Atmospherics

	Formula	Boiling Point C	Freezing Point C
R728	N_2	-196	-210
R740	Ar	-186	-189
R14	CF_4	-128	-184
R23	CF_3H	-82	-155
R116	C_2F_6	-79	-94
R125	C_2F_5H	-49	-103
R218	C_3F_8	-37	-160
R134a	$C_2F_4H_2$	-26	-97
C318	C_4F_8	-6	-39
R610	C_4F_{10}	-2	-
R236FA	$C_3F_6H_2$	-1	-94

The synthesis of a process cycle and the definition of its working fluid(s) result from numerous considerations. A physical limitation imposed upon any mixed gas refrigeration system is that the freezing point of any major component can not be higher than the minimum cycle temperature that that component may experience. In order to minimize the cost and complexity of a mixed gas working fluid, the number of compounds should be limited to those critical to refrigeration circuit function. In general, compounds of similar boiling point should be differentiated based upon freezing point and those compounds exhibiting superior pure component refrigeration performance at the subject operating pressures. In general, such criteria indicate a preference toward lower molecular weight compounds. Given these criteria, an immediate complication to system design is apparent (see Table 1). There is a noticeable lack of compounds with boiling points near ambient and freezing points near –100 C. In general, non-flammable HFC's with 4+ carbons exhibit freezing/pour points above those necessary to supply refrigeration between –70 and –110 C. A search for compounds with boiling points over 0 C indicated that several fluoroether compounds satisfy both the flammability criteria and boiling/freezing point criteria (Tuma, 2000). The HFE-347E (+34 C boiling point, -119 C freezing point) was selected as the high temperature refrigerant component for this analysis.

3. PROCESS DEVELOPMENT

The process cycle shown in Figure 1 resulted from a simultaneous consideration of application demands relative to viable refrigerants (Howard, 2003). Cycle design results from an integrated consideration of performance, cycle cost and operability analysis. The process shown employs two, cascaded, mixed-gas refrigerant circuits. The cold circuit serves to absorb the refrigeration load. The high temperature circuit serves to absorb the condensing load from both the warm and cold circuits. In Figure 1 the high temperature circuit compresses the gas to an elevated pressure of 1300-2400 kPa. The gas is partially condensed against an ambient utility. The vapor liquid mixture is subsequently completely condensed and subcooled by passage through the primary heat exchanger. The fluid is flashed and serves to absorb the heat of condensation from both the incoming warm and cold circuit fluids. The vaporized warm circuit fluid is extracted and compressed as noted. The cold circuit compressor pressurizes the refrigerant mixture to a pressure in the range of 1300-2400 kPa. The gas is then desuperheated and condensed within the primary heat exchanger. The cold refrigerant is subsequently directed to the evaporator where it is flashed and completely vaporized. The vaporized refrigerant is directed back to the primary heat exchanger, superheated and compressed.
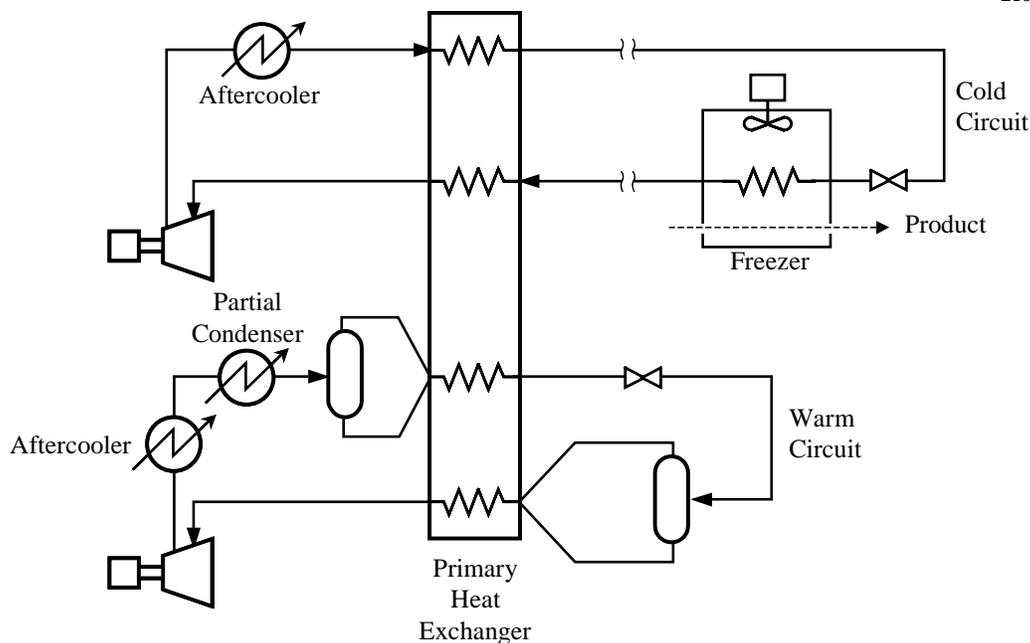
Figure 1: Dual Circuit Process

Initial cycle configurations contemplated a single circuit system design. However, the partial vaporization of the refrigerant mixture in remote evaporators presents several problems. First, the presence of high boilers reduces the heat transfer rate in the evaporator. Second, motivating the two-phase fluid back to the primary heat exchanger becomes problematic if significant process range-ability is necessary. In particular, the design point pressure drop must be increased in order to motivate the refrigerant mixture at low refrigeration load. In order to solve these problems, the process of Figure 1 was devised. Since the cold circuit fluid is completely vaporized in the evaporator, issues with two-phase flow were eliminated whilst improving overall evaporator performance. In addition, circuit segregation enables the operating pressure ranges for each circuit to be increased thereby mitigating the impact of pressure drop upon overall cycle performance.

The operational state of the process shown in Figure 1 is naturally dependent upon the ambient utility temperature and the desired evaporator temperature (range). In addition, the design variables requiring definition include the selection of n - 1 components (for each circuit), the 4 system pressures and the cold end temperature of the primary heat exchanger. In addition, the primary heat exchanger's minimum approach (or UA) must be defined. Given consideration of boiling point and the desired temperature rise across the evaporator, the most effective cold circuit mixture was found to comprise R740/R14/R23. This set of compounds was shown to provide both appropriate temperature glide and sufficient pressurization of the cold circuit. Given consideration of power, freezing point and boiling point, the most effective warm circuit components were found to be R740/R14/R23/R125/HFE-347E. The total number of compositions that must be defined for this system is 6. The total number of independent variables required to define the operational state is 15 (6 compositions, 4 pressures, the cold end temperature and approach of the primary heat exchanger, the ambient utility temperature/approach and evaporator inlet and outlet temperature).

4. PROCESS OPTIMIZATION

Steady state simulation of the dual circuit process reveals that the system is non-linear and that optimization presents significant challenges. Conventional non-linear optimization methods are difficult to implement because of model reliability. It was finally decided to pursue a combination of heuristics and a sequential linear search. The compressors represent the largest capital expense for this process. By maximizing the operating pressures and pressure ratios for each circuit, the compression equipment cost is minimized. In addition, the compressors are limited in available compression ratio. Given these factors it was decided to pursue a solution that constrained the high and low side pressures. Given the limited number of viable evaporator refrigerants, cold circuit fluid definition

is basically constrained by the need for complete evaporation. As for the warm circuit, it is found that the presence of a small fraction of deep condensable gas such as argon effectively facilitates the desired cold-end temperature difference (required to operate the primary heat exchanger). In addition, because heat rejection is accomplished primarily through the condensation of the warmest component (HFE-347E), there is substantial motivation toward maximizing its content. Maximization of the warm component reduces overall circuit mass flow and hence the compressor cost. Given the ambient utility temperature, primary heat exchanger approach and the low-side pressure (of the warm circuit), the maximum amount of HFE-347E can be computed directly. These considerations leave only the composition of the three interior boiling components (R14, R23, R125) of the warm circuit fluid as undefined. By this approach, the compositional optimization problem is reduced to two independent variables.

Numerous simulations were conducted and a contour map illustrating the results is shown in Figure 2. As noted the optimization can be reduced to finding the distribution of the three interior components (R14, R23 and R125). Figure 2 depicts normalized efficiency (COP/COP_{min}) relative to the point of minimum power consumption. The compositional axes are for R23 and R125. The change in R14 may be computed directly by difference.
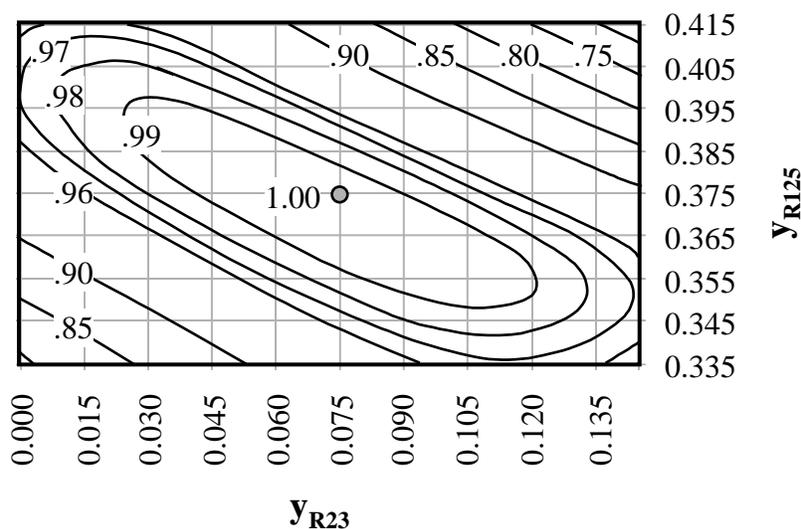

Figure 2: Contour Map of Relative Efficiency

Inspection of the above plot indicates a wide region where thermodynamic efficiency is within 1% of the highest attainable. The leftmost axis represents the loci of points where R23 is eliminated from the mixture. The figure indicates that the removal of R23 represents at least a 3% total cycle power penalty. Given consideration of the incremental capital for maintaining R23 as a component, it was retained in the mixture. The point of maximum efficiency indicates features of the process that are characteristic of all the optima observed for this cycle. Figure 3 depicts the composite heat exchange curves for the primary heat exchanger corresponding to the point of maximum process efficiency (y_{R23}, y_{R125} [=] 0.075, 0.375). Inspection of Figure 3 indicates that the optimal refrigerant composition results in at least two internal primary heat exchanger pinch points.

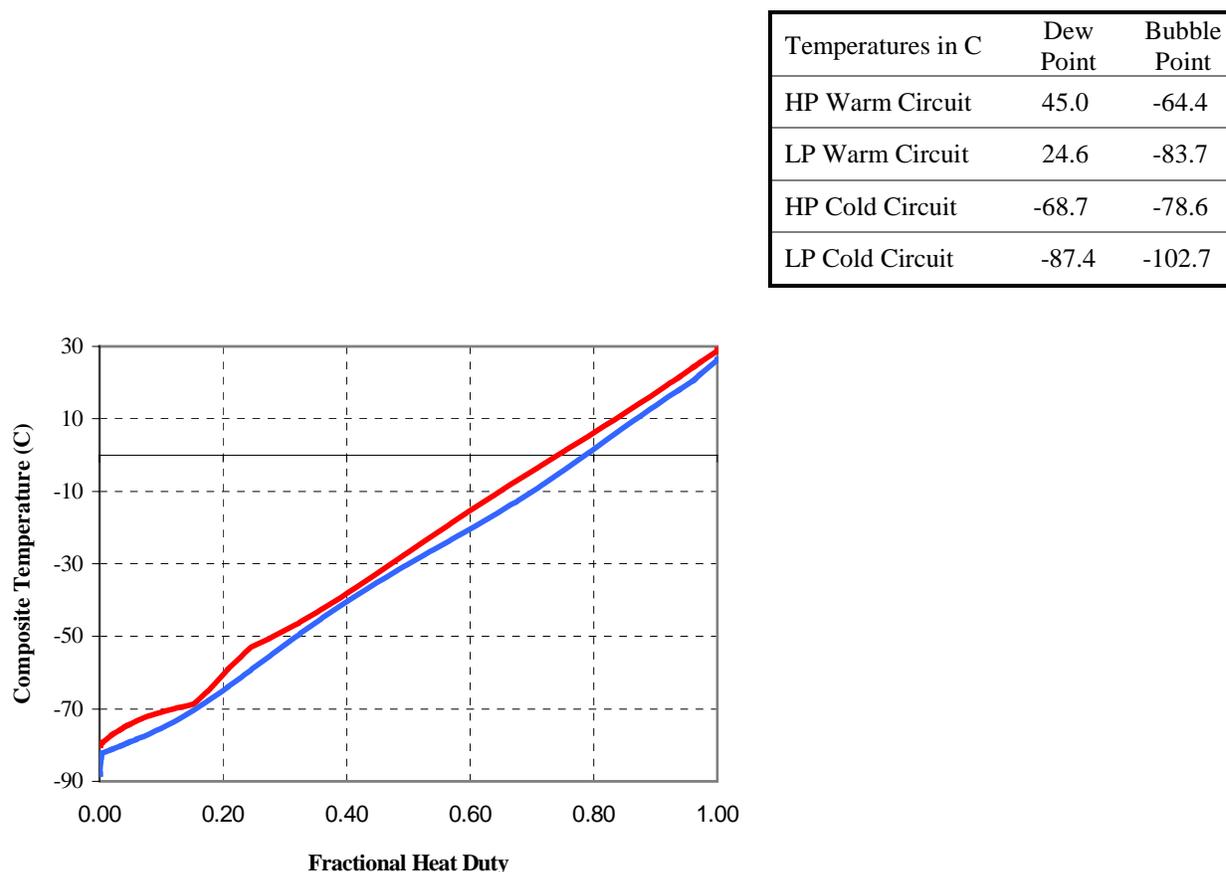| Temperatures in C	Dew Point	Bubble Point
HP Warm Circuit	45.0	-64.4
LP Warm Circuit	24.6	-83.7
HP Cold Circuit	-68.7	-78.6
LP Cold Circuit	-87.4	-102.7

Figure 3: Primary Heat Exchanger Composite Temperature Curves

Inspection of the saturation points of the incoming refrigerant streams indicates that optimal operation of the dual circuit process is achieved when the bubble point of the condensing warm circuit fluid resides above the dew point of the condensing cold circuit. In this way, the condensing load is most evenly distributed across the heat exchanger. The vaporizing warm circuit serves to absorb the latent heat of condensation for both circuits. Minimum cycle power consumption is achieved when the irreversibility of the overall heat exchange is considered. The staged condensation approach enables the creation of multiple internal primary heat exchanger pinch points. Given this finding the optimization of subsequent refrigerant mixtures was accelerated because a wide range of mixtures can be dismissed which do not satisfy these criteria.

5. TEMPERATURE-BALANCED DISTRIBUTION OF LATENT HEAT

As noted, the optimization algorithm included a combination of heuristics and sequential linear search. For this particular application, R14, R23 and R125 are the major interior components. The relative quantities of Argon and HFE-347 can be computed directly given the primary heat exchanger's minimum approach and the ambient utility

(condensation temperature). Inspection of Figure 2 illustrates how lines of constant efficiency are essentially parallel over large ranges (away from the optimum). This is a direct result of the need to maintain a temperature-balanced distribution of latent heat.

Inspection of Figure 3 indicates that the warming composite curve is approximately linear with respect to temperature. The warming composite curve is determined primarily by the energy absorbed by the vaporizing warm circuit fluid. The superheat of the cold circuit fluid absorbs only 5 to 10% of the duty required to condense the high-pressure streams. Since each component of the warm circuit mixture delivers refrigeration over a reasonably narrow temperature range (as defined by its boiling point at the given pressure), the total molar energy absorbed (Q) can be effectively weighted with respect to temperature range (where f_i is a non-dimensional weighting factor). In equation (1), the molar latent heat of vaporization (ΔH_i) is that observed for the pure fluid at the circuit operating pressure.

$$\Delta H_i y_i = f_i Q \qquad (1)$$

In equation (1), the end point temperatures of the primary heat exchanger and the boiling points of the interior two components can be used to determine the energy weighting factors (f_i). Each weighting factor may be computed by dividing the temperature range between any two points (e.g. the cold-end temperature and the boiling point of R23) by the total temperature difference existing across the primary heat exchanger. By observation, the total latent heat of vaporization (Q) is essentially constant. Equation (1) can therefore be rearranged and the respective component mole fractions related to one another.

$$\Delta H_i y_i / f_i = \Delta H_j y_j / f_j \qquad (2)$$

By rearranging Equation (2) and taking the partial derivative of composition (at constant pressure) an equation for a temperature-balanced change in composition is obtained. Equation (3) provides a finite difference equation relating a change in any one component to another.

$$\Delta y_i = (f_i / f_j)(\Delta H_j / \Delta H_i)\Delta y_j \qquad (3)$$

Table 2 summarizes the three distinct temperature ranges associated with the primary heat exchanger of Figure 3.

Table 2 – Temperature Weighting Factors
PHX WE = +26.1 C, PHX $T_{WE} - T_{CE}$ = +108.3 C

	Temperature C	ΔH kj/kgmole	ΔT Range C	f_i
R14 (PHX Cold End)	-82.2	9500	44.9	0.414
R23 (boiling point)	-37.4	14070	42.4	0.392
R125 (boiling point)	+5.1	15640	21.0	0.194

The data shown in Table 2 can be used to determine how to optimally traverse the efficiency contours of Figure 2. As an example, the difference equation relating changes in R23 with respect to R125 may be calculated.

$$\Delta y_{R23} = 2.25\ \Delta y_{R125} \qquad (4)$$

The slope of the constant efficiency contour lines of Figure 2 is approximately 2.2. This fact supports the validity of this approach to optimization. Therefore, the compositional optimization of the three interior components of the warm circuit fluid employed a two-step process. The first step involved a rough partitioning of R125 and R14. The second step involved a sequential linear search along a vector defined by equation (4). A simple mole balance assuming no change in the HFE and Argon content of the mixture defined the relative change in R14 as the optimization moved along the subject vector.

6. CONCLUSIONS

A novel dual circuit, mixed gas refrigeration process has been developed for non-energy related applications such as food freezing and pharmaceutical manufacture. The subject cycle addresses needs unique to refrigeration system

operation wherein refrigeration load is spatially removed from the machinery room. From steady state simulation, it can be concluded that the optimal component mixture is coincident with achieving at least two interior primary heat exchanger pinch points. More particularly, such pinch points are effectively created upon a staged condensation of the high-pressure mixtures.

A combined heuristic and numerical approach to process optimization has been developed. It has been found that the number of independent design (optimization) variables can be reduced through consideration of compression and primary heat exchanger constraints. A number of component compositions can be specified through application of such constraints. Working fluid component optimization can be further reduced to a partitioning of interior components. Through simple thermodynamic considerations and process simulation, it has been shown that component optimization should proceed along a vector that maintains the same relative distribution of latent heat with respect to temperature (as specified by component boiling points, the ambient utility and the primary heat exchanger's cold-end temperature). The subject approach has resulted in a substantial reduction in engineering efforts required for full system specification.

NOMENCLATURE

ΔH	molar latent heat of vaporization	(kj/kgmole)		**Subscripts**
y	component mole fraction	(–)	i, j	mixed gas component identifier
f	weighting factor	(–)		
Q	heat transferred	(kj/kgmole)		

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