

# Determining the minimum energy requirement of an LNG process New insights into the impact of the vapour liquid equilibrium

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**Abstract:** The paper provides a detailed first principles analysis of a process of liquefaction of natural gas in which the refrigeration compressors are driven by electric motors. The aim is to determine and understand the impact of the operation of the refrigeration cycles on the power consumption of the process. This study gives a detailed insight into the relationship between the discharge pressure of the compressors and the thermodynamic performance of the refrigeration cycles. By doing this, the findings of this research highlight the importance of the vapour liquid equilibrium. The results show that, for a given production rate, there is a minimum in the power consumption when the discharge pressures are close to the refrigerant saturation points. The paper provides a discussion and analysis of the advantages and disadvantages of operating at such points.

## 1. INTRODUCTION

As natural gas meets around the 23% of the global energy needs, the process for liquefying natural gas (LNG process) has increasingly become more important over the last two decades (BP plc (2018); Enerdata (2018)). In the LNG process, natural gas is cooled down to  $-162^{\circ}\text{C}$ , so that it liquefies, facilitating its storing and transportation. The operation uses refrigeration to remove the heat from the natural gas and release it to the environment. Depending on the capacity, typical power consumption ranges from 30MW to 200MW (Linde AG, 2018).

LNG plants rely on electrical energy. However, as mentioned by Devold et al. (2006), LNG industries are not always placed near reliable power supplies, and most of them depend on the electrical power produced on-site using commercial gas turbines. Consequently, LNG processes have to operate as efficiently as possible in terms of electricity consumption. Additional drivers for efficiency are economic revenues and emerging energy policies derived from the 2020 Energy Strategy of the European Commission (European Commission, 2008).

Currently, the leading LNG manufacturers are using processes by Air Products & Chemicals (Air Products & Chemicals, 2013), ConocoPhillips (ConocoPhillips, 2016), and Linde (Linde AG, 2018). A refrigeration process uses a refrigerant in a closed cycle involving Joule-Thomson expansion, absorption of heat from the LNG, compression, and exchange of heat with the environment, typically the sea. The refrigerant reaches its saturation point and presents a Vapour and Liquid Equilibrium (VLE) during the Joule-Thomson effect. This VLE has a significant influence on the enthalpies of the refrigerants, which ultimately influence the consumption of the plant. Thus, an understanding of the VLE is crucial in the modelling of the electrical power consumed by the process.

The motivation of this paper is to analyse and understand the impact of the VLE of the refrigerants on electrical power consumption, for a specified LNG flow rate and product composition.

This analysis makes it possible to determine the minimum electrical power consumption for any given combination of LNG flow rate and product composition.

Previous works (Kanoğlu, 2002; Remelje and Hoadley, 2006; Vatani et al., 2014), have researched the LNG plant using an equation of state for mixtures of real fluids whose streams can either present vapour or liquid. However, their work did not examine in-between conditions in which the stream presents a VLE. Shirazi and Mowla (2010) performed an analysis giving insight into the necessary thermodynamic equations to describe VLE. However, the VLE calculated parameters of the fluids but did not calculate physical properties when a VLE appears in a stream. Additionally, the models chose the temperatures in such a manner that there was no VLE present in the process. The Linde process was examined recently by Xuan et al. (2018), which explored the impact of the product flow rate on electricity consumption and the exit temperature of the liquefied natural gas. During that analysis, the authors noted the effect of the VLE on the electrical power consumption and the compressor discharge pressures. The analysis revealed a gap of knowledge concerning the impact of the VLE on the energy consumption of the LNG process. This paper now provides a comprehensive analysis of the relationship between the VLE and the LNG operating points for the Linde process. The results give new insights into the minimum achievable energy consumption for a given product flow rate and exit temperature. They show that operating closer to the VLE could potentially give a power saving of up to 17.5%. In a large LNG installation, this could reduce the power requirement by up to 35 MW.

The paper gives a detailed analysis of electrical power consumption of operation either side of the VLE. The physical insights from the model enable systematic selection of robust and energy-efficient operating points for the LNG process. The focus is on the Linde process patented by Stockmann et al. (2001), which uses a mixed fluid cascade process, in which

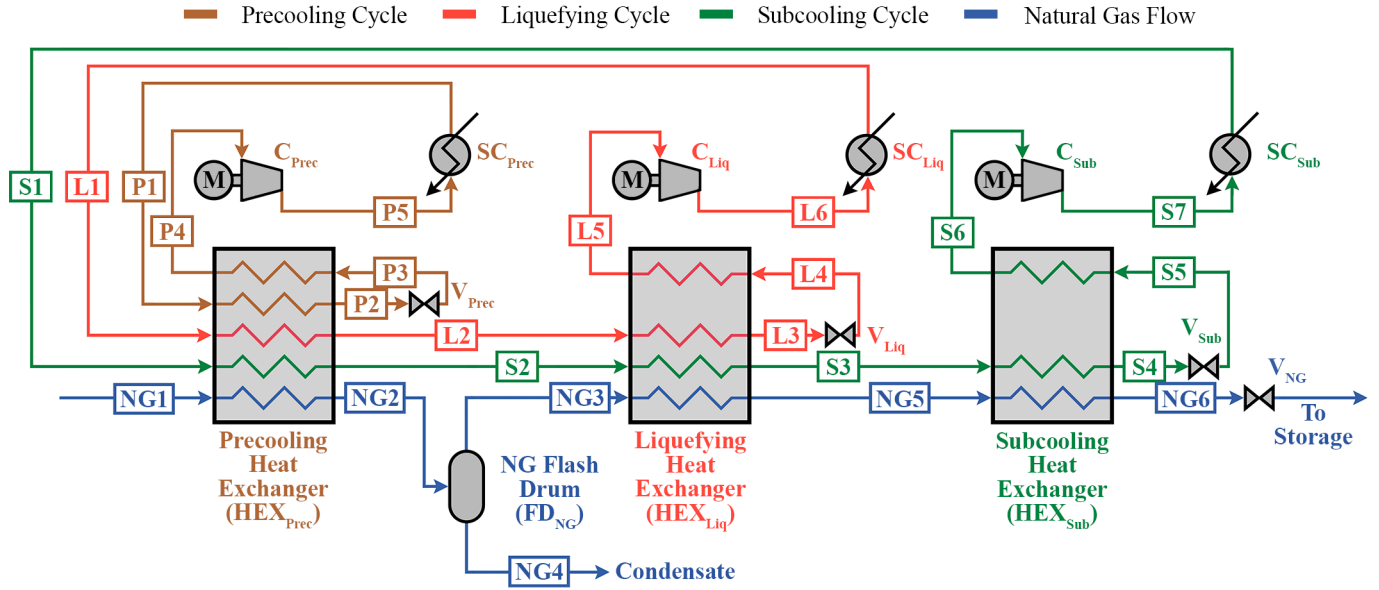


Fig. 1. Liquefied Natural Gas process. The picture is a representation of the process introduced in the patent by Stockmann et al. (2001), and it is based on the mixed fluid cascade process by Linde (Linde AG, 2018).

each refrigerant is not mixed with the rest, solely exchanging heat for cooling the natural gas. This mass isolation between refrigerants enables a detailed analysis of how the VLEs of the refrigeration fluids affect the electrical consumption.

The refrigerants used in the liquefaction are mixtures of hydrocarbons, and consequently, the fluid properties have to be accordingly modelled using an adequate equation of state. This paper implements the Redlich-Kwong Soave (RKS) (Soave, 1972) EoS along with the Rachford-Rice (RR) equation for accurate calculation of the properties of fluids. Ikeda and Schaefer (2011) stated that to model a mixture of hydrocarbons, either Peng Robinson or the RKS could be used. This paper uses the RKS EoS for modelling the LNG process.

This paper is structured as follows:

- Section 2 describes the process and gives essential information about the process and its components.
- Section 3 formulates the mathematical model, giving emphasis to the saturation points that define the VLE. This section also discusses the assumptions made while modelling the process.
- Section 4 presents results from solving the model. It shows the impact of the pressure of the refrigerants on the electrical consumption, presenting the steps for achieving such results. The results are validated against the typical operating points of working LNG processes.
- The analysis in section 5 discusses the mechanisms whereby the pressure affects the electrical consumption of the process and demonstrates why VLE has a significant impact on the consumption of the plant.
- The paper ends with a conclusion in Section 6.

## 2. LNG PROCESS

### 2.1 The process

Figure 1 shows the mixed fluid cascade process model studied in this research. In this process, natural gas is liquefied by

passing through three heat exchangers ( $HEX_{Prec}$ ,  $HEX_{Liq}$  and  $HEX_{Sub}$ ), one corresponding to each of the three refrigeration cycles that are represented in brown (precooling refrigerant), red (liquefying refrigerant), and green (subcooling refrigerant). Figure 1 also shows the natural gas streams (blue), where NG1 is the feed, and NG6 the liquefied product. The natural gas enters at 30 bars, and after the liquefaction, it is decompressed to 1 bar. Additionally, the natural gas enters a condensation stage ( $FD_{NG}$ ) between  $HEX_{Prec}$  and  $HEX_{Liq}$  for removing some heavier hydrocarbons present in the natural gas feed.

The process in Figure 1 is based on the one by Linde AG (2018) and Stockmann et al. (2001). Each cycle in the process has its refrigerant with its composition, corresponding to an appropriate combination of heat capacity and saturation points:

- **Precooling (Brown):** This refrigerant lowers the temperature of the natural gas, and the liquefying and subcooling refrigerants to  $-35^{\circ}\text{C}$ . The composition of the precooling refrigerant consists of ethane (20%) and propane (80%).
- **Liquefying (Red):** This refrigerant lowers the temperature of the natural gas to  $-100^{\circ}\text{C}$ , at which temperature and pressure, it becomes liquid. The liquefying refrigerant also cools the subcooling refrigerant to  $-100^{\circ}\text{C}$ . The composition of the liquefying refrigerant consists of ethane (85%), with small amounts of methane (5%) and propane (10%).
- **Subcooling (Green):** This refrigerant lowers the temperature of the liquefied natural gas to  $-162^{\circ}\text{C}$ . Subcooling is needed to keep the LNG liquid state after the final decompression. The composition of the subcooling refrigerant consists of methane (40%), ethane (30%), and ethylene (30%).

This introduction of the refrigerant cycles does not include any information about the pressures because the next sections will discuss the effect of the pressure of the refrigerants on the electrical power consumption of the plant. The absorbed heat is released into the sea through the sea coolers ( $SC_{Prec}$ ,  $SC_{Liq}$ , and  $SC_{Sub}$  in Figure 1). The temperature of the refrigerants at the exit of the sea-water coolers is  $10^{\circ}\text{C}$ . The model assumed a

cold sea temperature appropriate to the Arctic region, where a significant proportion of future natural gas resources are located.

The subcooling refrigerant has lighter components than the liquefying refrigerant, and the liquefying refrigerant has lighter components than the precooling refrigerant. Lighter components have lower saturation points, where saturation point refers to the temperature and pressure at which a VLE occurs. The Joule-Thomson expansion requires a VLE to be present in the refrigeration cycle, so the temperature achieved by the refrigeration cycle is lower when the saturation point of the refrigerant is lower.

The rotating machinery used for compressing the refrigerants is driven by electric motors, which are the primary electrical consumers in this operation. An ideal refrigeration cycle removes  $Q_{\text{Rem}}$  from the source and releases  $Q_{\text{Rel}} = W + Q_{\text{Rem}}$  to the sink, where  $W$  is the electrical power consumption.  $Q_{\text{Rem}}/W$  depends only on the temperatures of the source (the natural gas) and sink (the sea). If these temperatures do not vary, the heat removed from the natural gas is proportional to the electrical consumption of the refrigeration compressor. However, in reality, the refrigeration cycle is not ideal.

## 2.2 Effect of the discharge pressure

Enthalpy mainly depends on the temperature and the composition of a stream, whereas the pressure has a minor effect on the enthalpy. Nevertheless, the pressure has a significant impact on the saturation point. If the temperature of the considered stream does not change, the refrigerant might undergo a phase change, causing a considerable change of enthalpy. This phase change is one of the keys in the Joule-Thomson cycle seen in Figure 2, which illustrates a generic pressure-enthalpy ( $P-h$ ) diagram for a refrigeration cycle. The figure also shows isotherms, and it highlights the region where the VLE exists. Enthalpies are crucial since they are used to measure the heat (the form of enthalpy used for changing the temperature or phase of a stream) or the electrical power consumption (the form of enthalpy used by the motors attached to the compressors).

Figures 2 to 4 illustrate the effects of varying the pressure on the specific enthalpies of a cycle that present a VLE. Each figure shows a mode of operation for the precooling cycle, and each mode has a different compressor discharge pressure. There are five points for each mode of operation corresponding to streams P1 to P5. The three modes of operation are:

- An operation representing a reference case where stream P1 is liquid (Figure 2).
- An operation representing a case where stream P1 presents a VLE (Figure 3).
- An operation representing a case where stream P1 is liquid, but at a lower pressure than the reference pressure (Figure 4).

### Effects of pressure in a reference case scenario

Figure 2 illustrates the  $P-h$  diagram for a case in which stream P1 is liquid, and its pressure is above the saturation point. The pressure in stream P1 is the same as the discharge pressure of the precooling compressor, corresponding to stream P5. P2 is the stream that exits the first heat exchanger ( $\text{HEX}_{\text{Prec}}$ ) after releasing its heat. The pressure of P2 is also the same as the pressure in P1. P3 is the stream exiting the isenthalpic expan-

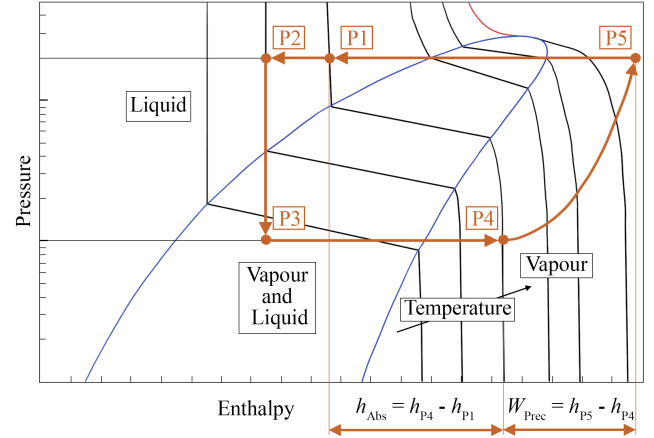


Fig. 2. Joule-Thomson cycle undergone by the precooling refrigerant. For the given temperature, the discharge pressure causes stream P1 to be liquid.

sion valve. The valve maintains the same enthalpy and lowers the pressure. After exiting the  $\text{HEX}_{\text{Prec}}$ , P4 is compressed in  $\text{C}_{\text{Prec}}$ , raising its pressure to the same pressure as P5. P5 cools down in  $\text{SC}_{\text{Prec}}$  with constant pressure and results in P1, so the cycle is complete.

The horizontal axis in Figure 2 includes two differences of enthalpies  $h_{\text{Abs}} = h_{\text{P4}} - h_{\text{P1}}$ , and  $w_{\text{Prec}} = h_{\text{P5}} - h_{\text{P4}}$ , both variables in  $\text{kJ kmol}^{-1}$ . The difference  $h_{\text{Abs}}$  represents the specific heat that the precooling refrigerant can absorb from the natural gas, and the liquefying and subcooling refrigerants. The difference  $w_{\text{Prec}}$  represents the specific electrical power consumption needed for compressing stream P4 until the refrigerant reaches the pressure in stream P5. Both  $h_{\text{Abs}}$  and  $w_{\text{Prec}}$  are specific measurements, so they have to be multiplied by the flow rate to obtain the total heat that the precooling refrigerant can absorb ( $H_{\text{Abs}}$  in W), and the total electrical power consumption used by the precooling compressor ( $W_{\text{Prec}}$  in W).

### Effects of pressure when presenting a VLE case scenario

Figure 3 illustrates the same cycle as Figure 2, but in this case, the discharge pressure of the precooling compressor is lower, causing stream P1 to be at a VLE. Figure 3 shows this operation (yellow), and for contrast, it also shows the reference case cycle (brown). Each stream maintains the same temperature, so the new points are on the same isotherms as in the reference case.

In the VLE case scenario,  $w_{\text{Prec}}$  is lower than in the reference case scenario. Thus, the specific electrical power consumption needed for compressing the refrigerant is lower. On the other hand,  $h_{\text{Abs}}$  is also lower, so the amount of specific heat that the refrigerant can absorb decreases. The precooling refrigerant flow rate has to increase to compensate the decrease in  $h_{\text{Abs}}$ , otherwise the temperature of the natural gas, and the liquefying and subcooling refrigerants would increase. Increasing the flow rate of the precooling refrigerant increases the electrical power consumption of the compressor. Thus, in the VLE case, the decrease of  $w_{\text{Prec}}$  in the VLE case does not outweigh the decrease of  $W_{\text{Prec}}$ .

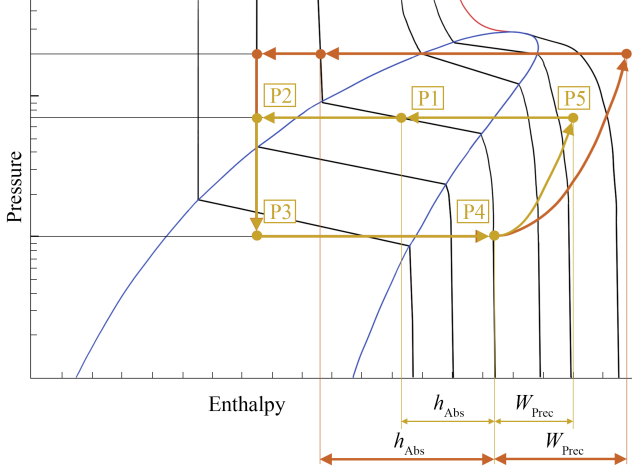


Fig. 3. Joule-Thomson cycle undergone by the precooling refrigerant (yellow) at a lower discharge pressure than the pressure in the reference case (brown), causing stream P1 to present a VLE.

### Effects of pressure in an optimal case scenario

Figure 4 illustrates the same cycle as Figure 2, but in this case, the discharge pressure of the precooling compressor causes P1 to be closer to the saturation point. In this case,  $w_{prec}$  is lower than in the reference case scenario, but  $h_{Abs}$  does not decrease as much as in Figure 3. Thus, the precooling refrigerant flow rate is virtually the same as in the reference case, whereas the electrical power consumed by the compressor decreases. Thus,  $W_{Prec}$  does not increase in the same manner it does in the VLE case.

### 2.3 Choosing the right refrigerant pressure

If the heat that the refrigerant can absorb is low, it must be compensated by increasing the refrigerant flow rate, which ultimately will increase the electrical power required by the compressor. Thus, it is necessary to find a discharge pressure that makes  $h_{Abs}$  as high as possible, and that makes  $w_{Prec}$  as low as possible. These theoretical arguments and their applicability are further discussed in sections 4 and 5.

In the VLE region, a slight change in the pressure has grave consequences on the enthalpy of a stream, and therefore, on the heat that the refrigerant can absorb. Outside this region, a slight change in the pressure makes almost no difference. Thus, determining the VLE region of the refrigerant is crucial for choosing the right discharge pressure.

There are three main factors to consider when choosing the discharge pressure of the compressor:

- It might change the phase of one or more than one streams.
- It has consequences on the heat absorbed by the refrigerants, and therefore, on the refrigerant flow rate.
- A higher pressure means a higher specific electrical power used by the compressor.

## 3. MATHEMATICAL MODEL OF THE LNG PROCESS

This section presents the mathematical model of the process. The following physical equations are a derivation of the thermodynamic equations from Poling (2007) and Nieto et al. (2013).

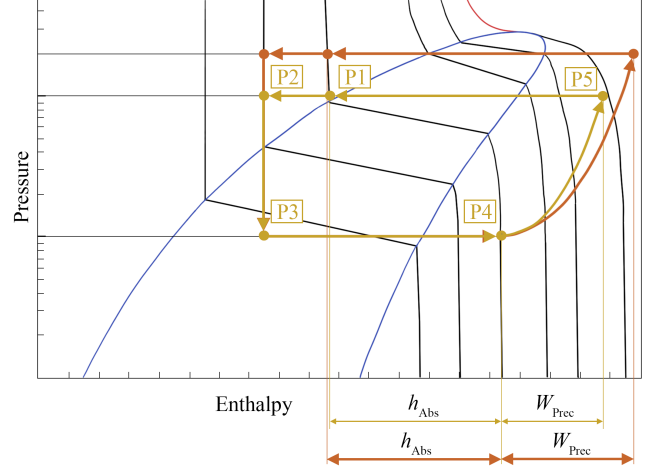


Fig. 4. Joule-Thomson cycle undergone by the precooling refrigerant (yellow) at a lower discharge pressure than the pressure in the reference case (brown), causing stream P1 to be liquid and closer to the saturation point.

### 3.1 Thermodynamic model: RKS Equations

The RKS equation is a three parameter EoS that relates the pressure, the molar volume and the temperature of a fluid, and it is widely used in the hydrocarbon field (Soave, 1972).

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m - b)} \quad (1)$$

where  $P$  is the pressure in Pa,  $V_m$  is the molar volume in  $\text{m}^3 \text{mol}^{-1}$ ,  $T$  is the temperature in K, and  $R$  is the ideal gas constant.  $a$ ,  $b$ , and  $\alpha$  are parameters characteristic of the RKS equation. Expressions for these can be found in (Soave, 1972).

The model uses the departure function because of the presence of real fluids. The departure function of a property is the difference between the value of the property for an ideal gas and its value for a real fluid. For the RKS equation, the departure enthalpy is:

$$h^{\text{Dep}} = (PV_m - RT) - \frac{a\alpha - T \frac{\partial a\alpha}{\partial T}}{b} \ln \left( \frac{V_m + b}{V_m} \right) \quad (2)$$

where  $\frac{\partial a\alpha}{\partial T}$  is derived according to the EoS used in the model. In this case, for the RKS:

$$\begin{aligned} \frac{\partial a\alpha}{\partial T} = & \sum_i \sum_j^C y_i y_j (1 - k_{ij}) \sqrt{a_i a_j} \\ & \times \left( -\frac{s_i}{2T_{ci} T_{ri}^{0.5}} - \frac{s_j}{2T_{cj} T_{rj}^{0.5}} \right. \\ & \left. + s_i s_j \frac{T_{rj}^{0.5} - 1}{2T_{ci} T_{ri}^{0.5}} + \frac{T_{ri}^{0.5} - 1}{2T_{cj} T_{rj}^{0.5}} \right) \end{aligned} \quad (3)$$

where  $T_{ci}$  is the critical temperature of component  $i$ , and  $T_{ri}$  is the reduced temperature of component  $i$ , and it is equal to  $T/T_{ci}$ . Appendix A shows a detailed derivation of Eqs. 2 and 3.

### 3.2 Thermodynamic model: vapour-liquid equilibrium

The vapour fraction and the composition in each phase are crucial for computing the thermodynamic properties in a VLE. The Muskat-McDowell (Muskat and McDowell, 1949) methodology or the Rachford-Rice (RR) equations (Rachford and Rice, 1952) can calculate both vapour fraction and compositions. This model uses the RR methodology and implements iterations for solving the initial assumption problem inherent to this kind of algorithm. The RR equations calculate the vapour fraction and the molar fractions of the components by solving first the vapour-liquid equilibrium ratio.

#### Vapour-liquid equilibrium ratio

The general form of the vapour-liquid equilibrium ratio is:

$$K_i = \frac{y_i}{x_i}$$

where  $K_i$  is the vapour-liquid equilibrium ratio,  $y_i$  is the mole fraction of  $i$  in the vapour, and  $x_i$  is the mole fraction of the same component in the liquid. The fugacities have to be the same between phases. For real fluids, they are calculated as:

$$f_i^L = \gamma_i^L x_i P_i^{\text{sat}}(T) \phi_i^{\text{V,sat}} \exp \left[ \frac{V_{m,i}^L [P - P_i^{\text{sat}}]}{RT} \right]$$

$$f_i^V = \phi_i^V y_i P$$

where  $f_i^L$  and  $f_i^V$  are the fugacities of component  $i$  in the liquid and in the vapour respectively.  $P_i^{\text{sat}}$  is the saturation pressure of component  $i$  at temperature  $T$ ,  $V_{m,i}^L$  is the molar volume of  $i$  in the liquid, and  $\phi_i^V$  is the fugacity coefficient. The variable  $\gamma_i^L$  is the activity coefficient of component  $i$ , and it can be calculated with the Wilson equation (Wilson, 1964) derived from the excess Gibbs energy. The activity coefficient depends on the interactions between components and it is calculated as:

$$\gamma_i^L = -\ln \left[ \sum_j^C x_j \Lambda_{ij} \right] + 1 - \sum_{k=1}^C \frac{x_k \Lambda_{ki}}{\sum_{j=1}^C x_j \Lambda_{kj}}$$

where  $\Delta_{ij}$  is the Wilson interaction parameter between  $i$  and  $j$ . The variable  $\Lambda_{ij}$  is not equal to  $\Lambda_{ji}$ , and  $\Lambda_{ii}$  is equal to zero. For the RKS, the fugacity coefficient is:

$$\ln \phi_i^V = \frac{b_i}{b} (Z - 1) - \ln \left[ Z \left( 1 - \frac{b}{V_m} \right) \right]$$

$$+ \frac{a\alpha}{bRT} \left( \frac{b_i}{b} - \frac{2}{a\alpha} \sum_j y_j (a\alpha)_{ij} \right) \ln \left[ 1 + \frac{b}{V_m} \right]$$

where  $Z$  is the compressibility factor. Thus, the vapour and liquid equilibrium ratio is:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^L P_i^{\text{sat}}(T) \phi_i^{\text{V,sat}} \exp \left[ \frac{V_{m,i}^L [P - P_i^{\text{sat}}]}{RT} \right]}{\phi_i^V P} \quad (4)$$

#### Rachford-Rice equation

The mass balance in a flash separator is:

$$F z_i = V K_i x_i + L x_i \rightarrow x_i = \frac{F z_i}{V K_i + L}$$

$$x_i = \frac{z_i}{1 + \frac{V}{F} (K_i - 1)}$$

where  $F$  is the feed flow rate in  $\text{kmol s}^{-1}$ ,  $z_i$  is the molar fraction of component  $i$  in the feed,  $V$  is the vapour flow rate in  $\text{kmol s}^{-1}$ , and  $L$  is the liquid flow rate in  $\text{kmol s}^{-1}$ . Considering that  $\sum_i^C (y_i - x_i) = 0$ , and that  $\frac{V}{F} = \psi$ :

$$\sum_i^C \frac{z_i (K_i - 1)}{1 + \psi (K_i - 1)} = 0 \quad (5)$$

where  $\psi$  is the vapour fraction, and  $z_i$  is the overall molar fraction of the stream. The model uses the Newton-Raphson iteration method, varying  $\psi$  until Eq. 5 is zero.

The critical properties and the acentric factors were extracted from Perry and Green (2008), while the remaining parameters (heat capacity coefficients, Wilson coefficients, and binary interaction parameters) were extracted from the Aspen database (AspenTech, 2015). These data are gathered in Xuan (2020), where the tables provide all the relevant data.

#### Compressor power

The overall consumption of the plant is calculated as the sum of the consumption of each compressor. The electrical power consumed by a compressor is equal to the difference of enthalpies between the discharge and the suction streams.

$$W_{\text{comp}} = \frac{H_{\text{out}} - H_{\text{in}}}{\eta_{\text{isen}}} \quad (6)$$

where  $W_{\text{comp}}$  is the electrical consumption of a single compressor in  $W$ ,  $H_{\text{out}}$  and  $H_{\text{in}}$  are, respectively, the enthalpy flow rate at the discharge stream and the suction stream in  $W$ , and  $\eta_{\text{isen}}$  is the isentropic efficiency, which depends on the compressor mechanical losses. The mechanical losses are released to the surroundings, and they can be measured as:

$$W_{\text{loss}} = W_{\text{comp}} - W_{\text{comp}} \eta_{\text{isen}} = W_{\text{comp}} (1 - \eta_{\text{isen}})$$

From Eq. 6, for the whole process:

$$W_{\text{Total}} = \sum_i W_{\text{comp},i} = W_{\text{Prec}} + W_{\text{Liq}} + W_{\text{Sub}}$$

where  $W_{\text{Prec}}$ ,  $W_{\text{Liq}}$ , and  $W_{\text{Sub}}$  are the electrical power consumptions of the precooling, liquefying, and subcooling compressors respectively. The enthalpy flow rate of a stream  $j$  is:

$$H_j = h_j F_j$$

where  $F_j$  is the compressor flow rate of stream  $j$  in  $\text{kmol s}^{-1}$ , and  $h_j$  is the specific enthalpy of stream  $j$  in  $\text{kJ kmol}^{-1}$ .

Table 1. Input values for the LNG process

| Natural Gas Stream | T(K)   | P(bar) | Precooling Cycle Stream | T(K)   | P(bar) | Liquefying Cycle Stream | T(K)   | P(bar) | Subcooling Cycle Stream | T(K)   | P(bar) |
|--------------------|--------|--------|-------------------------|--------|--------|-------------------------|--------|--------|-------------------------|--------|--------|
| 1                  | 298.15 | 30     | 1                       | 283.15 | =P5    | 1                       | 283.15 | =L6    | 1                       | 283.15 | =S7    |
| 2                  | 238.15 | 30     | 2                       | 238.15 | =P1    | 2                       | 238.15 | =L1    | 2                       | 238.15 | =S1    |
| 3                  | 238.15 | 30     | 3                       | Solv   | 2      | 3                       | 173.15 | =L2    | 3                       | 173.15 | =S2    |
| 4                  | 238.15 | 30     | 4                       | 260.15 | 2      | 4                       | Solv   | 2      | 4                       | 120.15 | =S3    |
| 5                  | 173.15 | 30     | 5                       | Solv   | Solv   | 5                       | 220.15 | 2      | 5                       | Solv   | 2      |
| 6                  | 107.15 | 30     | -                       | -      | -      | 6                       | Solv   | Ind    | 6                       | 185.15 | 2      |
| -                  | -      | -      | -                       | -      | -      | -                       | -      | -      | 7                       | Solv   | Ind    |

### Mass and energy balances

The model calculates the refrigerant flow rates by performing energy balances of the three heat exchangers. The following set of equations uses to the nomenclature in Figure 1:

$$F_{\text{Prec}} = \frac{F_{\text{NG1}}(h_{\text{NG2}} - h_{\text{NG1}})}{h_{\text{Abs}}^{\text{Prec}}} + \frac{F_{\text{Liq}}(h_{\text{L2}} - h_{\text{L1}}) + F_{\text{Sub}}(h_{\text{S2}} - h_{\text{S1}})}{h_{\text{Abs}}^{\text{Prec}}} \quad (7)$$

$$F_{\text{Liq}} = \frac{F_{\text{NG3}}(h_{\text{NG5}} - h_{\text{NG3}}) + F_{\text{Sub}}(h_{\text{S3}} - h_{\text{S2}})}{h_{\text{Abs}}^{\text{Liq}}} \quad (8)$$

$$F_{\text{Sub}} = \frac{F_{\text{NG5}}(h_{\text{NG6}} - h_{\text{NG5}})}{h_{\text{Abs}}^{\text{Sub}}} \quad (9)$$

where  $F_{\text{Prec}}$ ,  $F_{\text{Liq}}$ , and  $F_{\text{Sub}}$  are, respectively, the precooling, liquefying, and subcooling refrigerant flow rates in  $\text{kmol s}^{-1}$ . The enthalpies  $h_{\text{Abs}}^{\text{Prec}}$ ,  $h_{\text{Abs}}^{\text{Liq}}$ ,  $h_{\text{Abs}}^{\text{Sub}}$  follow the nomenclature of Figure 2, and they represent the specific heat that the refrigerants can absorb in  $\text{kJ kmol}^{-1}$ :

$$\begin{aligned} h_{\text{Abs}}^{\text{Prec}} &= h_{\text{P1}} - h_{\text{P4}} \\ h_{\text{Abs}}^{\text{Liq}} &= h_{\text{L2}} - h_{\text{L5}} \\ h_{\text{Abs}}^{\text{Sub}} &= h_{\text{S3}} - h_{\text{S6}} \end{aligned}$$

The mass balance in the natural gas flash evaporator ( $\text{FD}_{\text{NG}}$ ) is:

$$\begin{aligned} F_{\text{NG3}} &= F_{\text{NG2}}\psi_{\text{NG2}} \\ F_{\text{NG4}} &= F_{\text{NG2}}(1 - \psi_{\text{NG2}}) \end{aligned}$$

$F_{\text{NG6}}$  and  $F_{\text{NG5}}$  are equal to  $F_{\text{NG3}}$ .

### Overall energy balance

The heat absorbed from the natural gas is ultimately released into the sea by means of the three sea coolers ( $\text{SC}_{\text{Prec}}$ ,  $\text{SC}_{\text{Liq}}$ , and  $\text{SC}_{\text{Sub}}$ ). Considering the work exerted by the compressors, and the losses associated with the compressor work:

$$(H_{\text{P1}} - H_{\text{P5}}) + (H_{\text{L1}} - H_{\text{L6}}) + (H_{\text{S1}} - H_{\text{S7}}) = H_{\text{NG1}} - H_{\text{NG6}} - H_{\text{NG4}} + W_{\text{Total}}\eta_{\text{isen}} \quad (10)$$

Rearranging Equation 10, it can give the heat that the whole process discharges to the sea:

$$\begin{aligned} H_{\text{Sea}} &= (H_{\text{NG1}} - H_{\text{NG6}}) - H_{\text{NG4}} + W_{\text{Total}}\eta_{\text{isen}} \\ &= W_{\text{Total}}\eta_{\text{isen}} + H_{\text{LNG}} - H_{\text{NG4}} \end{aligned}$$

where  $H_{\text{Sea}}$  is the heat released to the sea, and  $H_{\text{LNG}}$  is the total heat absorbed from the natural gas by the refrigerants.

### 3.3 Assumptions and solution approaches

The following assumptions are made to solve the model:

- (1) All temperatures are fixed with exception of the temperatures of the streams exiting the compressors or the valves (P3, P5, L4, L6, S5, and S7).
- (2) There is no pressure drop due to the piping system.
- (3) The discharge pressures after the Joule-Thomson valves in the refrigerant cycles are fixed (P3, L4, and S5), even when the discharge pressures of the compressors vary.
- (4) The compressors are isentropic.
- (5) The natural gas at the beginning of the liquefaction (NG1) enters at 30 bar, and the model considers it constant throughout the whole liquefaction.

Assumption number 1 reflects industrial practice. The process is operated within a limited range of temperatures so that thermal stress does not jeopardize the facilities. The reason for not fixing the temperatures of the streams exiting the compressors or the valves is because they can be calculated. This would not change the degrees of freedom, because such a calculation would add an additional variable but also an additional equation for each stream.

Assumption 3 reduces the degrees of freedom in the model. The alternative would be to calculate these pressures by including the equations of the valves that relate the flow rate and the pressure ratio between the outlet and inlet of the valve. However, the electrical power consumption is not strongly dependent on the pressure ratio across the Joule-Thomson valve, considering that moving the right hand side isobar in Figure 2 does not have a grave consequence on the enthalpy at the exit of the Joule-Thomson expansion. Hence, the pressures are specified in order to simplify the calculations in equations 7 to 9.

Table 1 gives the input values used in the model. The simulations are performed for a production rate of  $15.5 \text{ kmol s}^{-1}$ , equivalent to 7.5 MTPA. The 'Ind' in the pressures column indicates that the variable is independent and must be assigned a value. The 'Solv' term indicates that the temperature and pressure are dependent variables that will be solved using equations present in the model, for instance the equations for the compressors and valves.

With the mentioned assumptions, and the assigned variables, the degrees of freedom of the process can be reduced to two. The model covers these two degrees to assign various values for the two discharge pressures to obtain the effect of the discharge pressure on the electrical power consumption. Thus, the results of the calculations:

- Find the electrical power consumption as a function of compressor discharge pressures.
- Give some deep physical insights into the relationship.
- Suggest the optimum operating point.

#### 4. RESULTS

The results are presented in Figures 5, 6 and 7. In all three pictures, following the pattern in Figure 1, the brown colour represents the precooling cycle, the red colour represents the liquefying cycle, and the green colour represents the subcooling cycle. So, for example, the red lines represent the liquefying streams, and the red shaded areas represent a range of pressures in which a liquefying stream presents a VLE.

The pressure of a stream does not have grave consequences on the enthalpy, unless a VLE is present. The change of enthalpy has grave consequences on the flow rate of the refrigerants (equations 7 to 9). Thus, the results are divided according to the heat exchangers, because the flow rates of the refrigerants are calculated according to the heat balance in the heat exchangers.

##### 4.1 Effects of the discharge pressures observed from the first heat exchanger

Figure 5 represents the effects of varying the discharge pressures of all refrigerant compressors on the precooling flow rate. The relevant pressures are the pressures of the streams related

to the first heat exchanger ( $HEX_{Prec}$  and streams P1, L1, L2, S1, and S2). The graphs do not consider stream P4 because the temperature and pressure in this stream are fixed.

The three graphs in Figure 5.a) show the effect of varying the precooling, liquefying, and subcooling pressures on the precooling flow rate. The reason for observing the flow rates is because the electrical power consumption of the compressors is directly proportional to the flow rate of the refrigerant.

The three graphs in Figure 5.b) show the vapour fraction of each refrigerant when its own discharge pressure varies. Hence, Figure 5.b1) shows the vapour fractions of stream P1 when the precooling refrigerant pressure varies, 5.b2) shows the vapour fractions of L1 and L2 when the liquefying pressure varies, and 5.b3) shows the vapour fractions of S1 and S2 when the subcooling pressure varies. These vapour fractions explain the behaviour of the precooling flow rate.

##### 4.2 Effects of the discharge pressures observed from the second heat exchanger

The two graphs in Figure 6.a) show the effects of varying the refrigerant pressures on the liquefying refrigerant flow rate. The relevant pressures in Figure 6 are the discharge pressures of the streams related to the second heat exchanger ( $HEX_{Liq}$  and streams L2, S2, and S3).

The two graphs in Figure 6.b) show the vapour fraction of each refrigerant when its own discharge pressure varies. Figure 6.b1) shows the vapour fraction of stream L2 when the liquefying pressure varies, and Figure 6.b2) represents the vapour fraction of streams S2 and S3 when the subcooling pressure varies.

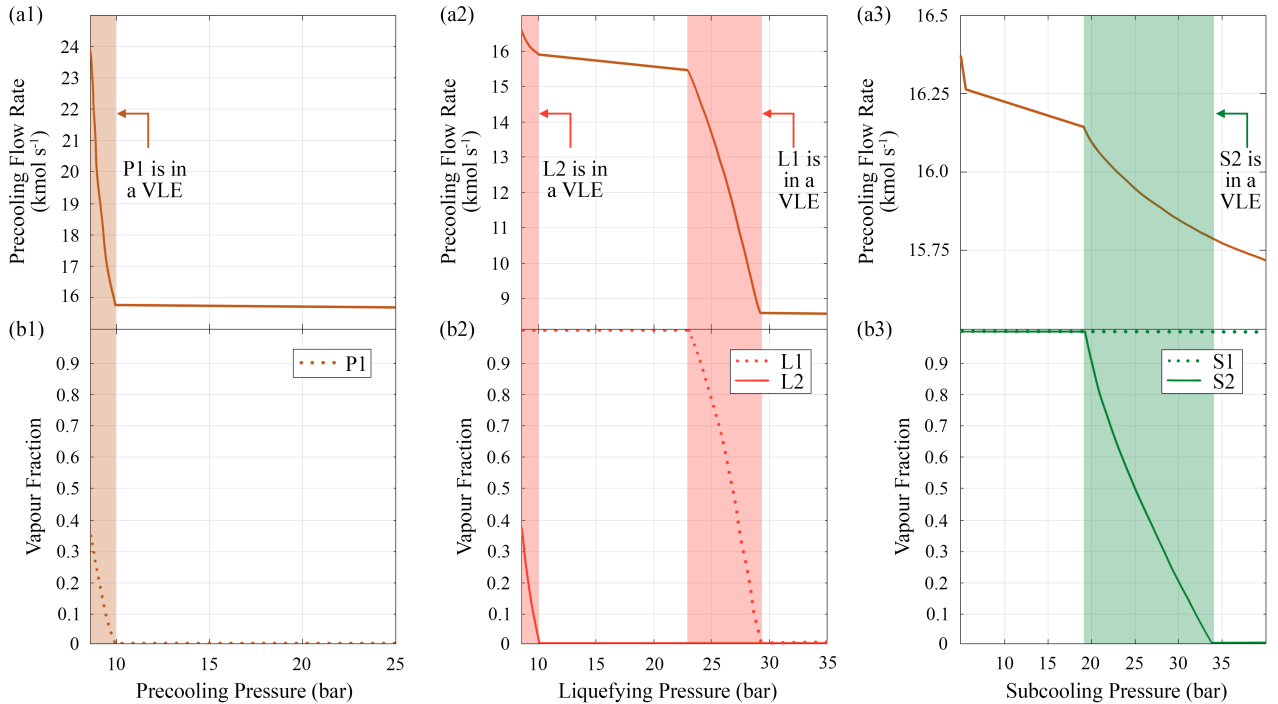


Fig. 5. Effect of varying the pressure of the refrigerants (bar) on (a) the precooling flow rate ( $\text{kmol s}^{-1}$ ), and (b) the vapour fractions in P1, L1, L2, S1, and S2. The shaded areas represent a stream undergoing a VLE.

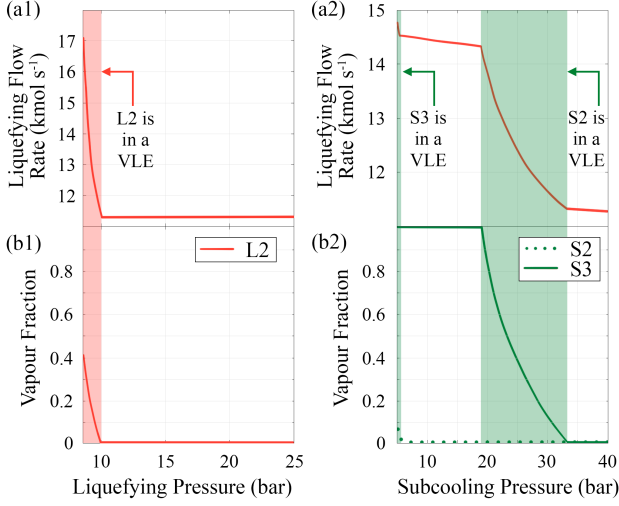


Fig. 6. Effect of varying the discharge pressure of the compressors of the refrigerants (bar) on (a) the liquefying refrigerant flow rate ( $\text{kmol s}^{-1}$ ) and on (b) the vapour fraction in streams L2, S2, and S3.

#### 4.3 Effects of the discharge pressures observed from the third heat exchanger

Figure 7.a) shows the effects of varying the subcooling pressure on the subcooling refrigerant flow rate. The relevant pressures in Figure 7 are the discharge pressures of the streams related to the third heat exchanger ( $\text{HEX}_{\text{Sub}}$  and stream S3). Thus, Figure 7.a) represents the effects of the subcooling pressure on the subcooling flow rate, and Figure 7.b) represents the vapour fraction of stream S3 when the subcooling pressure varies.

Figures 5, 6, and 7 show that the range of pressures in which the refrigerants present a VLE is limited, but within that range, the flow rate of the refrigerants can drastically change. The figures also show that the flow rate of the refrigerants present a plateau when the refrigerant presents only one phase. For example, observing Figure 5.b1) between 8 and 10 bars, stream P1 presents a VLE. Within this VLE, the flow rate, represented in Figure 5.a1), drops from around  $24 \text{ kmol s}^{-1}$  to  $16 \text{ kmol s}^{-1}$ . Above 10 bars, stream P1 does not undergo any phase change, and the precooling flow rate hits a plateau.

#### 4.4 Electrical power consumption of the compressors

The three graphs in Figure 8.a) illustrate the effects of varying the pressure of each refrigerant and the work that the corresponding compressor needs to exert to achieve the established pressure. In Figure 8, compressor choke (shaded areas) occurs when the operating discharge pressure is low, and the flow rate is high. The consequences of a prolonged choke operation can cause damage to the elements in the compressor, so the operation must avoid working in these areas. The model detects choke points by observing the isentropic efficiency of the compressor. Thus, this model programs the choke zone to occur when the isentropic efficiency drops below 65%. The fixed pressures are 15, 15, and 35 bars for the precooling, liquefying, and subcooling refrigerants represented by the circles in Figure 8.b). The model establishes these pressures because they leave a margin from the optimal point for possible disturbances. As explained in Section 5.3, this is the strategy followed in industry.

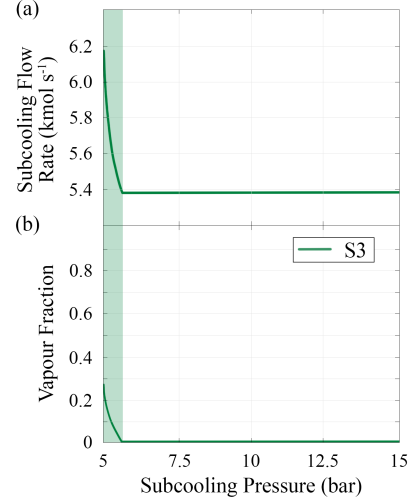


Fig. 7. Effect of varying the pressure of the subcooling refrigerant (bar) on (a) its flow rate ( $\text{kmol s}^{-1}$ ) and on (b) the vapour fraction in stream S3.

The discharge pressure also causes a change in the flow rate. Therefore, the model calculates the total electrical consumption of the plant by multiplying the values in Figure 8.a) by the flow rates given in Figures 5, 6, and 7. The three graphs in Figure 8.b) show the total consumption of the plant. As will be discussed, the discontinuities in 8.b) are given by the discontinuities in the flow rates.

## 5. DISCUSSION

This section discusses the results shown in the previous section, giving demonstrations why the pressures ultimately have effects on the flow rates and comparing the results with industrial practice.

### 5.1 Relationship between discharge pressure and flow rate

#### Relationship between a refrigerant discharge pressure and its own flow rate

Figures 5.a1) and 5.b1) show that P1 presents a VLE when the discharge pressure of the precooling compressor falls below 10 bars. The precooling refrigerant flow rate depends heavily on the discharge pressure of the precooling compressor. The explanation is in Eq. 7 and in Figure 3.

Eq. 7 states that the precooling flow rate is inversely proportional to  $h_{\text{Abs}}^{\text{Prec}} = h_{\text{P1}} - h_{\text{P4}}$ . The model fixes the pressure and temperature in stream P4, and consequently  $h_{\text{P4}}$  is fixed. Figure 3 showed that, if P1 falls within a VLE, a slight change in the pressure leads to a significant change in enthalpy. Therefore, a slight change in the discharge pressure causes a significant change in  $h_{\text{Abs}}^{\text{Prec}}$ , and thus, the precooling refrigerant flow rate changes.

Similarly, Figures 6.a1) and 6.b1) show that L2 presents a VLE when the discharge pressure of the liquefying compressor falls below 10 bars. The liquefying refrigerant flow rate depends heavily on the discharge pressure of the liquefying compressor. Eq. 8 showed that the liquefying refrigerant flow rate is inversely proportional to  $h_{\text{Abs}}^{\text{Liq}} = h_{\text{L2}} - h_{\text{L5}}$ . The properties of stream are fixed, so  $h_{\text{Abs}}^{\text{Liq}}$  varies when the pressure in stream L2

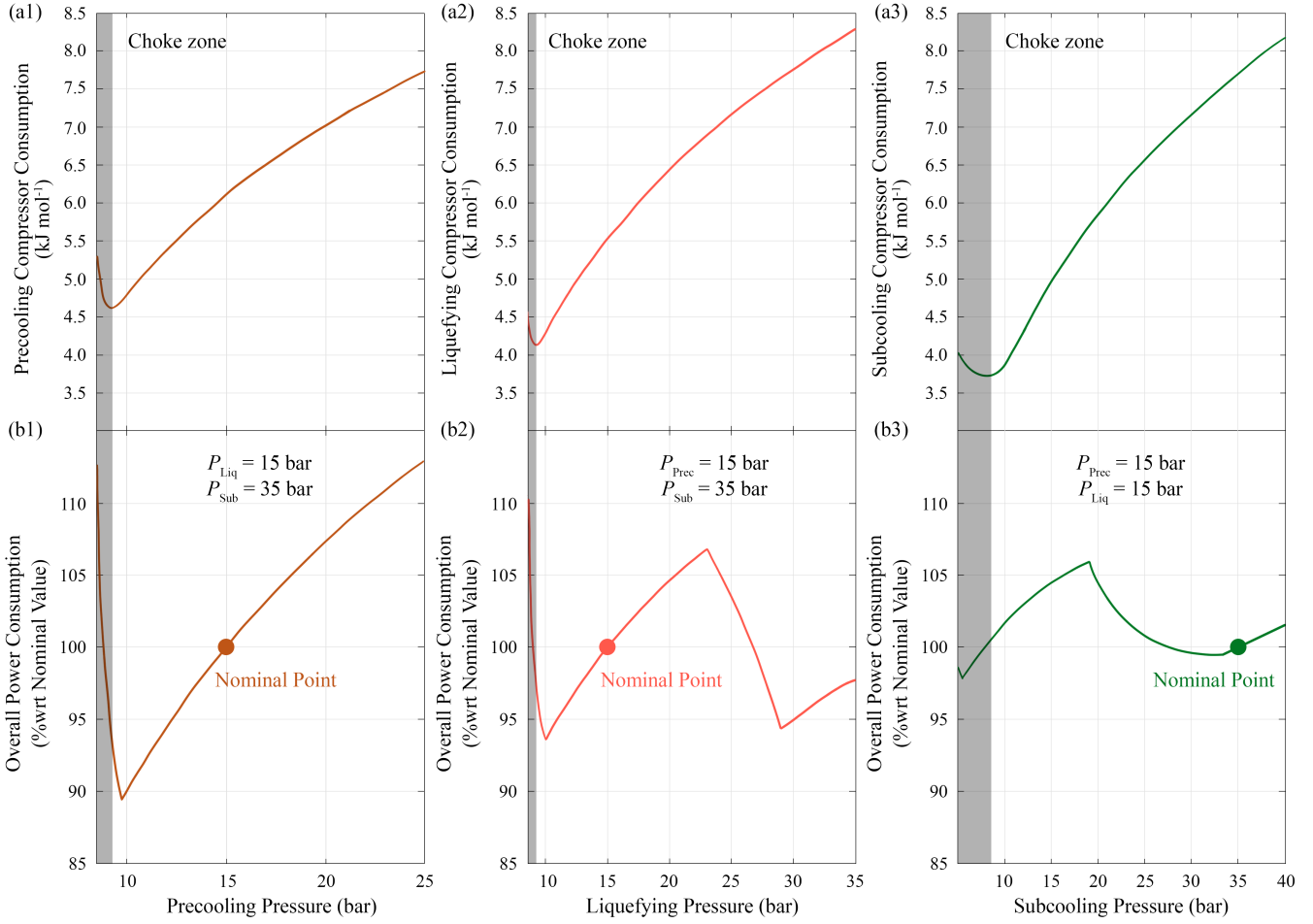


Fig. 8. Effects of varying the discharge pressure of the compressors (bar) on the (a) specific power consumption of the corresponding refrigeration cycle ( $\text{kJ mol}^{-1}$ ), and on the b) overall power consumption (% wrt nominal value).

changes. Consequently, the liquefying flow rate changes with a pressure variation.

The same reasoning can be applied to the subcooling cycle. Figure 7 shows that below 6 bars, S3 presents a VLE. The subcooling refrigerant flow rate varies if the pressure within that VLE varies.

#### Relationship between a refrigerant discharge pressure and other refrigerant flow rates

The precooling refrigerant flow rate is also influenced by the other pressures, but not in such an abrupt manner. Figure 5.a2) shows the relationship between the precooling refrigerant flow rate and the discharge pressure of the liquefying compressor. The graph shows that there are two steep slopes as the discharge pressure of the liquefying compressor varies. The left slope is located below 10 bars, and the slope on the right starts at 22.5 bars. These two slopes correspond to two phase changes. Observing Eq. 7, the terms related to the liquefying cycle are its flow rate  $F_{\text{Liq}}$ , and  $h_{\text{L1}} - h_{\text{L2}}$ . The terms are related to the steep slopes in the following manner:

- Liquefying pressure below 10 bars: The decrease of  $F_{\text{Liq}}$  reduces the precooling flow rate. Figure 6.a1) shows that the liquefying flow rate decreases because of a phase change in L2.

- Liquefying pressure between 22.5 bars and 29.5 bars: The specific enthalpy  $h_{\text{L1}}$  significantly reduces, and consequently,  $h_{\text{L1}} - h_{\text{L2}}$  decreases<sup>1</sup>. From Eq. 7, the precooling flow rate decreases for a decreasing  $h_{\text{L1}} - h_{\text{L2}}$ .

Figure 5.a3) plots the precooling flow rate when the discharge pressure of the subcooling compressor varies. The small slope when the subcooling pressure is below 6 bars is caused by the phase change in S3 shown in Figure 7, which decreases the amount of needed subcooling refrigerant flow rate. Consequently, the amount of heat to be removed from the subcooling refrigerant by the precooling refrigerant in  $\text{HEX}_{\text{Prec}}$  decreases, reducing the precooling refrigerant flow rate.

Figures 5, 6, and 7 showed that changing the discharge pressure of a specific refrigerant compressor affects all three refrigerant flow rates. Figure 8.b2) represents the total electrical power consumption when the liquefying pressure varies. There is a local minimum at 29.5 bars, but Figures 6.a1) and 6.a2) show that the liquefying refrigerant flow rate is not affected by the liquefying pressure. On the other hand, Figures 5.b1) and 5.b2) show that at that pressure, the precooling refrigerant flow rate reaches a plateau that leads to a low electrical power consumption. Thus, the local minimum at 29.5 bars in Figure 8.b2) is due to the decrease in precooling flow rate.

<sup>1</sup> Both terms have negative numerical values

## 5.2 Choosing the right refrigerant pressure

Figures 5, 6, and 7 show that the greater the discharge pressures of the compressors, the lower the flow rate. Figure 8 also showed that the greater the pressure, the greater the work the compressor has to exert.

Thus, the best place to operate is given by a discharge pressure that leads to the highest specific heat flow rate that the refrigerant can absorb, and at the same time leads to the lowest specific electrical power consumption exerted by the compressor.

Figures 5, 6, and 7 showed that, when the pressure is slightly greater than the saturation pressure, the flow rate decrease is not substantial. Hence, increasing the pressure will make almost no difference on the flow rate of the refrigerant. However, the power consumption of the corresponding compressor does increase.

For the subcooling cycle, Figure 7 shows that the ideal situation would be to operate the subcooling compressor at 6 bars. The ideal situation of 6 bars is not feasible due to choking constraints of the compressor observed in Figure 8. Hence, the operating point corresponds to the next saturation point pressure, which is the one undergone by stream S2 at 33 bars. Figure 6.a2) shows that increasing the subcooling compressor discharge pressure reduces the flow rate of the liquefying cycle.

Therefore, the operating point for optimizing the consumption should be slightly above the saturation pressure. This is, for the precooling compressor, slightly above 10 bars, for the liquefying compressor, slightly above 10 bars as well, and for the subcooling compressor, above 33 bars.

## 5.3 Comparison with industrial practice

In real practice, compressors operate at a discharge pressure as close as possible to the saturation point but maintaining a margin in case a disturbance takes place. The industrial practice establishes this operating point because, in the case of working

at the saturation pressure, a slight disturbance might cause the refrigerant to present a VLE. The undesirable consequence of a VLE is that the former liquid state of P1 becomes vapour partially, increasing its volume and applying sudden stress to the pipes, and simultaneously decreasing the amount of heat absorbed from the natural gas, and therefore, increasing the natural gas temperature.

The industrial practice is to operate at 15 bars for the discharge pressure of the precooling compressor, 15 bars for the discharge pressure of the liquefying compressor, and 35 bars for the discharge pressure of the subcooling compressor. Figure 9 shows the effects of varying the precooling and liquefying pressures on the total power consumption when the subcooling pressure is at its optimum. As shown in Figure 8, the optimal pressures for the precooling, liquefying, and subcooling are 9.8, 10, and 33 bars respectively. Figure 9 that the power consumption reduces to 82.5% giving a 17.5% reduction compared to the nominal power consumption at 15, 15, and 35 bars. In a large LNG plant, this corresponds to a reduction of 35 MW.

## 5.4 Suggestions for reducing electrical consumption

The results have pinpointed several ways to achieve lower electrical power consumption. Industrial practice could potentially be improved by working at an operating point in which the discharge pressures cause the streams entering the heat exchangers (P1, L2, and S3 in Figure 1) to be as close to the saturation points as possible. However, it is undesirable to allow a VLE, and development of a VLE has to be detected before it happens.

The authors suggest that a possible strategy could be to calculate the bubble point pressure according to the composition of the refrigerant and establishing a set point for the discharge pressure considering the calculated bubble point pressure. Figure 10 shows a simplified example of the suggestion for the precooling cycle in the LNG plant.

The controllers would be preprogrammed, so the calculations establish a proper set point for the discharge pressure. By setting this control loop, the cycle is prepared for possible disturbances, and therefore, the control system avoids the appearance of a VLE in P1, L2, and S3.

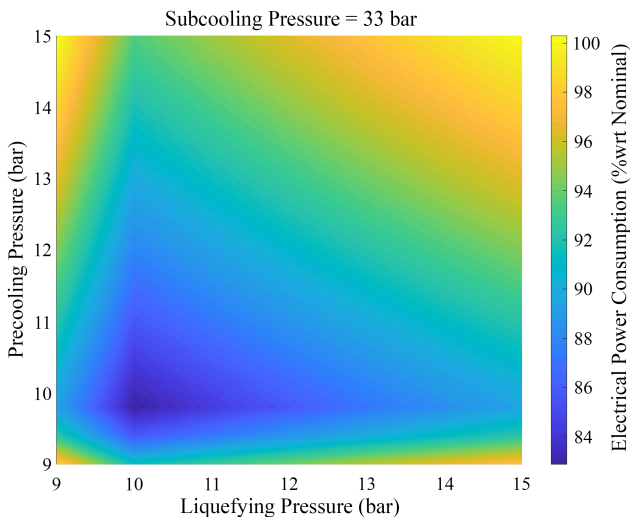


Fig. 9. Effects of varying the discharge pressure of the precooling and liquefying compressors (bar) on the overall power consumption of the plant (MW). The subcooling pressure is established at the optimal pressure found in Figure 8.b3) (33 bar)

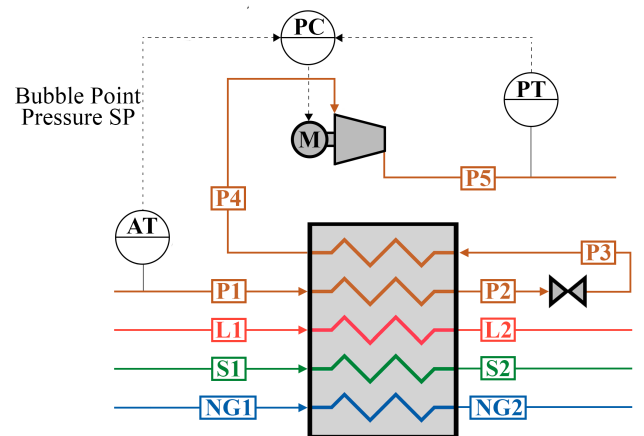


Fig. 10. Control system to enable an operation closer to the VLE. Controller PC adjusts the pressure of the discharge measured by PT to be equal to the set point. The set point is calculated as the bubble point of the refrigerant, based on a composition measurement and calculation (AT).

Figure 8.b3) showed that the overall consumption is at a minimum when the subcooling pressure is at 6 bars. However, that pressure cannot be achieved due to the already mentioned choke problems. Installing an anti-choke valve system can avoid the compressor from falling in the choke zone. Nevertheless, installing the anti-choke system affects the performance of the system by adding flow resistance in the discharge stream (Grace and Frawley, 2011), and hence, varying the pressure of the streams entering the heat exchangers. Thus, it would be necessary to perform a new assessment for this arrangement.

## 6. CONCLUSIONS

This paper has discussed how the electrical power consumption of an LNG plant is influenced by the VLE that can appear in the refrigerant cycles. The VLE is affected by the discharge pressure of the compressors.

The analysis is based on the process by Linde (Linde AG, 2018), using a combination of thermodynamic equations for a mixture of real fluids along with VLE equations. The developed model calculates refrigerant flow rates and electrical power consumption as functions of the discharge pressures of the compressors. The solutions show that the discharge pressure of the compressor has a great influence on the power consumption, especially when the discharge pressure causes a VLE to appear. It is important to avoid falling within the VLE region in said streams because its presence causes the electrical consumption of the plant to increase significantly. On the other hand, it has been found that the combination of discharge pressures that achieves a minimum electrical power consumption corresponds to the pressures just above the refrigerant saturation point pressures, which cause the stream to be liquid.

The process has to fulfil the requirements regarding the LNG characteristics trying at the same time to consume the minimum amount of electrical power. One of the intermediate links between the LNG characteristics and the electrical power consumption is the change of discharge pressure of the refrigerant compressors used in the Joule-Thomson cycle. This work has found that link and it has obtained a combination of pressures that achieves a minimum power consumption while meeting the process requirements of production and LNG final temperature.

The discharge pressure of a refrigerant compressor has an influence on the flow rates of the remaining refrigerant, giving a combination of possibilities for operating the compressors with the same electrical power consumption.

The insights of the first principles provided in the model have enabled an analysis of the electrical consumption of the LNG Linde process. The compressor discharge pressures have a great influence in operating the LNG process efficiently. These discharge pressures affect the appearance of VLE in the streams entering the heat exchangers. This paper has made suggestions on how to operate the plant for reducing the electrical power consumption, mentioning a control loop that causes the discharge pressure of the compressors to be just above the refrigerant saturation point pressure.

## ACKNOWLEDGEMENT

This work was supported by ABB under the the ABB Imperial College Strategic Alliance framework. The first author gratefully acknowledges full financial support for his PhD from ABB.

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## Appendix A. RKS EQUATIONS

This appendix includes the derivations of the variables corresponding to the RKS equations.

### A.1 Equation of State for single components and mixtures

The RKS equation of state is:

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m - b)}$$

where  $P$  is the pressure in Pa,  $V_m$  is the molar volume in  $\text{m}^3 \text{mol}^{-1}$ ,  $T$  is the temperature in K, and  $R$  is the ideal gas constant.  $a$ ,  $b$ , and  $\alpha$  are expressed as:

$$a = 0.427 \frac{(RT_c)^2}{P_c}$$

$$b = 0.0866 \frac{RT_c}{P_c}$$

$$\alpha = \left(1 + s \left(1 - \sqrt{\frac{T}{T_c}}\right)\right)^2$$

where  $T_c$  is the critical temperature in K,  $P_c$  is the critical pressure in Pa, and  $s$  is given by:

$$s = (0.48508 + 1.552\omega - 0.15613\omega^2)$$

where  $\omega$  is the acentric factor, which is a parameter characteristic of each component. The presented equations are applicable for a single component. For a mixture, the parameters follow the classical mixing rules as seen below:

$$a\alpha_{ij} = (1 - k_{ij})\sqrt{a_i a_j \alpha_i \alpha_j}$$

$$b = \sum_{i=1}^C b_i x_i$$

where  $k_{ij}$  is the binary interaction parameter between components  $i$  and  $j$ ,  $x_i$  is the mole fraction of component  $i$ ,  $x_j$  is the mole fraction of component  $j$ , and  $C$  is the total number of components in the mixture.

### A.2 Enthalpies

The enthalpies are obtained by solving the RKS equations. Because the model deals with real fluids, it is necessary to use the departure function, which is the difference between the value of the property for an ideal gas and its value for a real fluid. Thus, for the enthalpy:

$$h = h^{ideal} + h^{Dep} \quad (\text{A.1})$$

where  $h$  is the specific enthalpy of a stream in  $\text{kJ kmol}^{-1}$ ,  $h^{ideal}$  is the specific enthalpy in  $\text{kJ kmol}^{-1}$  if the stream were ideal, and whose equation is given by:

$$h^{ideal} = \sum_i y_i \int_{T_0}^T c_{p_i} dT$$

where  $y_i$  is the composition of component  $i$ ,  $c_{p_i}$  is the heat capacity in  $\text{kJ kmol}^{-1} \text{K}^{-1}$  and  $T_0$  is the base temperature in K. The heat capacity of each component ( $c_{p_i}$ ) is calculated using the following equation:

$$c_{p_i} = c_{p,0} + c_{p,1}T + \frac{c_{p,2}T^2}{2} + \frac{c_{p,3}T^3}{3} + \frac{c_{p,4}T^4}{4} + \frac{c_{p,5}T^5}{5}$$

where  $c_{p,x}$  are parameters characteristic of each component. Returning to Eq. A.1,  $h^{Dep}$  is the departure enthalpy in  $\text{kJ kmol}^{-1}$ , a departure function is calculated as:

$$f^{Dep} = \int_V^\infty \left[ T \left( \frac{\partial Z}{\partial T} \right)_V \frac{dV}{V} \right] + 1 - Z$$

where  $Z$  is the compressibility factor, which is:

$$Z = \frac{PV}{RT}$$

For the RKS gather, the departure enthalpy can be obtained as:

$$h^{Dep} = (PV_m - RT) - \frac{a\alpha - T \frac{\partial a\alpha}{\partial T}}{b} \ln \left( \frac{V_m + b}{V_m} \right)$$

where  $\frac{\partial a\alpha}{\partial T}$  is derived according to the EoS used in the model. In this case, for the RKS:

$$\frac{\partial a\alpha}{\partial T} = \sum_i \sum_j y_i y_j (1 - k_{ij}) \sqrt{a_i a_j} \times \left( -\frac{s_i}{2T_{ci}T_{ri}^{0.5}} - \frac{s_j}{2T_{cj}T_{rj}^{0.5}} + s_i s_j \frac{T_{rj}^{0.5} - 1}{2T_{ci}T_{ri}^{0.5}} + \frac{T_{ri}^{0.5} - 1}{2T_{cj}T_{rj}^{0.5}} \right)$$

These equations were modelled in Matlab, so that the research improves the reproducibility of its methodology by providing a higher transparency of the equations and easy access to the parameters of the components.