

1 **Development and Use of Exergy Efficiency for Complex**

2 **Cryogenic Processes**

3

4 Donghoi Kim and Truls Gundersen*

5 Department of Energy and Process Engineering, Norwegian University of Science and Technology (NTNU),

6 Kolbjørn Hejes vei 1B, NO-7491, Trondheim, Norway

7 Keywords: Exergy decomposition, Exergy efficiency, LNG process, Dual mixed refrigerant, Optimization

8 **Abstract**

9 In this paper, exergy efficiencies, which are effective performance parameters for cryogenic processes, are
10 categorized based on their exergy decomposition levels. However, the existing efficiencies are not standardized
11 for a variety of unit operations. Thus, the extension of the exergy transfer effectiveness (*ETE*) has been suggested
12 with a general mathematical expression. The extended *ETE* is defined by decomposing both thermo-mechanical
13 and chemical exergy to the chemical component level. A case study with a complex natural gas liquefaction
14 process and its optimization has also been performed. The results indicate that the extended *ETE* brings consistent
15 and accurate results for all types of units, also properly reflecting the changes in process performance after
16 optimization. Other efficiencies, however, struggle to measure the performance improvement for some equipment,
17 even showing decreases in their efficiency values.

18 **1. Introduction**

19 With the current focus on global warming and use of fossil fuels, energy efficiency is an important performance
20 measure in industrial plants. As a post-design tool, energy efficiency has been applied to various energy systems
21 in order to evaluate and compare them, thus finding opportunities to improve the processes. Such definitions of
22 energy efficiency are case-dependent based on the characteristics of a process, which means a general
23 mathematical expression for energy efficiency does not exist [1]. This may bring misinterpretations into the
24 definitions of energy efficiency and produce inconsistent results even for the same system. Thus, there is a need

25 for an objective performance parameter for energy conversion efficiency. Another limitation of using energy
26 efficiency is that it does not take energy quality into account when measuring process performance. Different
27 energy forms have different qualities, for example, the value of heat cannot be directly compared with the value
28 of power because the energy quality of the heat will vary, depending on the temperature level. In the case of
29 refrigeration processes where work is transformed into a cooling duty, there is no proper definition for energy
30 efficiency [2]. Instead, a coefficient of performance is used, which unfortunately gives equal values to heat and
31 power.

32 Unlike energy analysis, exergy accounts for both quantity and quality of various energy forms, which is why
33 exergy has been recommended as a measure of system performance [3]. Due to the characteristics of entropy
34 generation below ambient temperature, exergy efficiency is a good performance indicator, especially for low
35 temperature processes in a post-design phase. Regarding liquefied natural gas (LNG), specific power consumption
36 per produced amount of LNG is widely used to evaluate the performance of liquefiers, since there is no proper
37 energy efficiency definition for such processes. However, this value does not consider the cold energy of the
38 produced LNG. The LNG generally contains a significant amount of cold exergy (around 1000 kJ/kg), and this
39 exergy is utilized in many LNG terminals [4]. Thus, the cold energy of the produced LNG has to be included
40 when measuring the performance of the liquefaction process. In addition, the specific power consumption will
41 depend on local environmental conditions (i.e. climate). An LNG plant located in a warm climate region will
42 always show a larger power consumption than one in cold climate, even when they have exactly the same
43 processing system. In contrast, exergy can represent various energy forms in one standard (i.e. heat, work and
44 power), while considering the effect of the environment conditions, particularly temperature and pressure.
45 Therefore, exergy efficiency would be a good candidate to measure the performance of processes in order to have
46 an objective and consistent analysis.

47 Such an exergy efficiency can be formulated in various ways, but tends to fall into two main categories [1]. One
48 is the input-output efficiency, which is the ratio between the exergy leaving and entering the system. The input-
49 output efficiency is defined by a simple formulation and applicable to any types of processes, thus widely used
50 [5]. Yet, this efficiency definition may not be ideal for process evaluation and comparison [5-9]. The input-output
51 efficiency may show only a marginal difference with changes in process performance, since it is not focusing on
52 the task of a process. Thus, there have been various suggestions for exergy efficiency, considering the purpose of
53 a system [8, 10-13]. These are called the consumed-produced or task efficiencies, which is the second category of

54 exergy efficiency. The consumed-produced efficiency describes what is consumed to deliver a specific or targeted
55 product from a process.

56 Nevertheless, it is difficult to determine which efficiency definition is the right one to use due to their inconsistent
57 results for a typical process. Several definitions of the consumed-produced efficiency suggested in the literature
58 do not contain general mathematical expressions, thus causing room for different interpretations [14]. This has
59 resulted in different definitions of exergy efficiency for the same system, from small units to large systems such
60 as Joule Thomson valves, gas expanders, air separation units (ASUs), LNG processes and processes for offshore
61 platforms. [2, 5, 15-20]. Thus, there have been attempts to develop more generalized task efficiencies by removing
62 so-called transit exergy from consideration, which is defined as the amount of exergy that is preserved across a
63 system [13]. However, this definition requires a high calculation effort. Zanchini also formulated an exergy
64 efficiency that can generalize some of the task efficiencies, while being applicable for both flowing and non-
65 flowing systems [17]. Nguyen et al. suggested an efficiency for offshore platforms, which can cover various
66 processes with decomposition of exergy to the chemical component level [9]. None of the efficiencies mentioned
67 above have explicit definitions for cases where processes operate across or below ambient temperature.

68 Thus, a new general exergy efficiency, the Exergetic Transfer Effectiveness (*ETE*) was developed to handle all
69 operating conditions with less computational effort by defining exergy sources and sinks as consumed and
70 produced exergy [21]. The *ETE* also allows encapsulating the actual transfer of exergy in a process, indicating the
71 purpose of the system. Such careful definition is achieved by focusing on the effect of temperature and pressure
72 changes, and by decomposing exergy into different forms.

73 However, the use of the *ETE* has so far been limited to processes without chemical reactions or compositional
74 changes, simply because the decomposition of exergy forms to identify sources and sinks had not been developed
75 to include chemical exergy. Thus, this paper extends the *ETE* by including chemical exergy to cover all types of
76 processes at all operating conditions with a general mathematical expression. The extended *ETE* and other
77 consumed-produced efficiencies are then thoroughly classified and compared, indicating the characteristics of the
78 efficiency definitions. This paper also compares the *ETE* with the input-output efficiency and selected task
79 efficiencies, where generalized formulas have been suggested. The comparison is conducted by applying them to
80 a natural gas liquefaction process referred to as the dual mixed refrigerant (DMR) process. The DMR process is
81 a good candidate to study the capability of exergy efficiencies to manage changes in temperature, pressure and

82 chemical composition. This comparison of exergy efficiencies will provide guidance about a proper choice of
83 exergy efficiency based on their characteristics (classification). The mathematical optimization of the DMR
84 process is also performed to evaluate exergy efficiencies for the optimal operating conditions. Although exergy
85 efficiency is a post design tool to measure the improvement of systems, the comparison of the efficiency values
86 for the initial and the optimal operating conditions have not been made in previous literature. Thus, this paper
87 conducts the comparison in order to evaluate the performance of exergy efficiencies whether they properly reflect
88 the improvement of the process after optimization.

89 2. Exergy and exergy efficiency

90 2.1 Exergy

91 Exergy is the maximum available work obtained by bringing a system to equilibrium with its environment [22].
92 Thus, it is a function of both the state of the system and its environment. However, there are various exergy
93 classifications suggested with different exergy forms [21]. Thus, in this work, the classification suggested by
94 Marmolejo Correa and Gundersen is used with further decomposition of exergy [14].

95 Based on the classification, exergy of a material stream flowing through a system can be expressed by two
96 components, thermo-mechanical exergy (\dot{E}^{TM}) and chemical exergy (\dot{E}^{Ch}) as seen in Eq. (1) [13]. This will be
97 referred to as the *first level* of exergy decomposition. Due to the nature of the processes studied, kinetic, potential,
98 electrical and nuclear exergies are not considered.

$$\dot{E}^{\text{Total}} = \dot{E}^{\text{TM}} + \dot{E}^{\text{Ch}} \quad (1)$$

99 Thermo-mechanical exergy represents the available work obtained from the material stream by bringing it from
100 its original state to its environment temperature (T_0) and pressure (p_0) through reversible processes and is given
101 by:

$$\dot{E}^{\text{TM}} = \dot{H}(T, p) - \dot{H}(T_0, p_0) - T_0[\dot{S}(T, p) - \dot{S}(T_0, p_0)] \quad (2)$$

102 Thermo-mechanical exergy, also referred to as physical exergy in various literature [7, 8, 22], can be further
103 decomposed to temperature based exergy (\dot{E}^{T}) and pressure based exergy (\dot{E}^{P}) as seen in Eq. (3). These terms
104 indicate the temperature and pressure portions of the available work (\dot{E}^{TM}), respectively. Similar to thermo-

105 mechanical exergy, temperature based exergy and pressure based exergy can be defined by Eq. (4) and Eq. (5).
 106 This decomposition is not unique, thus it does not have a specific physical meaning. Nevertheless, it has proven
 107 advantageous when analyzing processes.

$$\dot{E}^{\text{TM}} = \dot{E}^{\text{T}} + \dot{E}^{\text{P}} \quad (3)$$

$$\dot{E}^{\text{T}} = \dot{H}(T, p) - \dot{H}(T_0, p) - T_0[\dot{S}(T, p) - \dot{S}(T_0, p)] \quad (4)$$

$$\dot{E}^{\text{P}} = \dot{H}(T_0, p) - \dot{H}(T_0, p_0) - T_0[\dot{S}(T_0, p) - \dot{S}(T_0, p_0)] \quad (5)$$

108 Chemical exergy is the reversible work obtained by bringing the material stream with environment temperature
 109 and pressure to equilibrium with the chemical composition of the environment. Thus, chemical exergy is
 110 independent of the temperature and pressure level of the material stream. Similar to thermo-mechanical exergy,
 111 chemical exergy has two parts, referred to as concentrational exergy (\dot{E}^{Conc}) and reactional exergy (\dot{E}^{Reac}) as
 112 introduced in Eq. (6).

$$\dot{E}^{\text{Ch}} = \dot{E}^{\text{Conc}} + \dot{E}^{\text{Reac}} \quad (6)$$

113 Concentrational exergy indicates the work required to separate a mixture into pure chemical components as seen
 114 in Eq. (7). The value of concentrational exergy for mixtures is negative due to the interactions between chemical
 115 components in real gases and the work needed to increase the partial pressure of each component separated from
 116 the mixture to environment pressure. For ideal gases and ideal mixtures, only the latter will remain in the
 117 expression for concentrational exergy. Concentrational exergy is also referred to as mixing exergy since it
 118 represents the reduction in exergy due to mixing pure components [6, 23].

$$\begin{aligned} \dot{E}^{\text{Conc}} &= \dot{H}(T_0, p_0) - \sum_i x_i \dot{H}_i^{\text{pure}}(T_0, p_0) - T_0 \left[\dot{S}(T_0, p_0) - \sum_i x_i \dot{S}_i^{\text{pure}}(T_0, p_0) \right] \\ &= RT_0 \sum_i \dot{n}_i \ln x_i \text{ for ideal gas and ideal mixture} \end{aligned} \quad (7)$$

119 For reference species in the environment, reactional exergy is the reversible work obtained from a pure component
 120 stream at T_0 and p_0 by bringing it to the partial pressure of the component in the environment (Eq. 8). Thus, the
 121 value of reactional exergy for reference species depends on the concentration of the species in the environment.
 122 In Eq. (8), $\bar{e}_{i,0}^{\text{Chem}}$ stands for the standard chemical exergy of component i at ambient conditions. In this work, the

123 reference species and concentrations were implemented from Szargut to calculate molar reaction exergy of a
 124 pure component, which is also referred to as the standard chemical exergy [24]. The standard chemical exergy for
 125 species not present in the environment will be calculated by an extra step, which is a reversible reaction to convert
 126 the non-reference components to reference components.

$$\dot{E}^{\text{Reac}} = \sum x_i \dot{n}_i \bar{e}_{i,0}^{\text{Chem}} \quad (8)$$

127 Then, the four components of exergy (\dot{E}^{T} , \dot{E}^{P} , \dot{E}^{Conc} , \dot{E}^{Reac}) are regarded as the *second level* of exergy
 128 decomposition. Finally, these exergy components can be further decomposed to the chemical component level in
 129 a mixture by performing numerical calculations, and this will be referred to as the *third level* of exergy
 130 decomposition in this paper. The partial molar exergy can be determined by Eq. (9) where EX is the set of exergy
 131 components in the *second level* decomposition. Fig. 1 shows an overview of exergy decompositions defined and
 132 used in this work. Based on this decomposition of exergy, various definitions of exergy efficiency can be
 133 categorized in the next section.

$$\bar{e}_i^m = \left(\frac{\partial \dot{E}_{\text{mixture}}^m}{\partial \dot{n}_i} \right)_{T,p,\dot{n}_l \neq i}, \quad m \in \text{EX} \quad (9)$$

134 Apart from the exergy carried by a process stream, heat can also flow into a system, having an exergy value as
 135 seen in Eq. (10). In this paper, the exergy of heat (\dot{E}^{Q}) is also included in the definitions of exergy efficiency in
 136 the next section in order to handle systems with heat input and output although it is not the case for the process
 137 candidate evaluated by the exergy efficiencies in this paper.

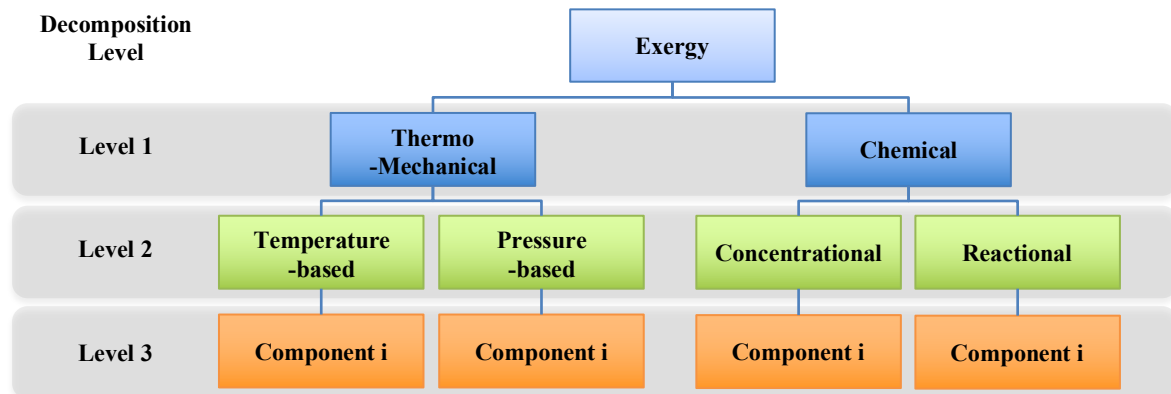
$$\dot{E}^{\text{Q}} = \dot{Q} \times \left(1 - \frac{T_0}{T} \right) \quad (10)$$

138 Use of an efficiency parameter helps to evaluate and compare processes with different operating conditions and
 139 configurations. For an objective comparison, applying an efficiency definition containing an explicit expression
 140 is essential to achieve consistent results as a performance parameter. Efficiencies having ambiguous definitions
 141 will leave room for different interpretations when applied to the same process. Thus, for exergy efficiency, several
 142 definitions have been suggested with general mathematical expressions for the sake of consistency [9, 13, 21].
 143 Such generalized equations for the definitions allow handling all types of processes that are experiencing changes
 144 in both thermo-mechanical and chemical exergies. Therefore, the following generalized exergy efficiencies were

145 selected and compared as performance indicators in this paper in order to evaluate their accuracy and consistency
 146 for a complex process.

147 2.2 Input-output exergy efficiency

148 One of the generalized exergy efficiencies can be classified as the input-output efficiency. This efficiency is
 149 expressed as the ratio between all the exergy leaving and entering the system as seen in Eq. (11).



150

151 Fig. 1. Decomposition of exergy for a material stream.

$$\eta_{in-out} = \frac{\sum \text{Exergy out}}{\sum \text{Exergy in}} \quad (11)$$

152 The input-output efficiency is regarded as a reasonable performance parameter for systems having most of the
 153 output streams as valuable products [1]. The input-output efficiency can also be an alternative to the consumed-
 154 produced efficiency. The task efficiency, which is another name for the consumed-produced efficiency, requires
 155 a definition of the necessary exergy inputs and the desired exergy products of a system. In addition, describing
 156 the consumption and production for dissipative units or complex processes will be even more challenging. The
 157 input-output efficiency, however, can be applied to any type of process due to the simple definition of the
 158 numerator and the denominator. On the other hand, the simplicity reduces the ability of the input-output efficiency
 159 to properly address the task or purpose of a system.

160 2.3 Consumed-produced exergy efficiency

161 There are also a number of exergy efficiencies classified as the consumed-produced type of efficiency. These
162 efficiencies address the task of a process and are expressed by the ratio between the produced and the consumed
163 amount of exergy:

$$\eta_{\text{consumed-produced}} = \frac{\text{Produced Exergy}}{\text{Consumed Exergy}} \quad (12)$$

164 Depending on the definition of the consumed and produced exergies, the value of the efficiency can vary. Kotas
165 [8] defined them as desired outputs and necessary inputs. Tsatsaronis [7] used exergy of products and exergy of
166 fuel for the definition of the task efficiency. The aforementioned definitions, however, do not have general
167 mathematical expressions. Thus, they may result in different interpretations. Therefore, the following task
168 efficiencies suggesting generalized formulas are in this paper considered candidates for evaluation of complex
169 processes having changes in temperature, pressure and chemical composition.

170 2.3.1 Coefficient of exergy efficiency

171 Brodyansky et al. [13] defined an exergy efficiency, offering general mathematical expressions for changes in
172 both thermo-mechanical and chemical exergy. It is called the Coefficient of Exergy Efficiency (*CEE*) and
173 expressed by subtracting the transit exergy from the inlet and outlet streams:

$$CEE = \frac{\sum \text{Exergy out} - \text{Transit Exergy}}{\sum \text{Exergy in} - \text{Transit Exergy}} \quad (13)$$

174 The transit exergy is the amount of exergy that does not undergo any change across a process. Thus, by subtracting
175 the transit exergy from the total exergy entering and leaving the system, the *CEE* only focuses on the amount of
176 exergy that is changed through the process, which is directly related to the task of the system. Table 1 shows the
177 formulas of transit exergy for thermo-mechanical, chemical, work and heat exergies. Here, work exergy will be
178 pure electricity or shaft work supplied or produced by turbo-machinery in a process. T_{\min} and T_{\max} are the lowest
179 and highest temperatures among the inlet and outlet streams of a system. Due to the detailed definition of the
180 thermo-mechanical transit exergy in the *CEE*, the ambient conditions are partly accounted for.

181 Table 1 Transit part of exergy components [13].

Transit exergy	
Thermo-mechanical exergy	
a. Systems operating above T_0 :	
$\dot{E}^{\text{tr}} = \min \begin{bmatrix} \dot{E}_{\text{in}}^{\text{TM}}(T_{\text{min}}, p_{\text{in}}) & \dot{E}_{\text{in}}^{\text{TM}}(T_{\text{min}}, p_{\text{out}}) \\ \dot{E}_{\text{out}}^{\text{TM}}(T_{\text{min}}, p_{\text{in}}) & \dot{E}_{\text{out}}^{\text{TM}}(T_{\text{min}}, p_{\text{out}}) \end{bmatrix}$	
b. Systems operating below T_0 :	
$\dot{E}^{\text{tr}} = \min \begin{bmatrix} \dot{E}_{\text{in}}^{\text{TM}}(T_{\text{max}}, p_{\text{in}}) & \dot{E}_{\text{in}}^{\text{TM}}(T_{\text{max}}, p_{\text{out}}) \\ \dot{E}_{\text{out}}^{\text{TM}}(T_{\text{max}}, p_{\text{in}}) & \dot{E}_{\text{out}}^{\text{TM}}(T_{\text{max}}, p_{\text{out}}) \end{bmatrix}$	
c. Systems operating across T_0 :	
$\dot{E}^{\text{tr}} = \min \begin{bmatrix} \dot{E}_{\text{in}}^{\text{TM}}(T_0, p_{\text{in}}) & \dot{E}_{\text{in}}^{\text{TM}}(T_0, p_{\text{out}}) \\ \dot{E}_{\text{out}}^{\text{TM}}(T_0, p_{\text{in}}) & \dot{E}_{\text{out}}^{\text{TM}}(T_0, p_{\text{out}}) \end{bmatrix}$	
Chemical exergy	
$\dot{E}^{\text{tr}} = \sum_i \dot{n}_i \min[\bar{e}_{\text{in},i}^{\text{Ch}}, \bar{e}_{\text{out},i}^{\text{Ch}}]$	
Work exergy	
$\dot{E}^{\text{tr}} = \min[\dot{E}_{\text{in}}^{\text{W}}, \dot{E}_{\text{out}}^{\text{W}}]$	
Exergy of heat	
$\dot{E}^{\text{tr}} = \min[\dot{E}_{\text{in}}^{\text{Q}}, \dot{E}_{\text{out}}^{\text{Q}}]$	

182 However, the CEE does not decompose thermo-mechanical exergy to the second or third level (see Fig.1), and
 183 chemical exergy is decomposed to the chemical component level without splitting it into concentrational and
 184 reactional exergy. This may give an inaccurate estimation of consumed and produced exergies. In addition, Table
 185 1 indicates that the calculation procedure for the transit part of thermo-mechanical exergy requires extra streams,
 186 which have different conditions than the original inlet and outlet streams. This will increase the computing effort
 187 for the CEE [15]. Due to the definition of transit work exergy, the CEE considers only net work as consumed or
 188 produced exergy.

189 2.3.2 Component-by-component exergy efficiency

190 As part of an effort to develop a performance parameter for offshore oil and gas processing, Nguyen et al. [9]
 191 developed an exergy efficiency with explicit formulas, which is referred to as the Component-by-Component
 192 exergy efficiency (called *CBC* in this paper). Eq. (14) represents the *CBC* where Z is the set of chemical
 193 components, I is the set of inlet streams, and O is the set of outlet streams. The *CBC* pays attention to the changes
 194 in partial molar thermo-mechanical exergy of each chemical component between inlet and outlet streams across
 195 a process ($\Delta \dot{E}_{j,k}^{\text{TM}}$) (Eqs. (15)-(17)). If the partial molar exergy value of an inlet stream is larger than the one of an
 196 outlet stream, the reduction will be considered as consumed exergy and vice versa. For Eq. (17), only multiple

197 inlet streams with one outlet stream or one inlet stream with multiple outlet streams are considered for a unit or a
 198 process.

$$CBC = \frac{\sum_j \sum_k (\Delta \dot{E}_{j,k}^{TM})^+ + \Delta \dot{E}^{Ch}}{\sum_j \sum_k (\Delta \dot{E}_{j,k}^{TM})^- + \dot{E}^{W_{net}} + \dot{E}^Q}, \quad i \in Z, j \in I, k \in O \quad (14)$$

199 where

$$(\Delta \dot{E}_{j,k}^{TM})^+ = \begin{cases} \sum_i \dot{n}_{i,j,k} (\bar{e}_{i,k}^{TM} - \bar{e}_{i,j}^{TM}) & \text{if } \bar{e}_{i,k}^{TM} > \bar{e}_{i,j}^{TM} \\ 0 & \text{if } \bar{e}_{i,k}^{TM} < \bar{e}_{i,j}^{TM} \end{cases} \quad (15)$$

$$(\Delta \dot{E}_{j,k}^{TM})^- = \begin{cases} 0 & \text{if } \bar{e}_{i,k}^{TM} > \bar{e}_{i,j}^{TM} \\ \sum_i \dot{n}_{i,j,k} (\bar{e}_{i,j}^{TM} - \bar{e}_{i,k}^{TM}) & \text{if } \bar{e}_{i,k}^{TM} < \bar{e}_{i,j}^{TM} \end{cases} \quad (16)$$

$$\dot{n}_{i,j,k} = \begin{cases} \dot{n}_{i,k} & \text{if } \dot{n}_{i,j} > \dot{n}_{i,k} \\ \dot{n}_{i,j} & \text{if } \dot{n}_{i,j} < \dot{n}_{i,k} \end{cases} \quad (17)$$

200 $\dot{n}_{i,j,k}$ represents the molar flow rate of component i flowing from the inlet stream j to the outlet stream k . The
 201 CBC is mainly intended for petroleum separation processes. Thus, the formula for exergy efficiency assumes that
 202 chemical exergy is always increasing and there is no heat produced in the separation process. The increment in
 203 chemical exergy ($\Delta \dot{E}^{Ch}$) is regarded as produced exergy, while the heat used in the separation is regarded as
 204 consumed exergy. This explains the numerator and denominator in Eq. (14). However, in the case of mixers, the
 205 total chemical exergy of the inlet streams will decrease due to reduction in concentrational exergy. Further, in the
 206 case of exothermic reactions, heat will be produced. Thus, in our work, the CBC exergy efficiency was modified
 207 to properly cover both positive and negative changes in chemical exergy and heat of reaction (Eqs. (18)-(20)). In
 208 addition, net work was regarded as consumed exergy since the original CBC does not consider the case where
 209 work is produced from a process. The CBC applies decomposition of thermo-mechanical exergy only to the
 210 component level (i.e. the *third level*). Without the *second level* decomposition of thermo-mechanical exergy, the
 211 effect of variation in temperature and pressure will not be correctly represented by the CBC . In addition, the
 212 efficiency does not consider further decomposition of chemical exergy, and this will result in inaccurate consumed
 213 and produced exergies.

$$CBC = \frac{\sum_j \sum_k (\Delta \dot{E}_{j,k}^{TM})^+ + (\Delta \dot{E}^{Ch})^+ + \dot{E}^{Q_{prod}}}{\sum_j \sum_k (\Delta \dot{E}_{j,k}^{TM})^- + (\Delta \dot{E}^{Ch})^- + \dot{E}^{W_{net}} + \dot{E}^{Q_{cons}}}, \quad (18)$$

214 where

$$(\Delta \dot{E}^{\text{Ch}})^+ = \begin{cases} \sum_k \dot{E}_k^{\text{Ch}} - \sum_j \dot{E}_j^{\text{Ch}} & \text{if } \sum_k \dot{E}_k^{\text{Ch}} > \sum_j \dot{E}_j^{\text{Ch}} \\ 0 & \text{if } \sum_k \dot{E}_k^{\text{Ch}} < \sum_j \dot{E}_j^{\text{Ch}} \end{cases} \quad (19)$$

$$(\Delta \dot{E}^{\text{Ch}})^- = \begin{cases} 0 & \text{if } \sum_k \dot{E}_k^{\text{Ch}} > \sum_j \dot{E}_j^{\text{Ch}} \\ \sum_j \dot{E}_j^{\text{Ch}} - \sum_k \dot{E}_k^{\text{Ch}} & \text{if } \sum_k \dot{E}_k^{\text{Ch}} < \sum_j \dot{E}_j^{\text{Ch}} \end{cases} \quad (20)$$

2.3.3 Exergy Transfer Effectiveness

Marmolejo Correa and Gundersen also suggested a generalized exergy efficiency that is particularly applicable to low temperature processes, called the Exergy Transfer Effectiveness (*ETE*) [21]. The efficiency defines the consumed and produced exergies as exergy sources and exergy sinks respectively:

$$ETE = \frac{\sum \text{Exergy Sinks}}{\sum \text{Exergy Sources}} \quad (21)$$

An exergy sink is an exergy component that increases across a unit or system, whereas an exergy source has a decrease in its exergy value. Thus, *ETE* can easily be formulated by knowing the changes of exergy components across a unit. *ETE* also considers the ambient temperature and pressure when decomposing thermo-mechanical exergy to the *second level*. This gives accurate efficiency estimation for a process operating across or below ambient temperature. Based on the definition of *ETE*, work and heat supplied to a system will be considered consumed exergy, while work and heat delivered from a system will be considered produced exergy. However, the original *ETE* only considered thermo-mechanical exergy, so it cannot be utilized for a process undergoing chemical reactions and compositional changes. Therefore, the *ETE* has been extended to handle such systems in this work. Due to the simple concept of exergy sinks and sources, the efficiency can vary with different combinations of exergy decomposition levels. Thus, in this work, the extended *ETE* includes decomposition of exergy to the *first*, *second*, and *third level*, called *ETE 1*, *ETE 2* and *ETE 3* respectively. *ETE 3* with exergy decomposition to the *third level* for both thermo-mechanical and chemical exergies can be expressed by Eqs. (22)-(26). For the *ETE*, we define a set for streams that operate across ambient:

$$\mathbb{S} = \{(j \in I, k \in O): T_j > T_0 > T_k \vee T_k > T_0 > T_j\} \quad (22)$$

Then for $m \in \text{EX}$ and $i \in \text{Z}$ we have:

$$ETE = \frac{\sum_m \sum_j \sum_k (\Delta \dot{E}_{j,k}^m)^+ + \dot{E}^{W\text{prod}} + \dot{E}^{Q\text{prod}}}{\sum_m \sum_j \sum_k (\Delta \dot{E}_{j,k}^m)^- + \dot{E}^{W\text{cons}} + \dot{E}^{Q\text{cons}}}, \quad (23)$$

233 where

$$(\Delta \dot{E}_{j,k}^m)^+ = \begin{cases} \sum_i \dot{n}_{i,j,k} (\bar{e}_{i,k}^m - \bar{e}_{i,j}^m) & \text{if } \bar{e}_{i,k}^m > \bar{e}_{i,j}^m \\ 0 & \text{if } \bar{e}_{i,k}^m < \bar{e}_{i,j}^m \end{cases}, \quad (24)$$

$$(\Delta \dot{E}_{j,k}^m)^- = \begin{cases} 0 & \text{if } \bar{e}_{i,k}^m > \bar{e}_{i,j}^m \\ \sum_i \dot{n}_{i,j,k} (\bar{e}_{i,j}^m - \bar{e}_{i,k}^m) & \text{if } \bar{e}_{i,k}^m < \bar{e}_{i,j}^m \end{cases}, \quad (25)$$

234 However, for $(j, k) \in \mathbb{S}$

$$(\Delta \dot{E}_{j,k}^T)^+ = \sum_i \dot{n}_{i,j,k} \bar{e}_{i,k}^T, \quad (26)$$

$$(\Delta \dot{E}_{j,k}^T)^- = \sum_i \dot{n}_{i,j,k} \bar{e}_{i,j}^T. \quad (27)$$

235 For *ETE 1* and *ETE 2*, Eqs. (23)-(27) do not contain subscript i and EX will be $\{\dot{E}^{\text{TM}}, \dot{E}^{\text{Ch}}\}$ and $\{\dot{E}^{\text{T}}, \dot{E}^{\text{p}}, \dot{E}^{\text{Conc}},$

236 $\dot{E}^{\text{Reac}}\}$ respectively. The set \mathbb{S} indicates the cases where units or systems are operated across the ambient

237 temperature. With Eqs. (23)-(27), ETE can accurately evaluate the performance of processes operating across T_0 .

238 For equipment or processes with multiple inlets and outlets, exergy can still be decomposed to the third

239 (component) level, but then a summation of the inlet streams on one hand and the outlet streams on the other hand

240 will replace the exergy sources and sinks in the exergy efficiency calculations.

241 All exergy efficiencies discussed in this paper can then be classified based on the level of exergy decomposition

242 and whether ambient temperature is considered, as shown in Table 2. The classification will help to indicate the

243 characteristics of the efficiency definitions, and thereby identifying the reasons for their possibly poor accuracy

244 as performance indicators.

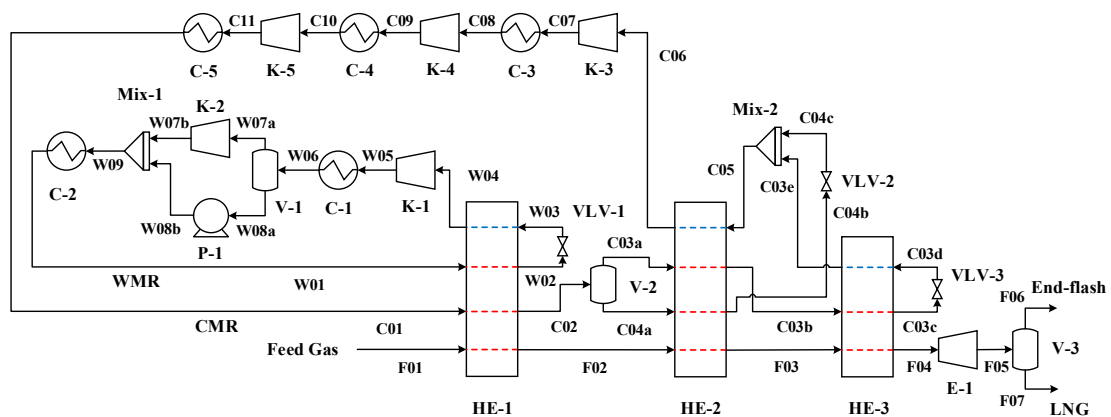
245 Table 2 Classification of exergy efficiencies.

	Exergy Decomposition Level		T_0 consideration
	Thermo- Mechanical	Chemical	
Input-output	X	X	X
<i>CEE</i>	1	3*	✓
<i>CBC</i>	3*	1	X
<i>ETE 1</i>	1	1	X
<i>ETE 2</i>	2	2	✓
<i>ETE 3</i>	3	3	✓

246 *Level 2 decomposition not included

247 **3. Design basis and optimization**

248 For the evaluation of the selected exergy efficiencies, the dual mixed refrigerant (DMR) process for liquefaction
 249 of natural gas was studied as a representative of cryogenic systems, having multiple cycles with two mixed
 250 hydrocarbon refrigerants [25]. The process flow diagram is shown in Fig. 2, and the simulations were performed
 251 with Aspen HYSYS V9 [26]. A pre-treated natural gas having small amounts of heavier hydrocarbons (F01) is
 252 fed to heat exchanger HE-1 and pre-cooled together with the cold mixed refrigerant (CMR) and the warm mixed
 253 refrigerant (WMR). The pre-cooled WMR (W02) is then subject to Joule Thomson throttling in valve VLV-1 to
 254 reduce its temperature and returned to HE-1. The heated WMR from the heat exchanger (W04) is pressurized
 255 through multi-stage compression and intercooling so that the WMR after further cooling in C-2 and HE-1 can
 256 produce sufficient cold duty for HE-1 by throttling. If liquid forms in intercooler C-1, it is sent to pump P-1 to
 257 boost the pressure level. The feed stream from the first heat exchanger (F02) is passed through HE-2 and HE-3 to
 258 be liquefied and sub-cooled before it is depressurized by liquid expander E-1, discharging the two-phase stream
 259 (F05). The mixture is separated into vapor (F06) and liquid (F07) products by phase separator V-3. The pre-cooled
 260 CMR (C02) is responsible for the liquefaction and the sub-cooling of the feed gas. The liquid part of the stream
 261 (C04a) is further cooled by heat exchanger HE-2 and depressurized by valve VLV-2 in order to liquefy the feed
 262 stream in the second heat exchanger. The vapor part of the CMR (C03a) is cooled in the second and third heat
 263 exchanger and throttled to sub-cool the feed gas in HE-3, and the rest of the cold energy is delivered to HE-2.
 264 Table 3 and Table 4 show simulation conditions and design parameters used in this work.



265

266 Fig. 2. The DMR process flow diagram [25].

267 The DMR process was optimized to minimize the net power consumption. As key decision variables, the
 268 compositions of the WMR (ethane, propane and n-butane) and the CMR (nitrogen, methane, ethane and propane
 269 were varied during optimization. Besides, the discharge pressures of the turbo-machinery in the system were
 270 selected as variables. The outlet temperatures of heat exchangers HE-1 and HE-2 were also manipulated so that
 271 the heat exchanger cold duties can be varied. The three cryogenic heat exchangers were constrained to a minimum
 272 temperature difference of 3 K, considering the trade-off between the capital and operating costs of the process [27,
 273 28]. A minimum superheating of 5 K was also applied to compressor inlet streams to prevent liquid formation at
 274 the inlet of the equipment, which is a proper value for the optimization of the DMR process [29]. The liquid
 275 expander E-1 and the phase separator V-3 are not affected by the optimization since the operating conditions of
 276 these units are not selected as optimization variables in this work. The optimization is performed by SQP
 277 (sequential quadratic programming), which is a local solver. The detailed process stream data for the initial case
 278 and the final case (optimal solution) are listed in Table 5 and Table 6.

279 Table 3 Simulation conditions for the DMR process.

Description	Unit	Value
Feed gas flow rate	kmol/s	1
Feed gas temperature	°C	22
Feed gas pressure	bar	60
LNG temperature	°C	-157.9
LNG pressure	bar	1.4
Feed gas composition		
Nitrogen	mol %	1.01
Methane	mol %	91.59
Ethane	mol %	4.93
Propane	mol %	1.71
i-Butane	mol %	0.35
n-Butane	mol %	0.40
i-Pentane	mol %	0.01

280 Table 4 Design parameters for the DMR process.

Process parameters	Unit	Value
Equation of state	-	Peng-Robinson
Compressor polytropic efficiency	%	78
Expander adiabatic efficiency	%	87
Cooler outlet temperature	°C	22
Total Δp in heat exchangers	bar	0.6
Δp in vessels (liquid/vapor outlet)	bar	0.1/0.2
Pressure drop in coolers	bar	0.1

281

282 Table 5 Stream conditions for the initial case of the DMR process.

Stream	Vapor Fraction [-]	T [°C]	p [bar]	\dot{n} [kmol/s]	\dot{E}^T [kW]	\dot{E}^P [kW]	\dot{E}^{Conc} [kW]	\dot{E}^{Reac} [kW]
F01	1.00	22.0	60.0	1.00	0.7	9 749.7	-960.1	892 561.4
F02	1.00	-33.5	59.7	1.00	355.3	9 739.1	-960.1	892 561.4
F03	0.00	-115.7	59.4	1.00	4 568.2	9 729.1	-960.1	892 561.4
F04	0.00	-148.0	59.4	1.00	6 697.2	9 728.3	-960.1	892 561.4
F05	0.06	-157.0	1.5	1.00	15 187.5	969.3	-960.1	892 561.4
F06	1.00	-158.1	1.3	0.06	209.9	38.5	-50.2	46 785.4
F07	0.00	-157.9	1.4	0.94	15 099.4	749.0	-871.7	845 776.0
W01	0.17	22.0	17.9	1.22	9.1	7 459.1	-3 108.5	2 382 943.2
W02	0.00	-33.5	17.6	1.22	876.0	7 445.4	-3 108.5	2 382 943.2
W03	0.02	-36.5	4.4	1.22	3 894.9	4 285.6	-3 108.5	2 382 943.2
W04	1.00	10.8	4.1	1.22	29.6	4 083.9	-3 108.5	2 382 943.2
W05	1.00	47.5	8.6	1.22	74.4	6 131.6	-3 108.5	2 382 943.2
W06	0.97	22.0	8.5	1.22	6.9	6 100.6	-3 108.5	2 382 943.2
W07a	1.00	21.5	8.3	1.18	1.8	5 841.3	-2 969.7	2 285 541.2
W07b	1.00	63.3	18.0	1.18	616.5	7 281.4	-2 969.7	2 285 541.2
W08a	0.00	21.6	8.4	0.04	0.3	162.7	-98.5	97 402.0
W08b	0.00	22.5	18.0	0.04	0.1	166.4	-98.5	97 402.0
W09	1.00	55.7	18.0	1.22	613.0	7 463.4	-3 108.5	2 382 943.2
C01	1.00	22.0	48.5	1.34	1.5	11 901.1	-4 057.6	1 644 174.9
C02	0.30	-33.5	48.2	1.34	1 257.2	11 886.6	-4 057.6	1 644 174.9
C03a	1.00	-33.6	48.0	0.40	134.0	3 699.1	-964.2	334 107.9
C03b	0.00	-115.7	47.7	0.40	1 980.9	3 694.0	-964.2	334 107.9
C03c	0.00	-148.0	47.7	0.40	2 845.3	3 693.6	-964.2	334 107.9
C03d	0.14	-158.4	3.9	0.40	4 997.6	1 316.7	-964.2	334 107.9
C03e	0.79	-118.7	3.8	0.40	1 595.0	1 311.6	-964.2	334 107.9
C04a	0.00	-33.5	48.1	0.94	853.5	8 094.0	-2 734.0	1 310 067.0
C04b	0.00	-115.7	47.8	0.94	3 767.4	8 086.7	-2 734.0	1 310 067.0
C04c	0.11	-124.7	3.8	0.94	8 306.2	3 045.9	-2 734.0	1 310 067.0
C05	0.32	-123.4	3.8	1.34	10 235.0	4 359.5	-4 057.6	1 644 174.9
C06	1.00	-41.2	3.6	1.34	525.6	4 113.6	-4 057.6	1 644 174.9
C07	1.00	28.4	10.6	1.34	1.3	7 594.9	-4 057.6	1 644 174.9
C08	1.00	22.0	10.5	1.34	1.0	7 565.3	-4 057.6	1 644 174.9
C09	1.00	68.8	20.3	1.34	215.4	9 573.7	-4 057.6	1 644 174.9
C10	1.00	22.0	20.2	1.34	1.1	9 559.3	-4 057.6	1 644 174.9
C11	1.00	86.9	48.6	1.34	482.4	11 905.9	-4 057.6	1 644 174.9

283

284

285

286 Table 6 Stream conditions for the final case of the DMR process.

Stream	Vapor Fraction [-]	T [°C]	p [bar]	\dot{n} [kmol/s]	\dot{E}^T [kW]	\dot{E}^P [kW]	\dot{E}^{Conc} [kW]	\dot{E}^{Reac} [kW]
F01	1.00	22.0	60.0	1.00	0.7	9 749.7	-960.1	892 561.4
F02	1.00	-30.6	59.7	1.00	313.7	9 739.1	-960.1	892 561.4
F03	0.00	-118.1	59.4	1.00	4 705.2	9 729.1	-960.1	892 561.4
F04	0.00	-148.0	59.4	1.00	6 697.2	9 728.3	-960.1	892 561.4
F05	0.06	-157.0	1.5	1.00	15 187.5	969.3	-960.1	892 561.4
F06	1.00	-158.1	1.3	0.06	209.9	38.5	-50.2	46 785.4
F07	0.00	-157.9	1.4	0.94	15 099.4	749.0	-871.7	845 776.0
W01	0.00	22.0	15.1	0.90	5.4	4 696.0	-2 412.9	1 940 490.6
W02	0.00	-30.6	14.8	0.90	574.8	4 690.7	-2 412.9	1 940 490.6
W03	0.02	-33.6	3.7	0.90	2 397.8	2 774.7	-2 412.9	1 940 490.6
W04	1.00	18.2	3.4	0.90	5.4	2 596.4	-2 412.9	1 940 490.6
W05	1.00	59.1	8.3	0.90	295.0	4 251.8	-2 412.9	1 940 490.6
W06	0.55	22.0	8.2	0.90	6.0	4 237.0	-2 412.9	1 940 490.6
W07a	1.00	21.5	8.0	0.50	0.7	2 437.3	-1 236.3	959 704.2
W07b	1.00	55.6	15.2	0.50	146.0	3 011.0	-1 236.3	959 704.2
W08a	0.00	21.6	8.1	0.40	2.6	1 526.0	-927.5	980 786.4
W08b	0.00	22.3	15.2	0.40	0.7	1 553.2	-927.5	980 786.4
W09	0.49	44.0	15.2	0.90	205.1	4 697.5	-2 412.9	1 940 490.6
C01	1.00	22.0	41.4	1.31	1.4	11 260.5	-3 752.4	1 678 086.8
C02	0.30	-30.6	41.1	1.31	1 266.4	11 243.3	-3 752.4	1 678 086.8
C03a	1.00	-30.7	40.9	0.40	119.4	3 510.1	-897.0	367 764.7
C03b	0.00	-118.1	40.7	0.40	2 109.3	3 504.2	-897.0	367 764.7
C03c	0.00	-148.0	40.6	0.40	2 906.3	3 503.7	-897.0	367 764.7
C03d	0.07	-152.9	4.1	0.40	4 907.7	1 353.6	-897.0	367 764.7
C03e	0.70	-121.1	4.0	0.40	1 928.9	1 348.8	-897.0	367 764.7
C04a	0.00	-30.7	41.0	0.92	861.6	7 673.2	-2 514.4	1 310 322.1
C04b	0.00	-118.1	40.8	0.92	3 908.8	7 663.9	-2 514.4	1 310 322.1
C04c	0.06	-121.9	4.0	0.92	8 140.4	3 091.7	-2 514.4	1 310 322.1
C05	0.25	-121.1	4.0	1.31	10 388.0	4 442.4	-3 752.4	1 678 086.8
C06	1.00	-33.7	3.8	1.31	406.7	4 214.1	-3 752.4	1 678 086.8
C07	1.00	32.3	10.6	1.31	6.0	7 445.9	-3 752.4	1 678 086.8
C08	1.00	22.0	10.5	1.31	1.0	7 417.0	-3 752.4	1 678 086.8
C09	1.00	74.4	22.1	1.31	273.8	9 613.6	-3 752.4	1 678 086.8
C10	1.00	22.0	22.0	1.31	1.1	9 600.9	-3 752.4	1 678 086.8
C11	1.00	68.3	41.5	1.31	238.8	11 266.3	-3 752.4	1 678 086.8

287

288

289

290 **4. Results**

291 This chapter shows the values of the selected exergy efficiencies for both the initial and the final cases of the
 292 DMR process in order to illustrate the improvement of the process and the accuracy of the efficiencies. Regarding
 293 the coolers, the exergy efficiencies were not measured since the heat from the compressor discharge streams is
 294 absorbed by cooling water, and its exergy is wasted to the environment. Thus, the coolers do not have any
 295 produced exergy.

296 **4.1 Compressors**

297 Table 7 indicates that all consumed-produced type of efficiency definitions give reasonable (similar) values for
 298 the compressors, whereas the input-output efficiency shows values close to 100 %. As seen in Table 8, the
 299 chemical exergy of hydrocarbons is significantly larger than other exergy components, thus diluting the effect of
 300 other exergy components in the input-output efficiency. This also results in a negligible change in the value of the
 301 input-output efficiency between the initial and final cases. The changes in compressor performance as measured
 302 by other efficiency definitions are also relatively small except for compressor K-2 and exergy efficiency *ETE 3*.

303 Table 7 Exergy efficiencies of compressors for the initial and final cases [%].

Unit Operating condition Case	K-1		K-2		K-3		K-4		K-5	
	Across T_0		Across T_0		Across T_0		Across T_0		Across T_0	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Input-output	99.98	99.97	99.98	99.98	99.95	99.95	99.97	99.96	99.96	99.97
<i>CEE</i>	78.51	78.96	79.14	78.92	78.31	78.27	79.40	79.57	79.96	79.38
<i>CBC</i>	78.27	78.91	79.12	78.90	75.37	75.90	79.40	79.57	79.95	79.37
<i>ETE 1</i>	78.27	78.91	79.12	78.90	75.37	75.90	79.40	79.57	79.95	79.37
<i>ETE 2</i>	78.51	78.96	79.14	78.92	78.30	78.27	79.40	79.57	79.96	79.38
<i>ETE 3</i>	78.51	78.96	83.84	83.08	78.30	78.27	79.40	79.57	79.96	79.38

304 In conclusion, the input-output efficiency will give inaccurate optimization results for equipment handling
 305 hydrocarbons. In Table 8, the final case for compressor K-1 produces less thermo-mechanical exergy, while also
 306 consuming less compression power, compared to the initial case. The decrease in compression power (consumed)
 307 is larger than the decrease in thermo-mechanical exergy (produced), thus the performance of the compressor is
 308 improved. However, the input-output efficiency has a small decrease after optimization, whereas all consumed-
 309 produced type of efficiencies show an increase. During compression, the equipment consumes less cold
 310 temperature based exergy due to the warmer inlet temperature below ambient and produces more hot temperature

311 based exergy as a result of the warmer outlet temperature above ambient. However, the input-output efficiency
 312 may not catch this effect of thermo-mechanical exergy since it is based on total exergy, while the portion of
 313 thermo-mechanical exergy in total exergy is negligible, compared to chemical exergy.

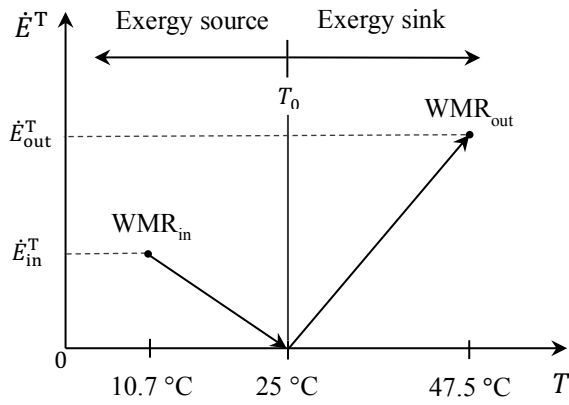
314 Table 8 Exergy decomposition for compressor K-1 in the initial and final cases.

Case	Unit	Initial			Final		
		In	Out	Δ	In	Out	Δ
T	[°C]	10.8	47.5	-	18.2	59.1	-
p	[bar]	4.1	8.6	-	3.4	8.3	-
Compression power	[kW]	2 673.5	-	-	2 464.7	-	-
\dot{E}^{TM}	[kW]	4 113.5	6 206.0	2 092.5	2 601.8	4 546.8	1 945.0
\dot{E}^T	[kW]	29.6	74.4	44.8	5.4	295.0	289.6
\dot{E}^P	[kW]	4 083.9	6 131.6	2 047.7	2 596.4	4 251.8	1 655.4
\dot{E}^{Ch}	[kW]	2 379 834.7	2 379 834.7	0.0	1 938 078.1	1 938 078.1	0.0
\dot{E}^{Conc}	[kW]	-3 108.5	-3 108.5	0.0	-2 412.9	-2 412.9	0.0
\dot{E}^{Reac}	[kW]	2 382 943.2	2 382 943.2	0.0	1 940 491.0	1 940 491.0	0.0
\dot{E}^{Total}	[kW]	2 383 948.2	2 386 040.7	2 092.5	1 940 679.9	1 942 624.9	1 945.0

315 When a compressor operates across ambient temperature, some of the consumed-produced efficiencies may also
 316 give inaccurate efficiency values if they do not decompose thermo-mechanical exergy into temperature and
 317 pressure based exergies. Table 7 shows that *CBC* and *ETE 1*, which only use total thermo-mechanical exergy
 318 without decomposition, have slightly lower efficiency values, compared to *CEE*, *ETE 2* and *ETE 3*, handling both
 319 temperature and pressure based exergies. Although *CEE* does not split thermo-mechanical exergy into temperature
 320 and pressure based terms, the use of transit exergy in *CEE* can have a similar effect as the decomposition into two
 321 terms.

322 The underestimated values of *CBC* and *ETE 1* are due to the nature of temperature based exergy across ambient
 323 temperature. As indicated in Table 9, compressor K-1 increases the stream temperature from 10.7 °C at the inlet
 324 to 47.5 °C at the outlet. Thus, the compressor operates across the ambient temperature of 25 °C. Fig. 3 shows that
 325 the temperature based exergy of the WMR that is compressed in K-1 is first reduced from the inlet temperature to
 326 the ambient temperature and then increased from T_0 to the outlet temperature. As a result, the WMR in K-1 is first
 327 a source (consumed exergy) and then becomes a sink (produced exergy) for the temperature based exergy.
 328 However, the thermo-mechanical exergy of the WMR increases monotonically across the compressor as seen in
 329 Table 9. This will give incorrect values for consumed and produced exergies in *CBC* and *ETE 1* due to the
 330 incomplete information about changes in temperature based exergy.

331 However, *CEE*, *ETE 2* and *ETE 3* only show marginal differences compared to *CBC* and *ETE 1*, while demanding
 332 larger computational efforts due to the decomposition of thermo-mechanical exergy [12]. Yet, the minor
 333 improvement of accuracy in the exergy efficiency may have a noticeable impact when analyzing optimization
 334 results. As seen in Table 7, *CEE*, *ETE 2* and *ETE 3* for K-3 show a slight reduction in their efficiency values after
 335 optimization, while *CBC* and *ETE 1* have the opposite trend, thus giving incorrect indications for the effect of
 336 optimization.



337

338 Fig. 3. Changes in temperature based exergy of compressor K-1 operating across T_0 .

339 Table 9 Exergy decomposition for the inlet and outlet streams of compressor K-1.

	Unit	Inlet	Ambient T_0	Outlet	Δ (Outlet-Inlet)
Temperature	[°C]	10.7	25	47.5	-
Pressure	[bar]	4.1	5.5	8.6	-
\dot{E}^{TM}	[kW]	4 113.5	4 911.9	6 206.0	2 092.5
\dot{E}^T	[kW]	29.6	0	74.4	44.8
\dot{E}^P	[kW]	4 083.9	4 911.9	6 131.6	2 047.7
\dot{E}^{Ch}	[kW]	2 379 834.5	2 379 834.5	2 379 834.5	0.0
\dot{E}^{Conc}	[kW]	-3 108.5	-3 108.5	-3 108.5	0.0
\dot{E}^{Reac}	[kW]	2 382 943.0	2 382 943.0	2 382 943.0	0.0
\dot{E}^{Total}	[kW]	2 383 948.0	2 384 746.4	2 386 040.5	2 092.5

340 One noticeable result is the larger efficiency value of *ETE 3* for compressor K-2. Generally, all the exergy
 341 components that include partial molar exergies increase through a compressor operating across ambient
 342 temperature. However, in the case of K-2, partial molar temperature based exergy shows a different behavior, and
 343 this affects the exergy sinks and sources in such a way that *ETE 3* is larger than other consumed-produced
 344 efficiencies. Even though *CBC* decomposes thermo-mechanical exergy to the component level, it has a different

345 behavior than *ETE 3*. Since *CBC* does not decompose partial molar thermo-mechanical exergy into temperature
 346 and pressure based terms, it will not account for the effect of temperature based exergy.

347 4.2 Throttling valves and the liquid expander

348 For throttling valves in Table 10, the input-output efficiency does not give meaningful efficiency values due to
 349 the large chemical exergy of the streams. *ETE 1* also fails to measure the performance of the valves, delivering a
 350 0 % efficiency value. Below ambient temperature, the purpose of a throttling valve is to reduce the temperature
 351 of a stream by reducing the pressure through the valve. Thus, pressure based exergy is converted to temperature
 352 based exergy across the valve, while having some exergy losses.

353 Table 10 Exergy efficiencies of valves and one expander for the initial and final cases [%].

Unit	VLV-1		VLV-2		VLV-3		E-1	
Operating condition	Below T_0	Below T_0	Below T_0	Below T_0	Below T_0	Below T_0	Below T_0	Below T_0
Case	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Input-output	99.99	99.99	99.96	99.97	99.93	99.96	99.99	99.99
<i>CEE</i>	80.34	74.69	67.04	54.76	81.87	71.17	99.29	99.29
<i>CBC</i>	94.74	93.47	72.56	73.00	72.48	70.93	93.56	93.56
<i>ETE 1</i>	0.00	0.00	0.00	0.00	0.00	0.00	71.90	71.90
<i>ETE 2</i>	95.54	95.15	90.04	92.55	90.55	93.08	99.14	99.14
<i>ETE 3</i>	96.01	95.60	90.63	92.88	91.90	93.92	99.23	99.23

354 However, *ETE 1* only accounts for the changes in thermo-mechanical and chemical exergy. The former is always
 355 reduced due to the irreversibilities of the equipment (that are large for valves), thus it acts as consumed exergy,
 356 while the latter is not changed since there is no chemical reaction or compositional changes. As a result, there will
 357 be no produced exergy in this unit, resulting in a zero efficiency using the definition of *ETE 1*. The *CEE* and *CBC*
 358 efficiencies tend to underestimate the performance of the valves, compared to *ETE 2* and *ETE 3*. Similar to *ETE*
 359 *1*, the *CEE* and *CBC* efficiency definitions only use thermo-mechanical exergy without decomposition, which
 360 means that information about the conversion between temperature and pressure based exergies is lost. However,
 361 *CEE* and *CBC* avoid zero efficiency values for valves since the transit exergy and the partial molar thermo-
 362 mechanical exergy in their definitions are able to partly account for these effects.

363 In conclusion, the *CEE* and *CBC* may not properly measure the improvement in the performance of the valves
 364 after optimization. In the final case, all the valves except VLV-1 have higher exergy efficiencies for *ETE 2* and
 365 *ETE 3*. As seen in Table 11, the ratio by which pressure based exergy is converted to temperature based exergy is
 366 increased from 0.91 to 0.93 for VLV-3 with smaller exergy loss ($\Delta\dot{E}^{\text{Total}}$) in the final case, fulfilling the purpose

367 of a throttling valve operating below ambient temperature. In contrast, the values of *CEE* and *CBC* are
 368 significantly decreased after optimization for this valve. Therefore, decomposition of thermo-mechanical exergy
 369 into temperature and pressure based exergies is essential to calculate accurate exergy efficiencies for equipment
 370 operating below ambient temperature.

371 Table 11 Exergy decomposition for valve VLV-3 in the initial and final cases.

Case	Unit	Initial			Final		
		In	Out	Δ (Out-In)	In	Out	Δ (Out-In)
\dot{E}^{TM}	[kW]	6 538.9	6 314.2	-224.7	6 410.1	6 261.3	-148.8
\dot{E}^T	[kW]	2 845.3	4 997.6	2 152.3	2 906.3	4 907.7	2 001.3
\dot{E}^P	[kW]	3 693.6	1 316.7	-2 376.9	3 503.7	1 353.6	-2 150.1
\dot{E}^{Ch}	[kW]	333 143.7	333 143.7	0.0	366 867.7	366 867.7	0.0
\dot{E}^{Conc}	[kW]	-964.2	-964.2	0.0	-897.0	-897.0	0.0
\dot{E}^{Reac}	[kW]	334 107.9	334 107.9	0.0	367 764.7	367 764.7	0.0
\dot{E}^{Total}	[kW]	339 682.7	339 458.0	-224.7	373 277.8	373 129.0	-148.8

372 Liquid expanders operating below ambient temperature have two tasks. The primary task is to provide cooling
 373 (temperature based exergy) and the secondary task is to produce power. The source is pressure based exergy. Thus,
 374 the input-output efficiency, *CBC* and *ETE 1* are not appropriate efficiency definitions for such units because they
 375 have incomplete information about the conversion between pressure and temperature based exergies. The high
 376 values of *CEE*, *ETE 2* and *ETE 3* mean good conversion of pressure based exergy into temperature based exergy
 377 and work, explaining why liquid turbines are considered a good alternative to throttling valves for the end-flash
 378 step in LNG processes [30]. As mentioned earlier, the operating conditions of expander E-1 and the end-flash are
 379 not selected as optimization variables in this work. This is why the columns for initial and final efficiencies are
 380 identical in Table 10. Again, *ETE 1* is not able to properly measure the efficiency of turbines below ambient
 381 temperature.

382 4.3 Heat exchangers and mixers

383 In Table 12, all consumed-produced efficiencies have similar values for heat exchangers, and they are all improved
 384 after optimization, especially for HE-1. This is mainly due to the reduced values of *LMTD* for all the heat
 385 exchangers in the final case as seen in Table 13. The input-output efficiency again fails to produce meaningful
 386 values, approaching 100 % due to the large reactional exergy of hydrocarbons. Regarding *CEE* and *CBC*, they
 387 give slightly different values compared to *ETE 1*, *2* and *3*.

388 The two efficiency definitions *CEE* and *CBC* consider the effect of pressure drop as exergy sources only
 389 (consumed exergy) on both the hot and cold stream sides. However, below ambient temperature, the pressure drop
 390 for hot streams reduces the increment of thermo-mechanical exergy through a heat exchanger. In addition, cold
 391 streams have a larger decrease in thermo-mechanical exergy through a heat exchanger due to the pressure drop.

392 Table 12 Exergy efficiencies of heat exchangers and mixers for the initial and final cases [%].

Unit Operating condition Case	HE-1		HE-2		HE-3		MIX-1		MIX-2	
	Below T_0		Below T_0		Below T_0		Across T_0		Below T_0	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Input-output	99.98	99.99	99.98	99.98	99.97	99.99	99.99	99.99	99.99	99.99
<i>CEE</i>	60.33	82.47	89.94	92.12	87.81	93.44	84.54	94.25	98.76	98.77
<i>CBC</i>	59.95	82.28	90.01	92.48	87.92	93.76	77.74	91.19	98.36	98.72
<i>ETE 1</i>	59.95	82.24	89.91	92.10	87.81	93.44	99.85	99.95	99.98	99.98
<i>ETE 2</i>	59.95	82.24	89.91	92.10	87.81	93.44	99.85	99.95	99.99	99.98
<i>ETE 3</i>	59.95	82.24	89.92	92.37	87.81	93.44	87.19	92.72	98.73	98.99

393 Table 13 *LMTD* values of the heat exchangers [°C].

Unit Case	HE-1		HE-2		HE-3	
	Initial	Final	Initial	Final	Initial	Final
<i>LMTD</i>	12.31	3.88	5.19	4.04	8.87	4.63

394 As a result, *ETE 2* and *ETE 3* have a smaller exergy sink and a larger exergy source compared to *CEE* and *CBC*,
 395 thus decreasing the exergy efficiency of the heat exchangers. Nevertheless, this effect is marginal in this work
 396 since pressure drops in the heat exchangers are small. However, with large pressure drops, the effect can be
 397 significant [21].

398 Unlike units having no changes in chemical exergy, mixers have significant differences between efficiency
 399 definitions as shown in Table 12. The input-output efficiency gives almost 100 % efficiency, thus not properly
 400 showing the performance of the equipment. As mentioned in Section 2.3.3, *ETE 1* and *ETE 2* are defined in order
 401 to handle changes in both thermo-mechanical and chemical exergies by decomposing them to the *first* (\dot{E}^{TM} , \dot{E}^{Ch})
 402 and *second level* (\dot{E}^T , \dot{E}^P , \dot{E}^{Conc} , \dot{E}^{Reac}). However, they also give similar efficiency values as the input-output
 403 efficiency. Values for MIX-1 in Table 14 indicate that due to mixing, stream Inlet1 experiences an increase in
 404 reactional exergy (18,167.0 kW), which then becomes an exergy sink. At the same time, reactional exergy of
 405 stream Inlet2 decreases by the same amount and becomes an exergy source. Since the changes in reactional exergy
 406 of stream Inlet1 and Inlet2 are substantially larger than the variations in other exergy components, they dominate

407 both the exergy sink and source terms in the definition of *ETE 1* and *ETE 2*. Thus, they give efficiency values
 408 close to 100 %, since the sink and source sides of the reactional exergy are similar.

409 Table 14 Exergy decomposition for mixer MIX-1 in the initial case.

Stream	Inlet1	Inlet2	Outlet	Outlet1*-Inlet1	Outlet2*-Inlet2			
Flow [kmol/s]	1.1798	0.0406	1.2204	1.1798	0.0406			
Unit	[kJ/kmol]	[kJ/kmol]	[kJ/kmol]	[kJ/kmol]	[kW]			
\bar{e}^{TM}	\bar{e}^T	522.6	1.3	502.3	-20.3	-23.9	501.0	20.3
	\bar{e}^P	6 171.6	4 100.3	6 115.5	-56.1	-66.2	2015.2	81.8
\bar{e}^{Ch}	\bar{e}^{Conc}	-2 517.1	-2 426.9	-2 547.1	-30.0	-35.4	-120.2	-4.9
	\bar{e}^{Reac}	1 937 187.0	2 400 280.0	1 952 585.0	15 398.0	18 167.0	-447 695.0	-18 167.0
\bar{e}^{Total}	1 941 364.1	2 401 954.7	1 956 655.7	15 291.6	18 041.5	-445 299.0	-18 069.8	

410 *Outlet1 = $(m_{inlet1}/m_{outlet}) \times Outlet$, Outlet2 = $(m_{inlet2}/m_{outlet}) \times Outlet$

411 In contrast, *CEE*, *CBC* and *ETE 3* successfully give distinctive efficiency values for the units having chemical
 412 exergy changes. Due to the decomposition of chemical exergy to the chemical component level, *CEE* and *ETE 3*
 413 can prevent reactional exergy from dominating both exergy sink and source terms. After this decomposition, the
 414 efficiency definitions are able to account for the difference in partial molar reactional exergy between the inlet
 415 streams and the outlet stream for the mixer. The molar reactional exergy of each component, however, does not
 416 change because all the streams include the same components. However, the streams have different compositions,
 417 thus different molar concentrational exergy values for the components. In the case of chemical exergy in *CBC*,
 418 only the difference in chemical exergy between the sum of the two inlet streams and the outlet stream is considered.
 419 Since there is no chemical reaction happening in the unit, reactional exergy is cancelled, and only the changes in
 420 concentrational exergy are left in the difference between inlet and outlet.

421 Therefore, *CEE*, *CBC* and *ETE 3* can disregard the reactional exergy in efficiency calculations, resulting in
 422 meaningful performance values. However, the *CEE* and *CBC* efficiencies will not contain accurate information
 423 about the changes in partial molar temperature and pressure based exergies. In addition, for *CEE*, calculating the
 424 transit part of thermo-mechanical exergy across the units is required, and this demands a large computational
 425 effort, compared to *CBC* and *ETE 3* [15]. Hence, *ETE 3* has a clear advantage in measuring the performance of
 426 mixers compared to other efficiency definitions.

427 In an analysis of LNG processes, mixers appear to have no important thermodynamic purpose since the equipment
 428 is just mixing streams that are separated upstream. Thus, exergy analysis of mixers has either been omitted or just
 429 performed for an illustrative purpose [11, 31]. However, in the final cases in Table 12, all the consumed-produced

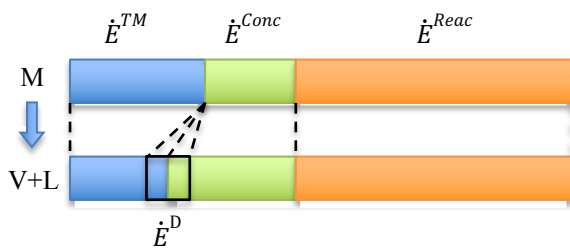
430 efficiencies clearly indicate a performance improvement of the mixers. Table 15 shows that the optimizer reduces
 431 the temperature difference between the two inlet streams. This results in a smaller amount of entropy generation
 432 in the mixer and thus higher exergy efficiency. Therefore, exergy analysis of mixers may be necessary to measure
 433 the performance improvement of the process.

434 Table 15 Operating temperatures of MIX-1.

Case	Initial			Final		
	Inlet-1	Inlet-2	Outlet	Inlet-1	Inlet-2	Outlet
Temperature [°C]	63.3	22.5	55.7	55.6	22.3	44.0

435 4.4 Phase separators and total process

436 Phase separators used in the LNG process have a similar trend in the efficiency values as mixers. Table 16
 437 indicates that efficiency definitions without the decomposition of chemical exergy to the *third level*, such as the
 438 input-output efficiency, *ETE 1* and *ETE 2*, give approximately 100 % efficiency values for the phase separators.
 439 During phase separation, the total amount of exergy remains the same if there is no pressure drop or heat exchange
 440 as illustrated in Fig. 4. However, the total concentrational exergy of the vapor and liquid streams increases since
 441 this exergy form is a measure of the degree of mixing. This increment is compensated by decreasing thermo-
 442 mechanical exergy, while keeping total exergy across the unit unchanged. Thus, the performance of phase
 443 separators depends on the conversion ratio from thermo-mechanical exergy to concentrational exergy.



444
 445 Fig. 4. Relationship between exergy components across a phase separator.

446 In addition, the amount of exergy destruction (indicated by \dot{E}^D in Fig. 4) due to pressure drop affects temperature
 447 based, pressure based and concentrational exergies. This means that decomposition of exergy at least to the *second*
 448 *level* ($\dot{E}^T, \dot{E}^P, \dot{E}^{Conc}, \dot{E}^{Reac}$) is required to properly measure the performance of phase separators. Thus, *ETE 1* is
 449 not suitable for this type of equipment. In addition, a phase separator will split a stream into two outlet streams,

450 one with higher and one with lower molar reactional exergy compared with the inlet stream. This makes reactional
 451 exergy dominating both the exergy sink and source terms in *ETE 2*, giving close to 100 % efficiency.

452 In contrast, *CEE*, *CBC* and *ETE 3* give reasonable efficiency values for the phase separators since they can
 453 disregard the large values of reactional exergy in both the consumed and produced exergy terms in the same way
 454 as for mixers. However, *CEE* and *CBC* tend to underestimate the efficiency values due to lack of detailed
 455 information about changes in temperature and pressure based exergies, showing the superiority of *ETE 3*.

456 Table 16 Exergy efficiency of phase separators and the total process for the initial and final cases [%].

Unit	V-1		V-2		V-3		Process	
Operating condition	below T_0		below T_0		below T_0		below T_0	
Case	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Input-output	99.99	99.99	99.99	99.99	99.99	99.99	99.02	99.34
<i>CEE</i>	60.93	95.95	99.52	99.42	98.98	98.98	63.13	71.66
<i>CBC</i>	51.30	95.14	99.64	97.01	83.22	83.22	42.98	52.68
<i>ETE 1</i>	99.67	99.98	99.99	99.99	99.76	99.76	64.02	72.44
<i>ETE 2</i>	99.67	99.98	99.99	99.99	99.78	99.78	73.26	80.18
<i>ETE 3</i>	71.00	96.85	99.75	97.89	84.61	84.61	63.43	71.92

457 Similar to the case with mixers, *CEE*, *CBC* and *ETE 3* also in general indicate performance improvement of phase
 458 separators after optimization. The task of phase separators is to divide an inlet stream into a vapor and a liquid
 459 stream. Table 17 indicates that the optimizer manipulates the LNG process to have more even molar flow rates in
 460 the vapor and liquid outlet streams, while having constant pressure drop as indicated in Section 3, Table 4. This
 461 means a larger degree of separation is achieved for the same pressure drop in the final case. As mentioned in
 462 Section 3, the operating conditions of the end-flash (V-3) are not selected as optimization variables in this work,
 463 resulting in identical efficiency values for the initial and final case.

464 Table 17 Vapor fraction in phase separators.

Unit	V-1		V-2	
Case	Initial	Final	Initial	Final
Vapor fraction	0.966	0.553	0.298	0.301

465 In the DMR process studied in this paper, the feed gas undergoes changes in both thermo-mechanical and chemical
 466 exergies, producing LNG and off-gas from the end-flash as products. The feed and product streams are all below
 467 ambient temperature. Like other equipment having changes in chemical exergy, the significant quantity of
 468 chemical exergy dominates the inlet and outlet total exergy, making the input-output efficiency of the total process
 469 close to 100 % as seen in Table 16.

470 In contrast, all the consumed-produced efficiencies give more reasonable values for the performance of the LNG
471 process. The *CBC* underestimates the efficiency value compared to other efficiency definitions. In the LNG
472 process, the feed gas is cooled and liquefied below ambient temperature. This increases the temperature based
473 exergy of the feed and such increment becomes an exergy sink. The pressure based exergy of the feed gas is
474 reduced due to the end-flash step and this reduction is regarded as an exergy source. However, the *CBC* just
475 considers the changes in total thermo-mechanical exergy so it does not include the precise information about the
476 variation in temperature and pressure based exergies. This makes the *CBC* inaccurate for evaluation of LNG
477 processes. *ETE 1* and *ETE 2* overestimate the performance of the total process compared to other consumed-
478 produced efficiencies. Similar to the case with phase separators, *ETE 1* and *ETE 2* will not handle this process
479 properly since the two products experience considerable changes in molar reactional exergy compared to the feed
480 gas. This will dilute the effect of variations in other exergy components.

481 However, *CEE* and *ETE 3* give appropriate efficiency values for the LNG process by considering temperature and
482 pressure based exergies and the *third level* decomposition of chemical exergy. The difference between the two
483 efficiencies occurs since *ETE 3* counts the power consumed in the compressors as an exergy source and the power
484 produced in the liquid turbine as an exergy sink whereas *CEE* only considers the net work required/produced by
485 the turbo-machinery as an exergy source/sink. The compressors consume electricity, which is pure exergy, and
486 the liquid turbine produces power at the cost of pressure based exergy. Thus, exergy efficiencies using net work
487 will not recognize such transfer between pressure based exergy and power, and thus being thermodynamically
488 inaccurate. Therefore, *ETE 3* provides the most accurate value of exergy efficiency for LNG processes, especially
489 for processes with multiple products.

490 **5. Recommendation**

491 A case study with an advanced LNG process was performed to compare the selected exergy efficiencies, including
492 the input-output efficiency. The results demonstrate that the input-output efficiency shows values close to 100 %
493 and only marginal changes after the process optimization due to the large chemical exergy of the streams (typical
494 for hydrocarbon processes). Thus, the input-output efficiency does not provide meaningful efficiency values for
495 units and systems handling hydrocarbons, and thus poorly reflecting the changes in process performance.

496 In contrast, all the consumed-produced types of efficiency definitions gave reasonable values for all units and the
497 total process containing hydrocarbon streams. However, exergy efficiencies using thermo-mechanical exergy

498 without decomposition (only *first level* of exergy decomposition) such as *CEE*, *CBC* and *ETE 1* did not give
499 accurate efficiency values for equipment producing refrigeration duty (throttling valves and the liquid expander)
500 and units operating across ambient temperature. The inaccuracy of these efficiencies is caused by the inability to
501 account for the conversion between temperature and pressure based exergies, which is the main principle of
502 refrigeration and liquefaction processes such as natural gas liquefaction and natural gas liquid (NGL) extraction
503 processes. Thus, when the DMR process was optimized, the efficiencies using only the *first level* of exergy
504 decomposition give inaccurate changes in their values since they do not properly address the task of the system.

505 Although it can reflect the conversion between temperature and pressure based exergies, decomposing exergy to
506 the *second level* (*ETE 2*) also gave inaccurate efficiency values for units and the total process having compositional
507 changes. Nevertheless, *ETE 2* is recommended for systems having only temperature and pressure changes due to
508 the simple calculation method and the ability to handle all operating temperatures above, across and below ambient.

509 To properly account for the performance of equipment and processes having compositional changes, decomposing
510 exergy into the chemical component level (the *third level* of exergy decomposition, such as *ETE 3*) was required.
511 In the case of *CEE* and *CBC*, decomposing to the *third level* is only done for chemical exergy, not thermo-
512 mechanical exergy (temperature and pressure based exergy components). This is required for units or systems
513 operating across ambient temperature. In contrast, *ETE 3* delivered reasonable exergy efficiency values for all
514 types of equipment and systems at all operating conditions without information loss about exergy transfer, while
515 demanding minor calculation efforts compared to *CEE*. Therefore, *ETE 3* has a clear advantage in measuring the
516 performance of processes with changes in chemical exergy, giving consistent and reliable efficiency values even
517 for the evaluation of the improvement in optimized systems.

518 **6. Conclusion**

519 In this paper, consumed-produced type exergy efficiencies were classified according to the level of exergy
520 decomposition, in order to indicate the characteristics of the efficiency definitions. Due to the inaccuracy of the
521 task exergy efficiencies for different types of system with various operating conditions, this paper extends the
522 Exergy Transfer Effectiveness (*ETE*), by including chemical exergy. This modification is to offer general formulas
523 for processes having changes in temperature, pressure and chemical composition. The result is an exergy
524 efficiency containing accurate information about exergy transfer in processes. The *ETE* also properly reflects the
525 changes in process performance after optimization, which is the main task of an efficiency index as a post-design

526 tool for diagnosing industrial processes with respect to potential improvements. Thus, the use of the *ETE* is
527 recommended for cryogenic processes, while considering the appropriate selection of the exergy decomposition
528 level. The generalized formula also makes the ETE applicable for other unit operations such as chemical reaction,
529 combustion and membrane separation. Such applications are possible future works.

530 **Acknowledgements**

531 The authors would like to acknowledge Statoil for financial support.

532 **Nomenclature**

533 *Roman letters*

534 ASU = air separation unit

535 *CBC* = component by component exergy efficiency [%]

536 *CEE* = coefficient of exergy efficiency [%]

537 CMR = cold mixed refrigerant

538 DMR = dual mixed refrigerant

539 \dot{E} = exergy rate [kW]

540 \bar{e} = molar exergy [kJ/kmol]

541 *ETE* = exergy transfer effectiveness [%]

542 EX = set of exergy components

543 \dot{H} = enthalpy rate [kW]

544 I = set of inlet streams

545 L = liquid stream

546 *LMTD* = log mean temperature difference [K]

547 LNG = liquefied natural gas

548 M = two-phase stream

549 \dot{n} = molar flow rate [kmol/s]

550 O = set of outlet streams

551 p = pressure [bar]

552 \dot{Q} = Heat rate [kW]

553 R = universal gas constant [8.314 kJ/kmol K]

554 SQP = sequential quadratic programming

555 \dot{S} = entropy rate [kW/K]

556 T = temperature [K]

557 V = vapor stream

558 WMR = warm mixed refrigerant

559 x = mole fraction [-]

560 Z = set of chemical components

561 *Greek letters*

562 Δp = pressure drop [bar]

563 η = exergy efficiency [%]

564 *Subscripts and superscripts*

565 0 = ambient conditions

566 Ch = chemical exergy

567 Chem = standard chemical exergy

568 Conc = concentrational exergy

569 cons = consumed

570 Consumed-produced = consumed-produced type exergy efficiency

571 D = exergy destruction

572 i = chemical component
573 in = inlet
574 in-out = input-output exergy efficiency
575 j = inlet stream
576 k = outlet stream
577 l = chemical component
578 m = exergy component
579 mixture = multi-component stream
580 net = net work
581 out = outlet
582 p = pressure based exergy
583 prod = produced
584 pure = pure component
585 Q = exergy of heat
586 Reac = reactional exergy
587 T = temperature based exergy
588 TM = thermo-mechanical exergy
589 Total = total exergy of a stream
590 tr = transit exergy
591 W = work exergy
592
593
594

595

596 **References**

- 597 [1] Lior N, Zhang N. Energy, exergy, and Second Law performance criteria. *Energy*. 2007;32(4):281-96.
- 598 [2] Rian AB, Ertesvåg IS. Exergy Evaluation of the Arctic Snøhvit Liquefied Natural Gas Processing Plant in
599 Northern Norway—Significance of Ambient Temperature. *Energy & Fuels*. 2012;26(2):1259-67.
- 600 [3] Rosen MA, Dincer I, Kanoglu M. Role of exergy in increasing efficiency and sustainability and reducing
601 environmental impact. *Energy Policy*. 2008;36(1):128-37.
- 602 [4] Romero Gómez M, Ferreiro Garcia R, Romero Gómez J, Carbia Carril J. Review of thermal cycles exploiting
603 the exergy of liquefied natural gas in the regasification process. *Renewable and Sustainable Energy Reviews*.
604 2014;38:781-95.
- 605 [5] Kanoğlu M, Çengel YA, Dinçer İ. *Efficiency evaluation of energy systems*: Springer Science & Business
606 Media, 2012.
- 607 [6] Ghannadzadeh A, They-Hetreux R, Baudouin O, Baudet P, Floquet P, Joulia X. General methodology for
608 exergy balance in ProSimPlus® process simulator. *Energy*. 2012;44(1):38-59.
- 609 [7] Tsatsaronis G. Thermo-economic analysis and optimization of energy systems. *Progress in Energy and
610 Combustion Science*. 1993;19(3):227-57.
- 611 [8] Kotas TJ. *The Exergy Method of Thermal Plant Analysis*. 3 ed. London, The United Kingdom: Exergon
612 Publishing Company with Paragon Publishing, 2012.
- 613 [9] Nguyen T-V, Voldsund M, Elmegaard B, Ertesvåg IS, Kjelstrup S. On the definition of exergy efficiencies for
614 petroleum systems: Application to offshore oil and gas processing. *Energy*. 2014;73:264-81.
- 615 [10] Morris DR, Steward FR. Exergy analysis of a chemical metallurgical process. *Metallurgical Transactions B*.
616 1984;15(4):645-54.
- 617 [11] Bejan A, Tsatsaronis G, Moran M. *Thermal Design and Optimization*. 1 ed. New York, USA: John Wiley &
618 Sons, Inc., 1995.

- 619 [12] Lazzaretto A, Tsatsaronis G. SPECO: A systematic and general methodology for calculating efficiencies and
620 costs in thermal systems. *Energy*. 2006;31(8–9):1257-89.
- 621 [13] Brodyansky VM, Sorin MV, Goff PL. *The Efficiency of Industrial Processes: Exergy Analysis and*
622 *Optimization*. Amsterdam, Netherlands: Elsevier, 1994.
- 623 [14] Marmolejo-Correa D, Gundersen T. A comparison of exergy efficiency definitions with focus on low
624 temperature processes. *Energy*. 2012;44(1):477-89.
- 625 [15] Cornelissen RL. *Thermodynamics and sustainable development; the use of exergy analysis and the reduction*
626 *of irreversibility*. Enschede, Netherlands: Universiteit Twente, 1997.
- 627 [16] Voldsund M, Nguyen T-V, Elmegaard B, Ertesvåg IS, Kjelstrup S. Thermodynamic Performance Indicators
628 for Offshore Oil and Gas Processing: Application to Four North Sea Facilities. *Oil and Gas Facilities*.
629 2014;3(06):51-63.
- 630 [17] Zanchini E. A more general exergy function and its application to the definition of exergy efficiency. *Energy*.
631 2015;87:352-60.
- 632 [18] Najibullah Khan NB, Barifcani A, Tade M, Pareek V. A case study: Application of energy and exergy
633 analysis for enhancing the process efficiency of a three stage propane pre-cooling cycle of the cascade LNG
634 process. *Journal of Natural Gas Science and Engineering*. 2016;29:125-33.
- 635 [19] Tan H, Zhao Q, Sun N, Li Y. Enhancement of energy performance in a boil-off gas re-liquefaction system
636 of LNG carriers using ejectors. *Energy Conversion and Management*. 2016;126:875-88.
- 637 [20] Ghorbani B, Hamed M-H, Amidpour M, Shirmohammadi R. Implementing absorption refrigeration cycle
638 in lieu of DMR and C3MR cycles in the integrated NGL, LNG and NRU unit. *International Journal of*
639 *Refrigeration*. 2017;77:20-38.
- 640 [21] Marmolejo Correa D, Gundersen T. A new efficiency parameter for exergy analysis in low temperature
641 processes. *International Journal of Exergy*. 2015;17(2):135-70.
- 642 [22] Szargut J. International progress in second law analysis. *Energy*. 1980;5(8):709-18.
- 643 [23] Sato N. *Chemical Energy and Exergy*. Amsterdam, Netherlands: Elsevier Science B.V., 2004.
- 644 [24] Szargut J. Chemical exergies of the elements. *Applied Energy*. 1989;32(4):269-86.

- 645 [25] Roberts MJ, Agrawal R. Dual Mixed Refrigerant Cycle for Gas Liquefaction. US Patent 6269655 B12001.
- 646 [26] Aspen Technology Inc. Aspen HYSYS V9. Cambridge, USA: Aspen Technology Inc., 2016.
- 647 [27] Xu X, Liu J, Cao L. Optimization and analysis of mixed refrigerant composition for the PRICO natural gas
648 liquefaction process. *Cryogenics*. 2014;59:60-9.
- 649 [28] Austbø B, Gundersen T. Using Thermodynamic Insight in the Optimization of LNG Processes. *Computer
650 Aided Chemical Engineering*. 2014;33:1273-8.
- 651 [29] Kim D, Gundersen T. Constraint Formulations for Optimisation of Dual Mixed Refrigerant LNG Processes.
652 *Chemical Engineering Transactions*. 2017;61:643-8.
- 653 [30] Barclay M, Yang CC. Offshore LNG: The Perfect Starting Point for the 2-Phase Expander? *Proceedings of
654 Offshore Technology Conference (OTC 2006)*. Houston, USA: Offshore Technology Conference (OTC); 2006.
- 655 [31] Vatani A, Mehrpooya M, Palizdar A. Advanced exergetic analysis of five natural gas liquefaction processes.
656 *Energy Conversion and Management*. 2014;78:720-37.