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Research Paper

A Comparative Study of Inorganic Refrigerants for the Liquefaction of Natural Gas

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Abstract –*Quite a number of refrigerants exists which are used in Natural Gas liquefaction operations with differing techniques, configuration and dynamics. This paper comparatively studies the characteristics offour inorganic refrigerants including argon, krypton, xenon, and Nitrogenin the light of an organic refrigerant - propane pre-cooled mixed refrigerants (C_3MR). This study was achieved by first simulating an already existing liquefaction plant using ASPEN HYSYS 11.0 and then analyzing the above-mentioned refrigerantswith focus on Global Warming Potential, energy efficiency, exergy and coefficient of performance of the system. The result shows that Nitrogen requires the least energy at the compressors, and Krypton proves to be the best refrigerant for the chiller while Xenon provided the best cooling effect followed by C_3MR which has a high coefficient of performance. In the past, there has been previous studies analyzing alternatives for floating LNG plants, or small-scale liquefaction. Unlike previous studies, this research compares individual alternatives that has been used in past studies, in application to an existing baseload LNG plant and serves as a good reference for further research, study, and implementation.*

Key Words*: Liquefied Natural Gas, Exergy, Coefficient of performance, refrigeration, liquefaction, Aspen Hysys, Simulation.*

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I. INTRODUCTION

Natural gas is the world's fastest-growing main source of energy today. Natural gas used in 2005 was 2750bcm, or around 23% of the world's main energy consumption [1].The global energy market relies heavily on natural gas, and the primary source of energy is crude oil. Coal and natural gas make up about half of the nation's energy supply. Many gas resources are known to be polluted with considerable levels of hydrogen sulphide and carbon dioxide, according to data published in the literature, therefore, companies have to create technologies that enable the exploitation of these sectors in a lucrative manner. When the natural gas streams' carbon dioxide content is high, low-temperature methods are preferable over standard chemical or physical absorption for gas purification [2]. Recent years have seen a rise in interest in low-temperature techniques for removing carbon dioxide. The refrigeration section is critical in these types of operations, and it must get careful consideration throughout the design phase. Refrigeration cycles keep the system at the low temperatures required for these activities. Compressor refrigeration devices use mechanical or electric power to power these cyclical refrigeration operations[3].

There are a variety of methods available to provide cooling duty, and a variety of chemicals may be used as working fluids in refrigeration cycles, either as pure refrigerants or as refrigerants in mixtures. Natural refrigerants (such as hydrocarbons, ammonia, carbon dioxide, and so on) and manufactured refrigerants (such as ethylene glycol) are both used e.g, chlorofluorocarbons, hydro-chlorofluorocarbons, hydro-fluorocarbons [4]. The Montreal Protocol on Substances that Deplete the Ozone Layer, on the other hand, has restricted the use of synthetic refrigerants due to their negative impact on the environment. As a consequence, natural refrigerants have gotten more attention in the refrigeration sector as a whole. The selection of the most suitable refrigerant is dependent on the circumstances in which it will be used. In a variety of low-temperature applications such as LNG production, pure ethylene, methane, propane and ethane are employed as pure fluids in place of water [5].

II. MATERIALS AND METHODS

2.1 Design Basis

To achieve a basis and platform for comparison of the various Inorganic Refrigerants, the refrigeration system was modelled. The system comprised of a variety of equipment and chemical components. In this study, five distinct refrigerants were used; notably C3MR (propane mixed refrigerants), Argon, Krypton, Xenon, and Nitrogen in varying proportions. It was necessary to send the natural gas through many different types of cooling systems, and all designs were created using steady state condition.

2.2 Process and Plant Design

Components which must be incorporated to achieve a good simulation and design of the liquefaction system are stated as follows: Aspen HYSYS version 11, Separator, LNG Heat exchangers, Compressors, Depressurizer, Cooler, Valves, Tee (Header), Natural gas, Refrigerants (propane, and the inert gases).

2.3 C3MR Refrigeration Cycle

a. Process Description of C3MR Cycle

A simple C3MR cycle consists of a single level of propane precooling and a single heat exchanger for liquefaction. Compressed propane's temperature is lowered by air- or water-cooled HEs, and as a result, propane hits the bubble point. The refrigerant then passes via the throttling valve, suffers significant pressure and temperature drop, and returns to the saturated area. Following that, two stages are separated in the separator. The gaseous phase returns to the compressor, while the liquid phase enters the HE for precooling natural gas and mixed refrigerant. The combined refrigerant is then introduced into the separator. Due to the disparity in the boiling temperatures of constituents, two phases have distinct compositions. Thus, MCHE receives two streams of mixed refrigerant. Throughout the process, the temperature of natural gas drops precipitously and it reaches the saturated phase. The mixed refrigerant cools through the MCHEs and then experiences pressure and temperature reduction in the throttling valves, resulting in a returning cryogenic stream that causes natural gas to liquefy. In recent study, an enhanced cycle with three precooling temperature stages and two cryogenic heat exchangers was investigated. The propane separators operate at three different temperatures; the gaseous phase always returns to the compressors, while the liquid phase is separated into three streams. Two streams will be utilized to precool natural gas and mixed refrigerant, with one entering the throttling valve to achieve the desired temperature and pressure level. As a result, propane will be at the third level's lowest temperature. Utilizing refrigerants imposes a functional limitation. Each refrigerant in a cooling process may be cooled to its saturation temperature at atmospheric pressure, regardless of its functional pressure. Propane has a freezing point of -42°C, and hence the third level of the precooling step is set at -42°C. Aftercooler compresses and cools the mixed refrigerant, which then enters three precooling layers. Following that, it degrades and enters MCHEs. The gaseous phase cools and transforms into a liquid, at which point it enters the second stage. It cools down further in the second MCHE, and the exit stream enters the throttling valve, forming a cryogenic stream that initiates the chilling process in the second MCHE. After cooling in the first MCHE, the liquid phase reaches the throttling valve. Then, this stream and the returning stream from the second MCHE will mix and chill the first MCHE's other streams. Finally, all of the streams will be combined and sent into the compressor. It is critical that the input stream be superheated; no liquid should be allowed to reach the compressors. Natural gas enters the cycle at a specified pressure, which is critical to the system's performance and efficiency. Following three precooling stages and a mixed refrigerant stage, natural gas will pass through a throttling valve to reach atmospheric pressure, where it will be prepared for delivery to transport stations. After the last throttling valve, it must be below -157°C. The gaseous phase and its cold exergy may be used as a cold stream for certain industrial applications or recirculated.

When designing the processes, Aspen Hysys version 11 software was used, and the Peng Robinson thermodynamics equation of state was used throughout the whole process. Aspen HYSYS is a chemical process modeling and design software that is used by the process industries to model and create chemical process models [6].

The Peng-Robinson equation of state;

$$P = \frac{RT}{V_m - b} - \frac{a\propto}{V_m^2 + 2bV_m - b^2} \qquad (1)$$

$$a \approx 0.45724\frac{R^2T^2}{p_c} \qquad (2)$$

$$b \approx 0.07780\frac{RT^2}{p_c} \qquad (3)$$

$$\propto = \left(1 + k\left(1 - T_r^{\frac{1}{2}}\right)\right)^2 \qquad (4)$$

$$k \approx 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (5)$$

$$T_r = \frac{T}{T_c} \qquad (6)$$

P = pressure, T= temperature, V=volume, R= Gas constant, T_r = Reduced temperature, T_c =Critical Temperature, P_c = Critical Pressure, ω = Acentric factor.

The refrigerants utilized in this experiment is a combination of argon, krypton, xenon, nitrogen, gas. When simulating the process, the circumstances and compositions of the refrigerants were different from what was employed in the real process.

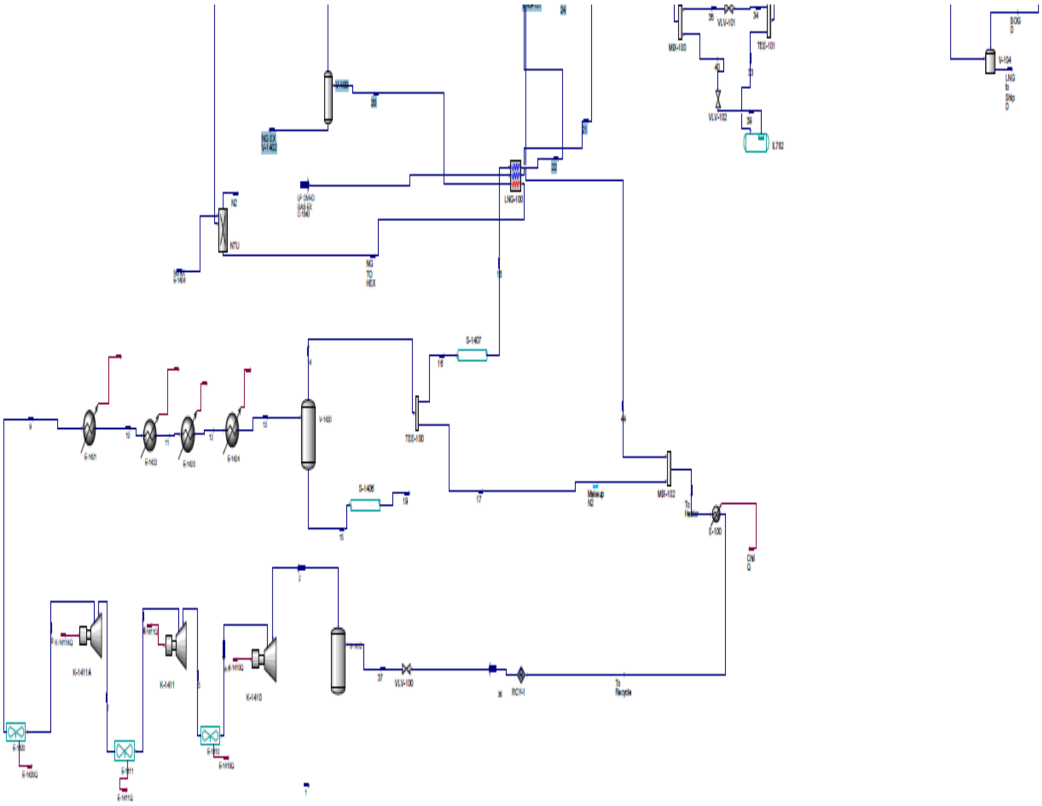

Figure 1: Simulation of Liquefaction Precooling Cycle for analysis

2.4 The Krypton Refrigeration Cycle

Table 1: Krypton Refrigerants Composition Krypton cycle

Components	**Mole Fraction**
Krypton	1

Table 2: Krypton Refrigerant Inlet Condition

Pressure [bar]	3
Temperature [°C]	181.5
Molar Flow [kgmole/h]	1494
Vapour/Phase Fraction	1

Table 3: Natural Gas composition

Components	**Mole Fraction**
Methane	0.9237
Ethane	0.0512
Propane	0.0192
i-Butane	0.0031
n-Butane	0.0024

Table 4: Natural Gas Inlet Process Condition

Pressure [Kpa]	5851
Temperature [°C]	-42
Molar Flow [kgmole/h]	3.830e+004
Vapour/Phase Fraction	1

i. Process Description of Krypton Cycle

In the design of the refrigeration system, krypton with the initial conditions was passed through a valve (VLV-100) to a separator (V-1410) where the overhead vapor was collected and sent through three compressors with inter-coolers placed in-between. The aim of the compressors is to raise the pressure of the gas to about 46.40 bar and the intercoolers are applied to maintain the temperature at about 40 ^{o}C. The cooled Krypton is sent to the first LNG heat exchanger (LNG-100) where it acts as a coolant in conjunction with propane. The two cooling streams were used to cool the natural gas stream from its initial temperature of -44.19 ^{o}C to -50 ^{o}C and sent to separator (V-100) to remove liquids, which might consist of heavy hydrocarbons. The overhead gas from separator (V-100) was sent to the second heat exchanger LNG-101. For this second heat exchanger, the coolants still remain krypton and propane. The overhead gas enters LNG-101 at -50 ^{o}C and exits at -132.0 ^{o}C, it then enters the third heat exchanger LNG-102 at -132.0 ^{o}C and exits at -132.0 ^{o}C, only xenon was used as the refrigerant for LNG-102. Although the LNG was completely formed after leaving the third heat exchanger, the temperature did not reach the determined temperature of -160.6 ^{o}C, the LNG was thus passed through a depressurier, to attain the required temperature of -160.0 ^{o}C, and to lower the pressure of the LNG before it was delivered to vessels that were built to operate at a lower pressure than the entering LNG pressure. LNG was passed through a pump, and stored into four different storage tanks. As a matter of safety, the boil-off gases from the storage section were diverted to Mix-103, where they are compressed and cooled before being recycled back to the component splitter unit, with the natural gas stream.

2.5 The Argon Refrigeration Cycle

Table 5: Refrigerants Composition for Argon Cycle

Components	**Mole Fraction**
Argon	1

Table 6: Argon Refrigerant Inlet Condition

Pressure [bar]	3.1
Temperature [^{o}C]	181.5
Molar Flow [kgmole/h]	1494
Vapour/Phase Fraction	1

Table 7: Natural Gas composition

Components	**Mole Fraction**
Methane	0.9237
Ethane	0.0512
Propane	0.0192
i-Butane	0.0031
n-Butane	0.0024

Table 8: Natural Gas Inlet Process Condition

Pressure [bar]	57.50
Temperature [^{o}C]	-42
Molar Flow [kgmole/h]	3.830e+004
Vapour/Phase Fraction	1

ii. Process Description of Argon Cycle

In the design of the refrigeration system, Argon with the initial conditions was passed through a valve (VLV-100) to a separator (V-1410) where the overhead vapor was collected and sent through three compressors with inter-coolers placed in-between. The aim of the compressors is to raise the pressure of the gas to about 46.40 bar and the intercoolers are applied to maintain the temperature at about 40 ^{o}C. The cooled Argon is sent to the first LNG heat exchanger (LNG-100) where it acts as a coolant in conjunction with propane. The two cooling streams were used to cool the natural gas stream from its initial temperature of -44.19 ^{o}C to -50 ^{o}C and sent to separator (V-100) to remove liquids, which might consist of heavy hydrocarbons. The overhead gas from separator (V-100) was sent to the second heat exchanger LNG-101. For this second heat exchanger, the coolants still remain Argon and propane. The overhead gas enters LNG-101 at -50 ^{o}C and exits at -132.0 ^{o}C, it then enters the third heat exchanger LNG-102 at -132.0 ^{o}C and exits at -132.0 ^{o}C, only Argon was used as the refrigerant for LNG-102. Although the LNG was completely formed after leaving the third heat exchanger, the temperature did not reach the determined temperature of -160.6 ^{o}C, the LNG was thus passed through a depressurier, to attain the required temperature of -160.0 ^{o}C, and to lower the pressure of the LNG before it was delivered to vessels that were built to operate at a lower pressure than the entering LNG pressure. LNG was passed through a pump, and stored into four different storage tanks. As a matter of safety, the boil-off gases from the storage section were diverted to Mix-103, where they are compressed and cooled before being recycled back to the component splitter unit, with the natural gas stream.

2.6 The Nitrogen Refrigerant cycle

Table 9: Refrigerants Composition for Nitrogen Cycle

Components	**Mole Fraction**
Nitrogen	1

Table 10: Nitrogen Refrigerants Inlet Condition

Pressure [bar]	3.1
Temperature [^{o}C]	-118.1
Molar Flow [kgmole/h]	1479
Vapour/Phase Fraction	1

Table 11: Natural Gas composition

Components	**Mole Fraction**
Methane	0.9237
Ethane	0.0512
Propane	0.0192
i-Butane	0.0031
n-Butane	0.0024

Table 12: Natural Gas Inlet Process Condition

Pressure [Kpa]	5851
Temperature [^{o}C]	-42
Molar Flow [kgmole/h]	3.830e+004
Vapour/Phase Fraction	1

iii. Process Description of Nitrogen Cycle

In the design of the refrigeration system, Nitrogen with the initial conditions was passed through a valve (VLV-100) to a separator (V-1410) where the overhead vapor was collected and sent through three compressors with inter-coolers placed in-between. The aim of the compressors is to raise the pressure of the gas to about 46.40 bar and the intercoolers are applied to maintain the temperature at about -90.0 ^{o}C. The cooled Nitrogen is sent to the first LNG heat exchanger (LNG-100) where it acts as a coolant in conjunction with propane. The two cooling streams were used to cool the natural gas stream from its initial temperature of -44.19 ^{o}C to -50 ^{o}C and sent to separator (V-100) to remove liquids, which might consist of heavy hydrocarbons. The overhead gas from separator (V-100) was sent to the second heat exchanger LNG-101. For this second heat exchanger, the coolants still remain Nitrogen and propane. The overhead gas enters LNG-101 at -50 ^{o}C and exits at -132.0 ^{o}C, it then enters the third heat exchanger LNG-102 at -132.0 ^{o}C and exits at -132.0 ^{o}C, only Nitrogen was used as the refrigerant for LNG-102. Although the LNG was completely formed after leaving the third heat exchanger, the temperature did not reach the determined temperature of -160.6 ^{o}C, the LNG was thus passed through a depressurier, to attain the required temperature of -160.0 ^{o}C, and to lower the pressure of the LNG before it was delivered to vessels that were built to operate at a lower pressure than the entering LNG pressure. LNG was passed through a pump, and stored into four different storage tanks. As a matter of safety, the boil-off gases from the storage section were diverted to Mix-103, where they are compressed and cooled before being recycled back to the component splitter unit, with the natural gas stream.

2.7 The Xenon Refrigeration Cycle

Table 13: Refrigerants Composition for Xenon Cycle

Components	**Mole Fraction**
Xenon	1

Table 14: Xenon Refrigerants Inlet Condition

Pressure [bar]	3.10
Temperature [^{o}C]	181.5
Molar Flow [kgmole/h]	1494
Vapour/Phase Fraction	1

Table 15: Natural Gas composition

Components	**Mole Fraction**
Methane	0.9237
Ethane	0.0512
Propane	0.0192
i-Butane	0.0031
n-Butane	0.0024

Table 16: Natural Gas Inlet Process Condition

Pressure [Kpa]	5851
Temperature [^{o}C]	-42
Molar Flow [kgmole/h]	3.830e+004
Vapour/Phase Fraction	1

iv. Process Description of Xenon Cycle

In the design of the refrigeration system, Xenon with the initial conditions was passed through a valve (VLV-100) to a separator (V-1410) where the overhead vapor was collected and sent through three compressors with inter-coolers placed in-between. The aim of the compressors is to raise the pressure of the gas to about 46.40 bar and the intercoolers are applied to maintain the temperature at about 40 ^{o}C. The cooled Xenon is sent to the first LNG heat exchanger (LNG-100) where it acts as a coolant in conjunction with propane. The two cooling streams were used to cool the natural gas stream from its initial temperature of -44.19 ^{o}C to -50 ^{o}C and sent to separator (V-100) to remove liquids, which might consist of heavy hydrocarbons. The overhead gas from separator (V-100) was sent to the second heat exchanger LNG-101. For this second heat exchanger, the coolants still remain Xenon and propane. The overhead gas enters LNG-101 at -50 ^{o}C and exits at -132.0 ^{o}C, it then enters the third heat exchanger LNG-102 at -132.0 ^{o}C and exits at -132.0 ^{o}C, only Xenon was used as the refrigerant for LNG-102. Although the LNG was completely formed after leaving the third heat exchanger, the temperature did not reach the determined temperature of -160.6 ^{o}C, the LNG was thus passed through a depressurizer, to attain the required temperature of -160.0 ^{o}C, and to lower the pressure of the LNG before it was delivered to vessels that were built to operate at a lower pressure than the entering LNG pressure. LNG was passed through a pump, and stored into four different storage tanks. As a matter of safety, the boil-off gases from the storage section were diverted to Mix-103, where they are compressed and cooled before being recycled back to the component splitter unit, with the natural gas stream.

III. RESULTS AND DISCUSSION

The results on the various processes (C_3MR, Krypton, Argon, Neon and Nitrogen) on the exergy, coefficient of performance of the refrigerants are displayed below in graphical and tabular forms.

3.1: Exergy Analysis

A. Analysis in Separators

Table 17: Exergy loss in Separators

PROCESS	V-100	V-1410	V-1420
C_3MR	0.00	0.10	0.00
KRYPTON	0.00	0.10	0.00
ARGON	-38.20	0.00	0.00
XENON	0.00	0.40	0.00
NITROGEN	0.00	1.40	0.00

Description: V-100: NG separator; V-1410: Refrigerant separator before Compressor; V-1420: Refrigerant separator after cooler

v. LNG Heat Exchangers

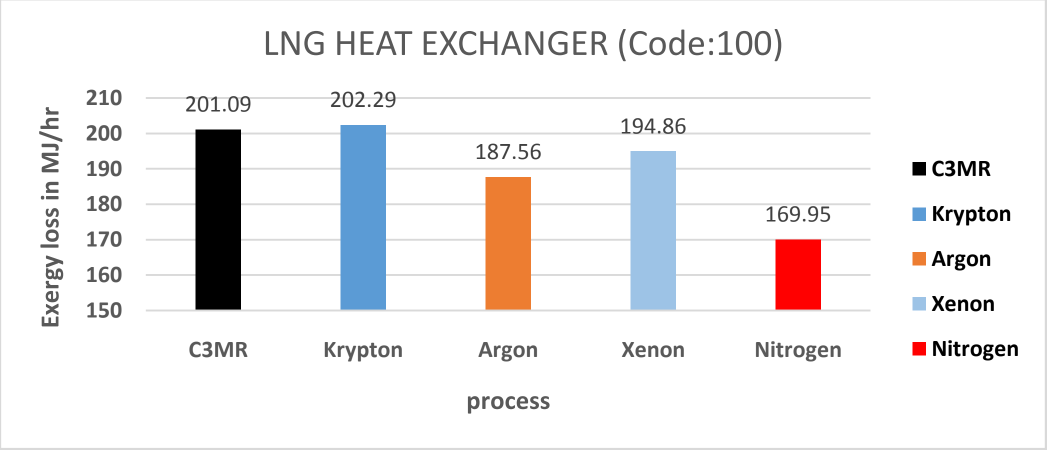

Figure 1 Exergy loss in LNG HEX 100 (HEX – Heat Exchanger)

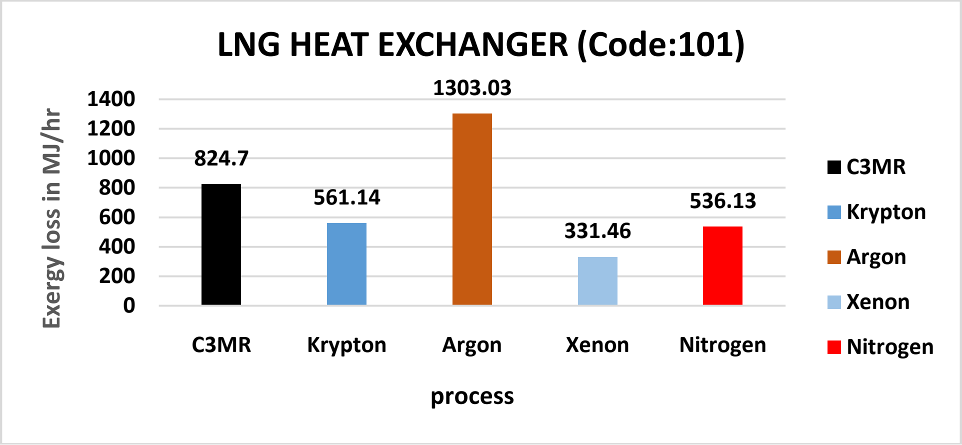

Figure 2: Exergy loss in LNG HEX 101

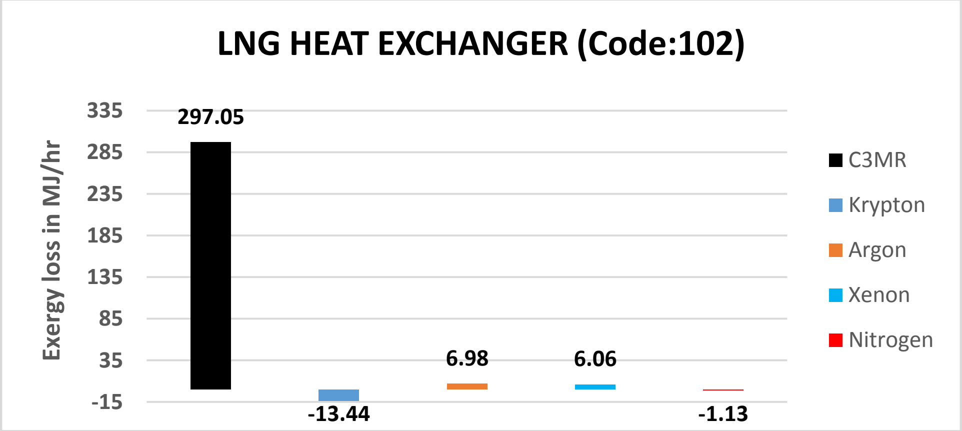

Figure 3: Exergy loss in LNG HEX 102

B. Valve and Expanders

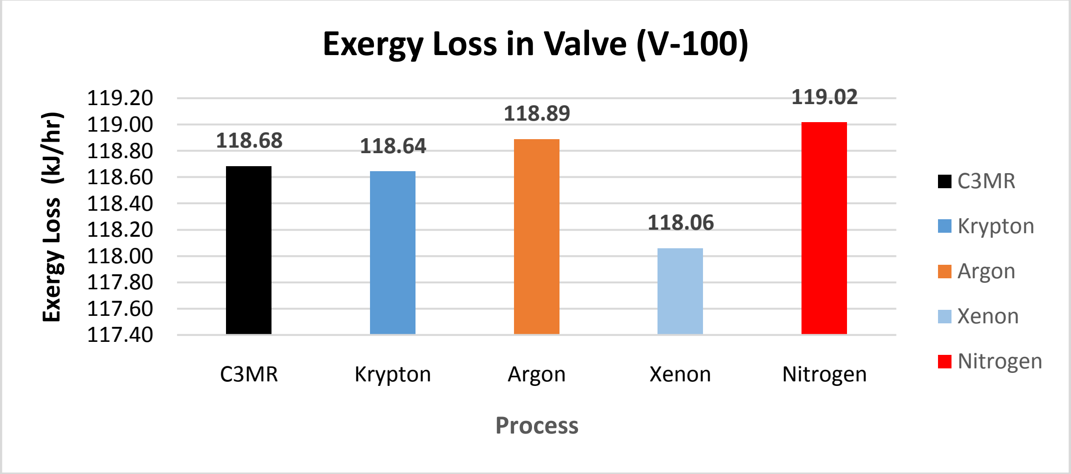

Figure 4: Exergy loss in valve V-100

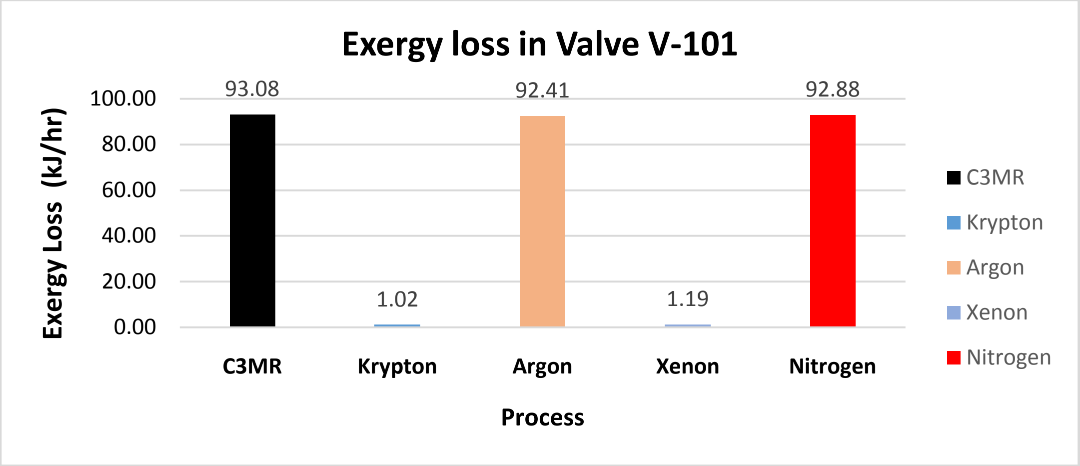

Figure 5: Exergy loss in valve V-101

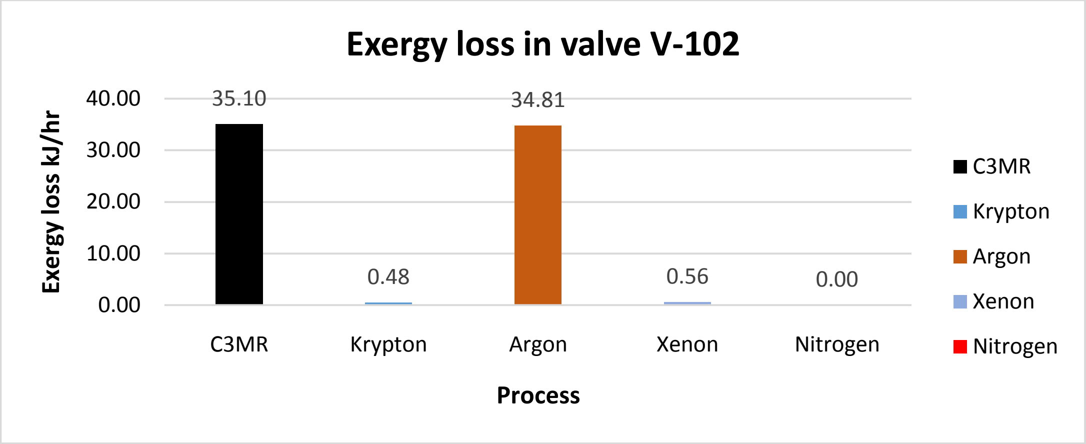

Figure 6: Exergy loss in valve V-102

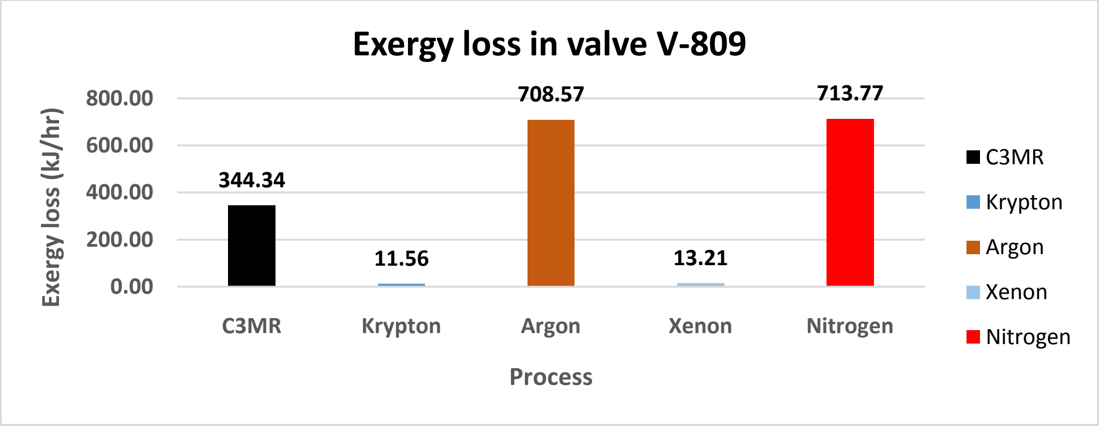

Figure 7: Exergy loss in valve V-809

vi. D Refrigerant compressor

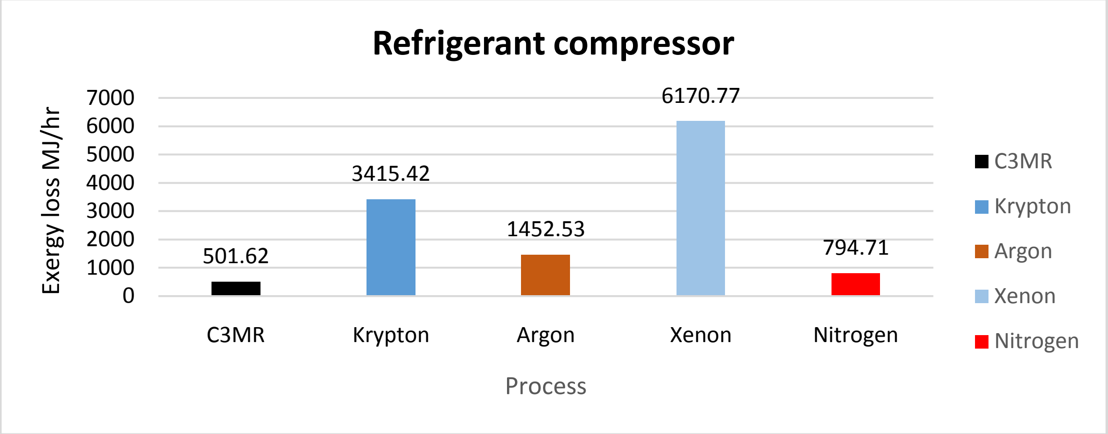

Figure8: Refrigerant compressor K1410

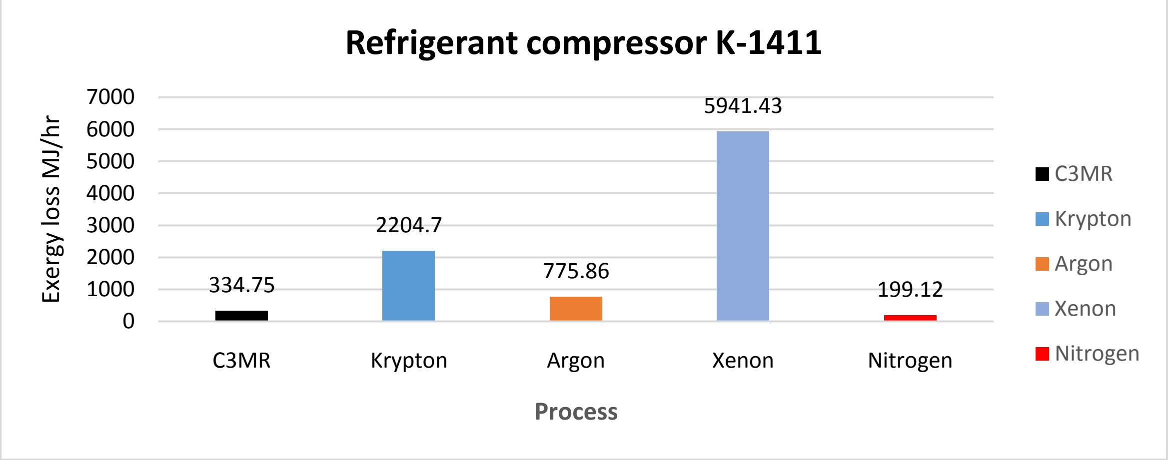

Figure 9: Refrigerant compressor K1411

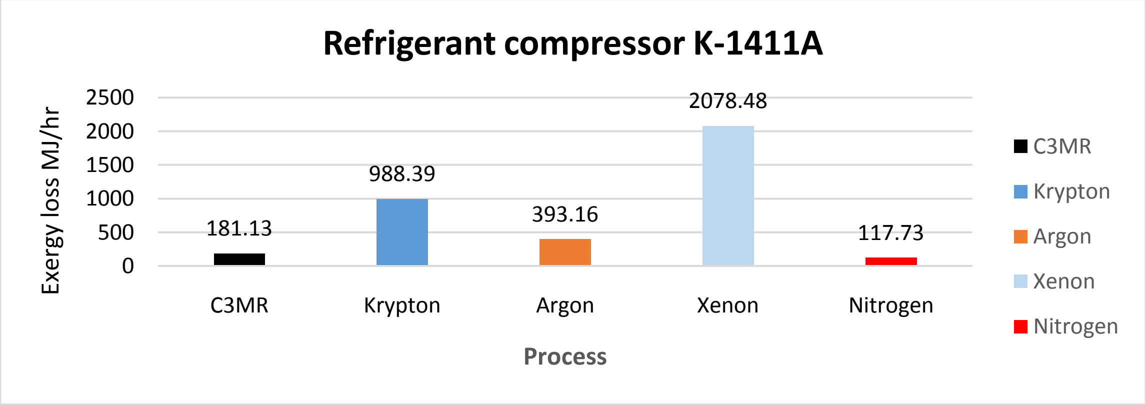

Figure 10: Refrigerant compressor K1411A

vii. E LNG Recycling Compressor

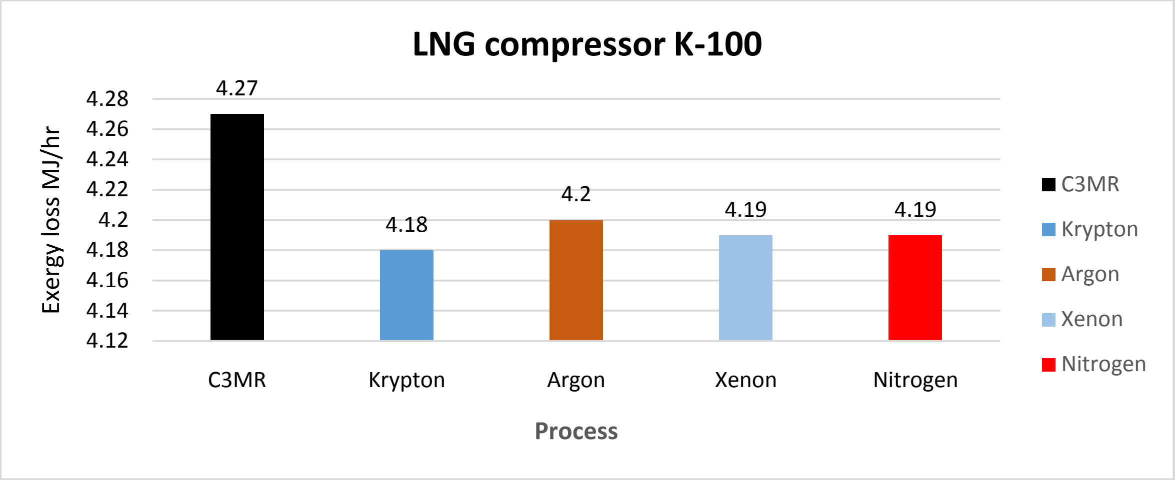

Figure 11: Refrigerant compressor K10

viii. F Exergy loss in Depressurizer

Table 18: Exergy loss in depressurizer

PROCESS	REFRIGERANT DEPRESSURIZER (IL 782) (kJ/hr)
C_3MR	3397.30
KRYPTON	34.60
ARGON	3352.90
XENON	57.80
NITROGEN	345439.20

ix. 3.2 Energy Requirement in compression, chilling and cooling section

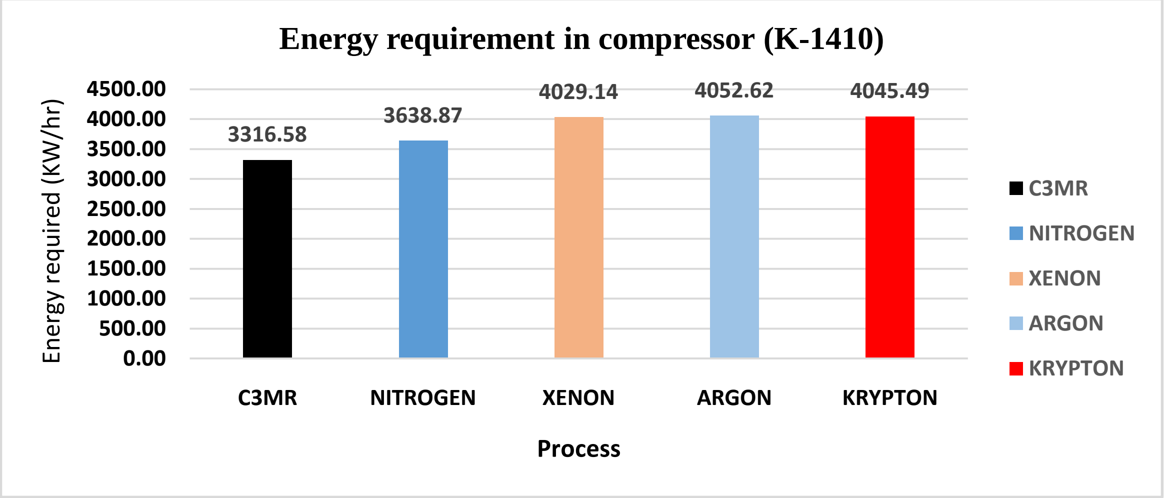

Figure 12: Energy requirement in compressor (K-1410)

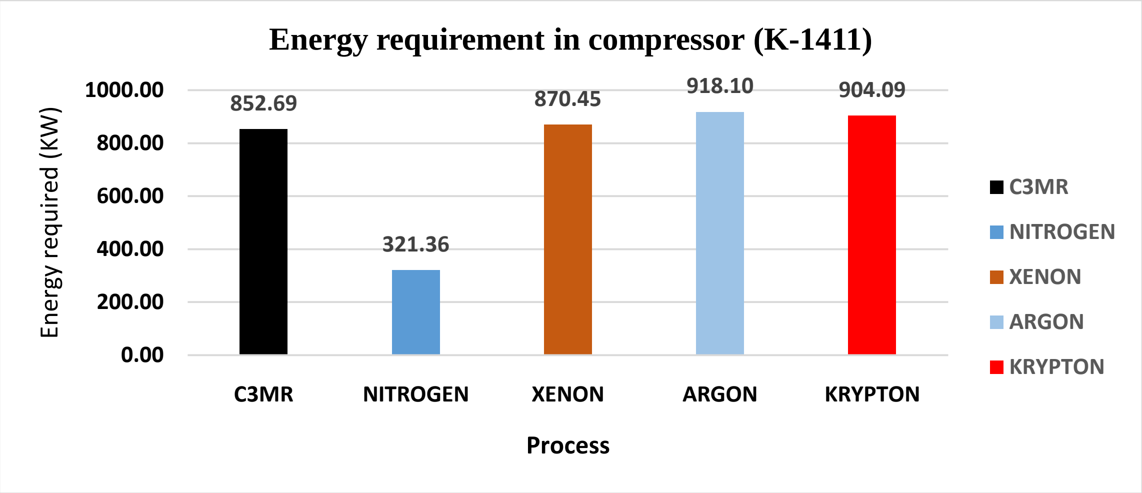

Figure 13: Energy requirement in compressor (K-1411)

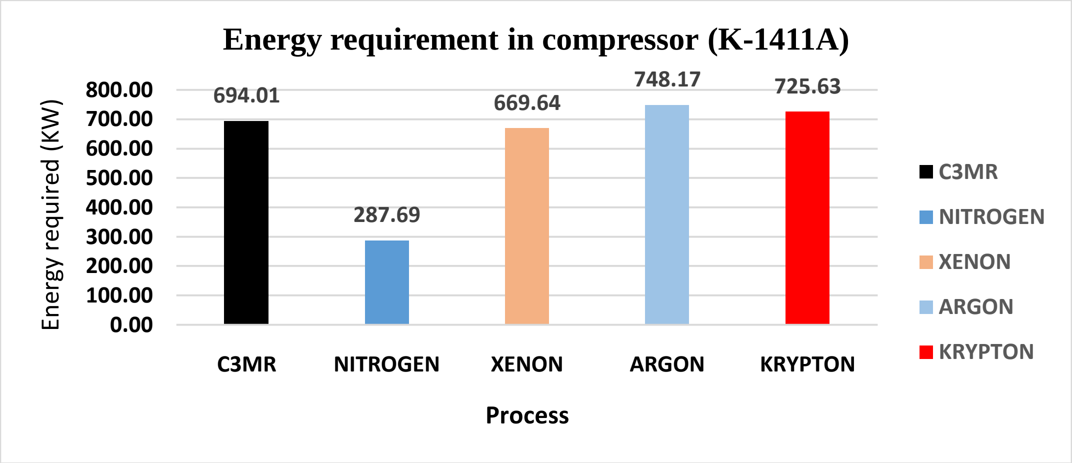

Figure 14: Energy requirement in compressor (K-1411)

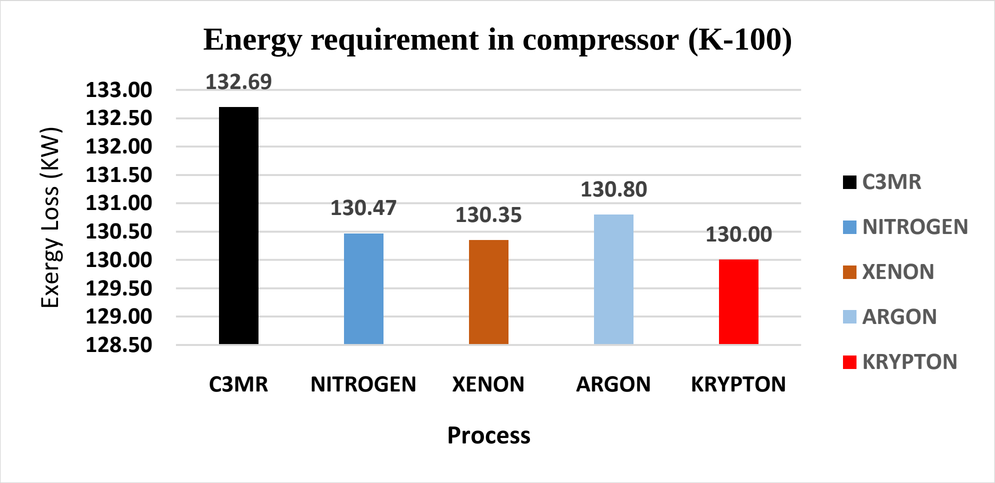

Figure 15: Energy requirement in compressor (K-100)

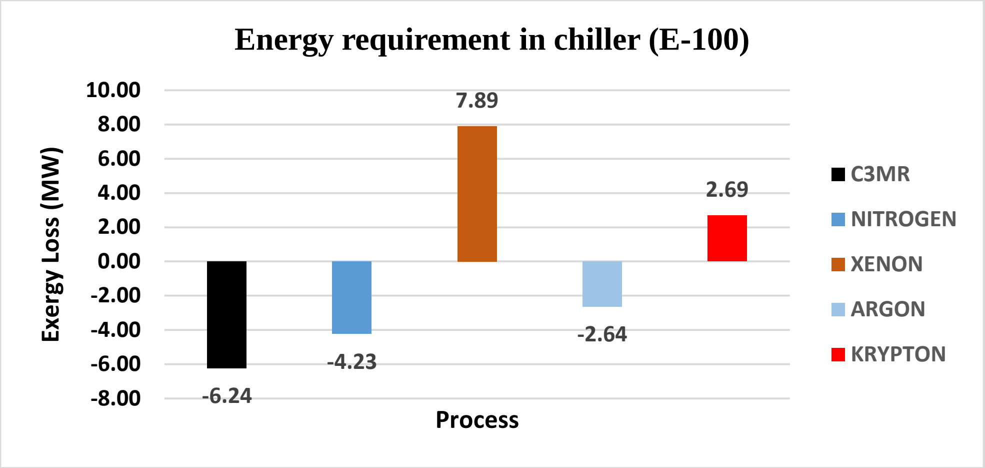

Figure 16: Energy requirement in chiller section (E-100)

x. 3.3 Percentage Exergy Efficiency

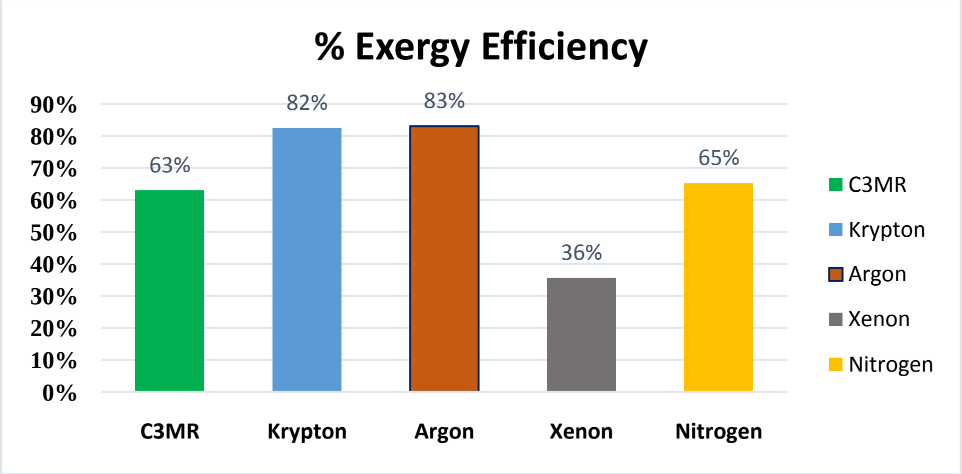

Figure 17: Percentage exergy efficiency

xi. 3.4 Coefficient of Performance of Refrigerants

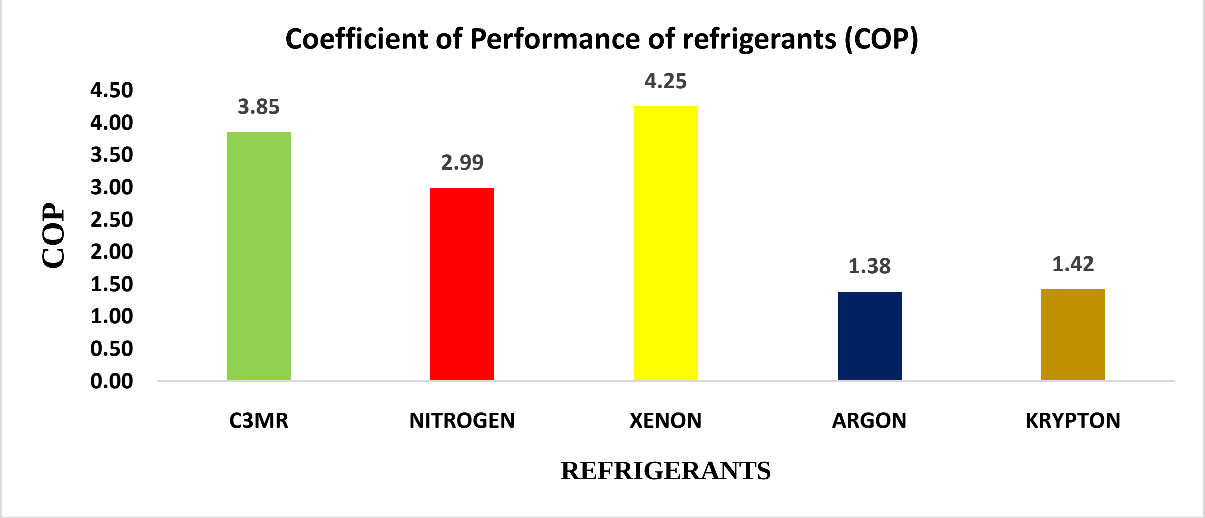

Figure 18: Coefficient of Performance

With this chemical process software (Aspen Hysys 11.0), separate designs with the same instruments were used and different refrigerants were administered. The first parameter was to check out the compatibility of each refrigerants using the designs. All refrigerants were compatible with the process equipment. First to be calculated was the exergy as required by the objectives. This was done on different equipment such separators, valve, compressors, LNG heat exchangers, and depressurizer used in each of the processes. Firstly, the exergy at the separator to present the refrigerant into two phase and separate the liquid to prevent the surge of the compressors, in Table 17. In Table 17, nitrogen lost the highest energy during phase separation, but argon used all available energy ready for the phase separation it is in equilibrium with the environment. Figure 1 - 3 displayed the LNG heat exchanger exergy analysis result. From the figures the Refrigerant with the most inability to use the available energy for the colling is argon with mean exergy loss of 499MJ/hr and next the conventional C_3MR (440.93MJ/hr).Figure 4 - 7 shows the exergy loss analysis of the valves through which the refrigerants passed through. Across the valve is to reduce the pressure. The Argon refrigerant has the highest exergy loss showing to its inability to make dowith available energy for the process. Figure 8 – 10 show the exergy loss in the compressor. From the analysis, Xenon refrigerant has the highest exergy loss amongst the studied refrigerants.

IV. CONCLUSION

It is important to evaluate and compare the performances of inorganic refrigerants in Natural Gas liquefaction process, as a way of drawing relevant insights vis-à-vis the merits and demerits of various materials refrigerants over another, as a means of providing a platform into which technological, environmental and economic decisions can be made.The refrigerant with the best cooling effect (COP) amongst all compared refrigerants is Xenon and then C_3MR due to their highCoefficient of Performance. On the other hand, Argon was seen to be most exergy efficient (Fig. 17).

REFERENCES

[1]. Haaf, S., & Henrici, H. (2003). Refrigeration Technology. Ullmann’s Encyclopedia of Industrial Chemistry, sixth ed. *Refrigeration Technology. Ullmann’s Encyclopedia of Industrial Chemistry, Sixth Ed.*, *31*, 209–312.

[2]. Hasan, M. M. F., Zheng, A. M., & Karimi, I. A. (2009). Minimizing Boil-Off Losses in Liquefied Natural Gas Transportation. *Industrial & Engineering Chemistry Research*, *48*(21), 9571–9580. https://doi.org/10.1021/ie801975q

[3]. Kidnay, A. J., & Parrish, W. R. (2006). Fundamentals of natural gas processing. *Fundamentals of Natural Gas Processing*.

[4]. Mehrpooya, M., Hossieni, M., &Vatani, A. (2014). Novel LNG-Based Integrated Process Configuration Alternatives for Coproduction of LNG and NGL. Industrial & Engineering Chemistry Research, 53(45), 17705–17721. https://doi.org/10.1021/ie502370p

[5]. Mokhatab, S., Poe, W. H., & Speight, J. G. (2015). Natural gas compression. Natural Gas Compression, 295–322.

[6]. Zhang, J., & Xu, Q. (2011). Cascade refrigeration system synthesis based on exergy analysis. *Cascade Refrigeration System Synthesis Based on Exergy Analysis*, 1901–1914.