A study of a cryogenic energy storage system for the integration of renewable energy sources

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A study of a cryogenic energy storage system for the integration of renewable energy sources

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A mon fils, Rayane

Venu au monde en cours de cette thèse

Et à qui j'enseignerai tout ce que j'ai appris de bon dans la vie

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Résumé

Dans le cadre des perspectives européennes H2020 de l'intégration des énergies renouvelables, des solutions de stockage de l'énergie électrique de masse s'imposent. Leur rôle principal est de stocker le surplus de production en électricité des énergies renouvelables en facilitant ainsi l'équilibrage du réseau électrique. Le stockage sous forme d'air liquide est l'une des technologies récemment étudiées répondant à cette problématique.

De ce fait, l'objectif global de cette thèse est de comparer deux systèmes de stockage à air liquéfié : système récupération à surchauffe, solution la plus étudiée, et un principe innovant de stockage d'air liquide mettant en œuvre une combustion lors de la récupération d'énergie. Pour conserver un impact faible sur l'environnement d'une telle technologie, les trois types de combustions dans l'unité de décharge étudiées ici sont : oxy-biogaz, oxy-gaz naturel et air-biogaz. L'oxy-combustion permet de réduire considérablement, voire d'éliminer totalement les émissions des NO_x. Grâce à la concentration importante en CO_2 dans les produits de combustion, elle facilite également le processus de post traitement des gaz d'échappement et la transformation du CO_2 en glace carbonique par la suite.

La comparaison consiste premièrement à établir une analyse thermodynamique incluant analyse énergétique et exergétique pour calculer les différents rendements et efficacités caractérisant le système. Comme il s'agit ici d'un processus de combustion, l'analyse thermodynamique inclue en particulier la modélisation et simulation de la chambre de combustion. Cette étape a été réalisée par la méthode de GRIMECH 3.0 incluant 53 espèces et 325 réactions. Par cette méthode, les émissions des gaz polluants de la combustion sont aussi quantifiées.

La deuxième partie de la comparaison repose sur une analyse de la performance environnementale. Les impacts environnementaux des 3 systèmes proposés sont évalués dans une approche d'Analyse de Cycle de Vie pour la partie opérationnelle (sans prendre en considération les étapes de matériaux/construction et destruction/recyclage). Un bilan de masse pour un point optimal choisi à l'issue de l'étude thermodynamique est établi. Trois méthodes « ReCiPe endpoint», « ReCiPe midpoint » et « Eco-cost » sont utilisées pour l'interprétation des résultats et la proposition des axes d'amélioration.

La dernière partie de la comparaison aborde le volet économique du système de stockage à air liquéfié sous forme d'une étude technico-économique pour un cas concret du système de stockage implanté dans un site industriel ayant des besoins en réfrigération utilisant l'energie photovoltaïque comme source d'énergie renouvelable. Une première partie consiste à proposer une optimisation des scénarios de distribution de l'énergie. Cette optimisation prend en considération le tarif d'électricité variable suivant la région, les données météorologiques ainsi que le rendement électrique du système de stockage. Les performances économiques sont ainsi évaluées à travers le retour sur investissement considérant les différents coûts d'investissement.

Mots clefs:

Liquid Air Energy Storage ; Energy Analysis ; oxy-fuel combustion ; Life Cycle Analysis; Techno-economic study

Abstract

As part of the H2020 European strategy of the renewable energy integration perspectives, grid-scale or large-scale Electric Energy Storage solutions have gained strategic role. Their major utility consists on balancing the electric grid by storing the surplus of energy from the renewable source. Liquid Air Energy Storage (LAES) is one of the newly studied storage solutions in this energy transition context.

Consequently, the global objective of the thesis is the comparison of two LAES storage systems: a direct expansion discharge cycle with super-heating process, and a discharge unit with the integration of a combustion process as innovation in this work. To preserve a reduced environmental impact of such a technology, three types of combustion are considered: oxy-biogas combustion, air-biogas combustion and oxy-natural gas combustion. The oxy-fuel combustion allows the reduction of considerable amount of NOx, or their total elimination. Thanks to high concentration in carbon dioxide, flue gases can be subject to a post treatment by means of carbon dioxide transformation into dry ice.

The comparison consists primarily, on the calculation of efficiencies as results of the energy and exergy analysis of four LAES configurations with a particular focus on the combustion modelling and simulation. For this reason, combustion was modeled separately for the rest of the system. This step was achieved by means of GRIMECH reaction scheme including 53 species and 325 reactions; emissions of pollutant gas was also quantified.

The second part of this comparison is related to the environmental performance of the LAES. Environmental impact of three innovative proposed systems are evaluated by a life cycle analysis method for the operational phase of the life cycle. A mass balance for an optimal operating point has been previously selected in the thermodynamic part of the study for the environmental simulation. Three methods are used for the interpretation: “ReCiPe midpoint”, “ReCiPe endpoint” and “Eco-cost”.

In the last step of the comparison, a techno-economic study of a real LAES trial implementation in an industrial site with PV power plant as renewable energy source is performed. The optimization of energy flow scenario based on meteorological parameters of the considered location, the electricity tariff as well as the efficiency of the LAES were considered. Economic performance is therefore evaluated through the payback period considering different investment costs.

Keywords:

Liquid Air Energy Storage ; Energy Analysis ; oxy-fuel combustion ; Life Cycle Analysis; Techno-economic study

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CHAPTER 1

INTRODUCTION

General introduction to the thesis

Aims of the work

1.1 General introduction

Today, within the energy transition global context, the share of renewable power generation is increasing. This engages pro-active discussions about new policies, regulations, market structures and industry strategies, particularly to support the stable integration of the highest possible shares of power generation from variable renewables (i.e. solar and wind) regarding their strong intermittency. Strategies are also needed to decarbonize high-energy consumers, from transport and industry to the buildings. The notion of decarbonization is a widely used vocabulary in recent studies/reports. It relates to the reduction of greenhouse gases (GHG) emission of the considered sector. This brings the role of electricity storage, and in particular large-scale storage systems, to highly prominent position in the leading strategy of the energy transition.

Although pumped hydro storage (PHS) dominates total large-scale electricity storage today, accounting for 96% of global installed capacity, there is a large portfolio of storage technologies, depending on the way energy is stored. The current deployment of compressed air energy storage (CAES) as a large-scale storage solution is 0.3% of the global capacity, concentrated in only a few large projects throughout the world. Conventional pumped hydro storage systems use two water reservoirs at different elevation, and compressed air technology requires typical underground storage cavities such as caverns or abandoned mines. So, the main drawbacks of these technologies are the dependence on geographical location and the large land footprint (Bisht, 2014; International Electrotechnical Commission).

Cryogenic Energy Storage (CES) is a relatively new option for energy storage. It makes use of low-temperature liquids (air or nitrogen) as an energy storage and transfer medium. CES can provide large scale, long duration storage and capacities between 5 to 1000 MWh (IEC, 2011) Inside this category, LAES (Liquid Air energy Storage) uses air as storage medium. The current state of LAES is still under development and demonstration stage since no commercial or pre-commercial plants have been built. Nonetheless, a small pilot plant was deployed and operated in Slough, UK, directed by Highview in 2015. More lately, British battery pioneers planned to build Europe's largest energy storage project of an LAES type that can store renewable energy for weeks rather than hours and they called it "Cryobattery". Highview claimed the cryobattery would cost about £110 per MWh of electricity, using a 200MW system, which would make it one of the cheapest energy storage technologies (Ambrose, 2019).

Apart from the environmental major advantage, CES has the benefit of the “co” or even “tri” energy recovery in some cases as CES can be coupled to more than one system. Moreover, cold from evaporation of liquid cryogen can be stored and reused in multiple applications. For example, CES can be associated to refrigeration plants and food processing systems by restituting some of the cold energy obtained from the evaporation. Considering that refrigerated warehouses for chilled and frozen foods are large energy consumers, this solution might generate economic benefits.

An additional technological development concerns the use of cryogenic process to capture CO_2 by combustion-post treatment. Captured CO_2 can be used under different forms: gaseous, liquid, solid or super critical for different applications: chemistry, refrigerated transport (dry ice), food and beverages industry, etc. Alternatively, liquid air or its components (liquid nitrogen, liquid oxygen and liquid argon) can be used in other applications in form of by-products, as it is the case of Dearman engine system where liquid air is used for powering the engine and cooling the refrigerated vehicle. Indeed, hybridization of LAES is opened to multiple opportunities as cryogenics have been used in superconductivity, rocketry, cryosurgery, cooled electronics since the 60’s, and nowadays even in food, medical and pharmaceutical industries.

In this context, a recent innovative European project CryoHub (CryoHub, 2019) has investigated and extended the potential of large-scale LAES by recovering the stored energy in two forms, electrical energy and cold energy for refrigerated warehouses. The surplus of electricity produced by Renewable Energy Sources (RES) is used to liquefy and store the air. Therefore, CryoHub project aims at providing grid balancing by storing energy from local intermittent RES, while meeting the cooling demand of a refrigerated food warehouse and recovering the waste heat from its equipment and components. Through the integration of LAES to a refrigerated warehouse, CryoHub intends to decarbonize the local electricity grid as LAES uses low carbon resources more effectively. The project is, yet under study and a demonstrator will be deployed by the end of 2020.

1.2 Aims of the work

The present PhD thesis is part of this H2020 European project. The current work has focused on newly developed LAES configurations. Two energy recovery systems are studied. The first one relies on an evaporation and super-heating process of liquid air while, in the second approach, a combustion process is integrated in the generation unit. For this combustion process, three cases will be analyzed: oxy-biogas combustion, oxy-natural gas combustion and air-biogas combustion. The involvement of biogas and oxy-combustion features is to maintain the environmental performance that mostly characterizes LAES compared to other storage technologies. A global study of the LAES including energy analysis, environmental impact and economic analysis will be carried out to assess the feasibility and perspectives of this technology in the nergy transition context.

The combination of the scientific papers has constituted the chapters of this report. They are organized as follows:

- Scientific background: to provide from a critical literature review a clear picture of the CES/LAES technology as well as a discussion of the cycle efficiencies depending on the process type.
- Thermodynamic performance analysis : to evaluate thermodynamic performance through energy and exergy analysis associated to polluting emissions analysis under the optimum operating conditions settings of the studied configurations
- Environmental performance of LAES: to assess the environmental impact through a Life Cycle Analysis method (LCA) of the operational phase.
- Energy optimization scenario and techno-economic analysis of the storage system in a real industrial implementation.

These articles aim at providing new knowledge in order to respond to the scientific questions that will be discussed at the outcome of the scientific background. A short introduction/transition section will be added at the beginning of each paper in which a diagram featuring input/output elements and developed methods will be presented.

CHAPTER 2

SCIENTIFIC BACKGROUND

Introduction to the review paper

The review paper

Conclusion and transition towards next chapter

Introduction to the scientific background paper

LAES thermodynamic performances reported in the literature are so far scattered due to different configurations and available external thermal energy sources (waste heat/cold); simulation's assumptions turbomachinery efficiencies, operating conditions .

The lack of experimental validation is also an issue and is due to very few realizations until now. One reason behind this lack of realization is the uncertainty payback periods for investors due to the important investment cost of machinery of a LAES demonstrator. Controversy related to the environmental aspect is another issue when a combustion process is included in the discharge part.

Up to date, no literature review of LAES technology has been made covering all investigation aspects on the subject.

This review tends to provide information on the different designs and configurations of Liquid Air Energy Storage systems. The primary objective of reviewing this technology is to evaluate its potential in the near future for the renewable energy integration in order to develop sustainable processes. Thermodynamic efficiency is also discussed as well as several ways to enhance the efficiency. One of the main ideas for the efficiency and profit enhancement proposed by this review is to recover two types of energy: cold cryogenic and electrical energy. The recovery of cold energy might be done by coupling the storage system to cold stores or refrigerated warehouses. The review paper also explores and discusses the possible integration in other processes to exploit the cryogenic energy of Liquid Air together with the main functionality of storing renewable energy source. **Figure 1.2.1** summarizes the above discussion in a schematic diagram.

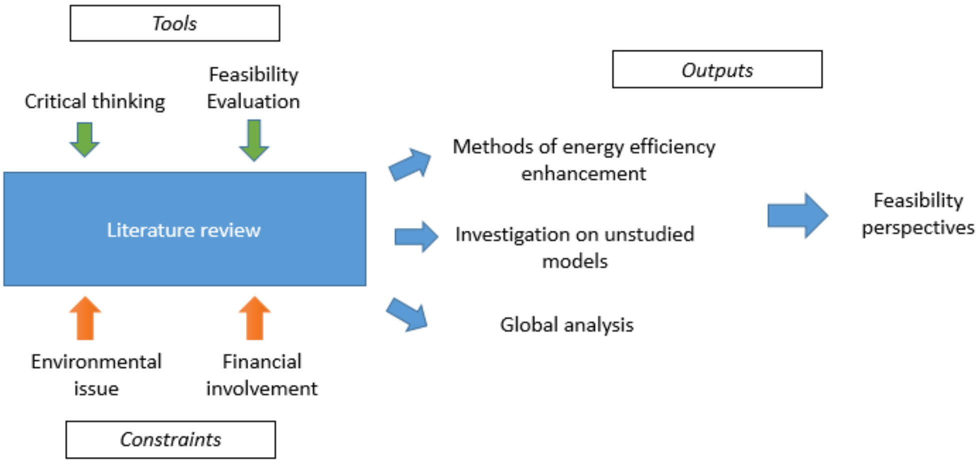

Figure 1.2.1 Schematic representation of the critical review paper

2.1 The review paper: Liquid Air Energy Storage (LAES) as a large-scale storage technology for renewable energy integration - A review of investigation studies and near perspectives of LAES

The literature review article has been published in the “International Journal of Refrigeration” (Damak et al., 2020)

Liquid Air Energy Storage (LAES) as a large-scale storage technology for renewable energy integration - A review of investigation studies and near perspectives of LAES

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Abstract

Electrical Energy Storage (EES) technologies have received considerable attention over the last decade because of the need to reduce greenhouse gas emission through the integration of renewable energy sources. Renewable sources have an intermittent power output to the electrical grid, thus EES represents a strategic solution in balancing electrical grids and enables the decarbonisation of the energy sector.

Cryogenic Energy Storage (CES) is a novel method of EES falling within the thermo-mechanical category. It is based on storing liquid cryogenic fluids after their liquefaction from an initially gaseous state. A particular form of CES, Liquid Air Energy Storage (LAES), has gained growing attention respect to other cryogens. The current state of LAES is still at the development and demonstration stage since no commercial or pre-commercial plants have been built. This technology has been developed in different ways throughout its history (from 1977), and, to the best of our knowledge, no review paper has been published so far about the CES topic.

Therefore, the present paper intends to provide a clear picture of the CES/LAES virtues in the literature as well as the challenges associated to the system to be commercially viable. For this purpose, this review includes: an investigation of the properties of cryogens and different CES processes as well as the main ways the system could be combined to other facilities to further enhance the energy efficiency, in particular the combination to a refrigerated warehouse with cold energy recovery from the cryogen evaporation.

Keywords:

Electrical energy storage, cryogenic energy storage, liquid air, renewable energy, global efficiency

Nomenclature

Ex Exergy (kJ kg^{-1})
h Enthalpy (kJ kg^{-1})
Liq liquefaction ratio
s Entropy (kJ kg^{-1})
P Pressure (bar)
T Temperature (K)
Wnet Net power (J kg^{-1})
Pc Power of compressor (J kg^{-1})
Pp Power of pump (J kg^{-1})
Pb Power of blower (J kg^{-1})

Subscripts

0 reference state
c critical
C cold
H hot
in input
l liquid state
out output

Acronyms

CAES Compressed Air Energy Storage
CCC Cryogenic Carbon Capture
CEEM Cryogenic Energy Extraction Method
CES Cryogenic Energy Storage
ECERS Enhanced Cryogen Exergy Recovery System
EES Electric Energy Storage
JT Joule Thompson
LA Liquid Air
LAES Liquid Air Energy Storage
LH Linde Hampspon
PHS Pumped Hydro Storage
RTE Round Trip Efficiency
TRL Technology Readiness Level

2.2 Introduction

Oil, coal and natural gas remain the world's leading sources of energy (IEA, 1998). According to World Energy Council, in 2015, the contribution of oil to the global primary energy consumption was 32.9%, while that of coal was 30% and natural gas accounted for 24% of the total (Kimmel and Cathery, 2010). The power generation sector contributes to 39% of CO_2 emissions worldwide and is more polluting than the transport and industry sectors (Kimmel and Cathery, 2010).

Renewable Energy Sources (RES) such as wind, solar or ocean energy (Li et al., 2010b) have a lower carbon footprint than conventional electrical energy and so have the potential to reduce carbon emissions if used effectively (Eurostat, 2017). Nowadays, around 7% of the energy produced comes from renewable sources (REN21, 2016). This value is projected to grow in the next years due to the global awareness of carbon-related environmental issues and the growing share of green technologies and governments' efforts to support the renewable energy sector.

However, the increased ratio of renewable energy generation may cause several issues in the electrical power grid considering the intermittent characteristic of RES. In fact its power generation is locally affected by weather patterns (IEC, 2011) and day/night cycle. Consequently, the use of Electrical Energy Storage (EES) is viewed as one potential way to support integration of variable RES (Luo et al., 2015). EES systems may also provide other useful services such as peak shaving, load shifting and supporting the realization of smart grids (Luo et al., 2015). In a study of electricity storage roadmap up to 2030, electricity storage facilities spreading tend to triple if countries double the share of renewables in the energy system mix (IRENA, 2017).

EES is not a single technology, but rather refers to a portfolio of technologies. Energy storage can be classified depending on the energy conversion and storage. Mainly electro-mechanical and thermal storage are widely used for the large-scale energy storage (IRENA, 2017). Pumped hydro storage (PHS) represented 96% in mid-2017 of worldwide installed electrical storage capacity followed by flywheels and Compressed Air Energy Storage technologies (IEC; IRENA, 2017). Conventional pumped hydro storage systems use two water reservoirs at different elevation, and compressed air technology requires underground storage cavities such as caverns or abandoned mines. So, the main drawbacks of these technologies are the dependence on geographical location and the large land footprint and therefore environmental concerns (ENEA_Consulting, 2012; IEC, 2011; IRENA, 2017).

Air has been recently regarded as a Cryogenic Energy Storage (CES) medium, whereby air is liquefied at around -195 °C and stored in insulated tanks (Antonelli et al., 2017). This technology is called Liquid Air Energy Storage (LAES). At off-peak times, energy produced by renewable sources is fed to an air liquefaction unit, while, when electrical energy is needed, the liquid air (LA) could be pumped, heated and expanded into turbines to generate power (Brett and Barnett, 2014).

Liquid air does not require important storage volumes considering significant energy density compared to that of PHS and CAES (Chen et al., 2009). Therefore, LAES is considered as a compact-technology. CAES footprint on_the ground "in principle" is not larger than LAES because the compressed air is stored underground therefore no more over ground land is used, but there are constraints on how close multiple storage caverns can be. Therefore, as stored energy increases, the overall footprint increases more substantially than with LAES. Moreover, LAES is one of the few storage technologies which can offer large scale storage without geographical restrictions (IRENA, 2017). This technology gives the possibility for energy "co-recovery", since cold from evaporation of liquid cryogen is not wasted. Cold can be reused in multiple applications, and particularly, in the case of sustainable refrigeration industry and food processing. Refrigerated warehouses for chilled and frozen foods are large energy consumers, and therefore, the reduction of their electrical consumption by restituting some of the cold from the evaporation (at temperature reaching -120°C) could greatly enhance the profitability of the whole combination.

Cycle efficiency, also known as the round trip efficiency, is the ratio of the system electricity discharged to the electricity stored during the charging phase. The round trip efficiency for the case of LAES is dependent on the effective management of heat flux, but can reach values higher than 80% under ideal circumstances (Luo et al., 2015)

The maturity of EES technologies is related to the level of commercialization, the technical risk and the associated economic benefits (Luo et al., 2015). The CES technology is at pre-commercial stage evaluated with Technology Readiness Level (TRL) at maximum nine (Hamdy et al., 2019). PHS is considered as a mature technology and CAES has already been deployed at commercial scale. On the other hand, LAES needs further development and is currently at industrial demonstration level.

Li (2011) made a thermodynamic assessment of the use of cryogen as a working fluid in an energy storage system and concluded that cryogens can be an efficient energy carrier and storage media. In the nineties, two hi-tech Japanese companies Hitachi Ltd. (Wakana et al., 2005) and Mitsubishi Heavy Industries, Ltd. (Kishimoto et al., 1998) investigated this technology and built prototypes to test the feasibility of a LAES system and assess practical performance. A few years later, Highview Power Storage Ltd (Highviewpower, 2017) built a small 350kW pilot plant initially located in Slough, UK, while the construction of a pre-commercial plant by the same company began on February 2015 and operation has started from April 2018.

This paper proposes a critical literature review of the LAES technology and its virtues comparing to other large-scale storage medium. Different liquefaction and energy recovery principles will be discussed in detail with reference to various studies found in the available literature. In the last part of the review, investigated methods of hybridization of the LAES will be also discussed in order to present the prospects of research and maturity development into LAES.

2.3 Cryogenic energy and liquid air as an energy carrier

A cryogen is a liquefied gas that boils at a temperature below -150°C (Li et al., 2010a). According to Li et al. (2010a), the energy stored in the cryogen is different from other heat storage : the energy stored in the cryogen is obtained from decreasing its internal energy and increasing its exergy. So, exergy analysis is more adapted to quantify the potential of stored cryogen than energy analysis.

In the study of the Enhanced Cryogenic Exergy Recovery System, Fyke et al. (1997) defined the exergy contained in cryogens as a thermomechanical exergy. This assumes that there are two components: "thermal exergy" - embodied by the large temperature difference with ambient and "mechanical exergy" - due to a possible pressure differential compared to ambient conditions. Cryogens can also embody chemical exergy, for example the chemical exergy of liquid methane is 48 times higher than its thermo-physical exergy, on the other hand liquid nitrogen does not have any chemical exergy and all exergy is in the thermo-mechanical exergy potential Li et al. (2010a). For example, calculation shows that liquid hydrogen has the highest exergy density using Eq. 1, up to $11912\mathrm{kJ/kg}$. While, the exergy embodied by liquid nitrogen could be up to $750\mathrm{kJ\ kg^{-1}}$. The latter figure is higher than the potential exergy of rock, which is around $455-499\mathrm{kJ\ kg^{-1}}$when used for storing sensible heat Li et al. (2010a). **Table 2.3.1** presents a comparison between thermodynamic properties of the most commonly used cryogens, values of critical properties of cryogens were taken from ASHRAE (1993). The values of exergy were calculated by the authors using the following formula:

$$Ex = \left[(h_l - h_0) - T_0(s - s_0)\right] \quad \mathbf{(1)}$$

where the index "l" refers to liquid state and "0" to reference state

Cryogens	Recovery process	Thermodynamic properties			Flammability Y/N
		Exergy available at liquid state (kJ kg^{-1})	*Critical point properties*		
			Tc (°C)	*Pc (bar)*	
Air	ASU	723	-135.65	37.7	No
Helium	Natural gas processing	6702	-267.85	2.3	No
Hydrogen	Hydrogen production methods	11912	-239.85	13	Yes
Methane	Natural gas processing / microbiological methods	1066	-82.05	46.4	Yes
Nitrogen	Air processing	750	-146.95	33.9	No
Oxygen	Air processing	621	-118.35	50.8	Yes

Table 2.3.1 : Thermodynamic properties of different cryogens

The very low values of critical temperature and relatively low critical pressure of cryogens play a major role during liquefaction, since the exergy lost during the heat exchange process is minimized when the fluid is cooled in supercritical conditions (Venkatarathnam, 2008).

In a practical aspect, air is obviously a non-flammable fluid compared to hydrogen or methane cryogens. However, there are some precautions when it comes to liquid air, because the oxygen fraction tends to separate and get locally enriched within the storage tank. Liquid air can even contain 50% of nitrogen and 50% of oxygen (CLCF, 2013) in some instances. Since oxygen reacts violently with most materials (EIGA, 2016), the potential fire and explosion hazards increase when oxygen concentration in liquid or gaseous air increases. In their report (EIGA, 2016), the European Industrial Gases Association claims that the maximum safe oxygen concentration in a confined space is 23.5% by volume. Consequently, in reference (CLCF, 2013), there are a list of safety measures to deal with oxygen enrichment: using suitable insulated tanks, monitoring oxygen content and keeping all types of organic materials away from the oxygen sources as they may combust in an oxygen rich environment. Furthermore, few air treatments operations are necessary before energy storage processing compared to hydrogen or nitrogen extraction for example. Finally, due to its instant availability and free use, air has the ultimate potential to the energy storing system as a cryogen.

Liquid air has attracted researchers working on large-scale energy storage based on cryogenic energy conversion. LAES is, henceforth, the particular form of CES where the energy conversion remains in Liquid Air transforming.

2.4 Process Principle

The idea of cryogenic energy storage was firstly proposed by E.M Smith, at university of New Castle in 1977 (Smith, 1977), and tested by Mitsubishi in 1998 (Kishimoto et al., 1998; Sciacovelli et al., 2017) using liquid air as cryogen. The principle of using this type of energy storage is based on 3 main steps shown in Figure 2.4.1: (i) liquefaction of gaseous air when energy is available at off-peak times, (ii) storing liquid air in insulated tanks and (iii) expansion of pumped liquid air through turbines to generate power at peak demand period (Abdo et al., 2015; Ameel et al., 2013; Antonelli et al., 2016; Guizzi et al., 2015; Kishimoto et al., 1998; Li et al., 2014; Morgan et al., 2015b; Sciacovelli et al., 2017; Smith, 1977)

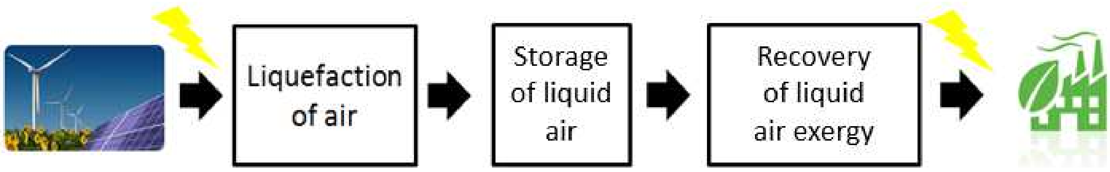

Figure 2.4.1: Principle of liquid air energy storage

The state-of-the-art of each of these subsystems will be described in next sections.

2.4.1 Cryogenic liquefaction cycle

In the literature, mainly 3 major cycles were studied for the liquefaction of cryogens, Linde Hampson cycle, Solvay cycle and Claude cycle (Abdo et al., 2015; Ameel et al., 2013; Atrey, 1998; Chang, 2015; D'Arsonval, 1898; Guizzi et al., 2015; Hamdy et al., 2017; Li, 2011; Sciacovelli et al., 2017; Venkatarathnam, 2008). In 1895, Car von Linde built the first industrial scale air liquefier (Agrawal and Herron, 2000). The Linde-Hampson (LH) liquefier is based on the Joule Thomson (JT) effect taking place in any throttling valve (Venkatarathnam, 2008). Petit (1995) referred to the efficiency of 11% and describes the efficiency of JT liquefaction cycle as “poor”. The JT expansion is responsible for a large loss of exergy due to the important pressure drop in an isenthalpic process. When the isenthalpic expansion device is replaced by an isentropic expansion device, an increase in the exergy efficiency of about 60% is achievable for a compression pressure of 200 bar (Venkatarathnam, 2008). The liquid yield increases considerably and this cycle is known as the Solvay liquefier. This can be done by means of a turbine instead of the JT valve, using a two-phase expander or a cryogenic expander (Kanoğlu, 2001). This technology was not available until recently because it requires accurate prediction of liquid fraction trajectories while it condenses in the expander. This was introduced at industrial scale in methane liquefaction plants with the advent of 3D, multiphase computational fluid dynamics.

T-s diagram of a Solvay cycle for air liquefaction is represented in Figure 2.4.2. The segments 1-2, 3-4 and 5-6 correspond to compression processes while 2-3, 4-5 and 6-7 represent the inter-cooler between compressors. Then, from 7 to 8 an external cold source and a part of returning non-liquefied gas is used to cool down the compressed air. The segment 8-9 is the non-isentropic expansion within a cryo-turbine where production of liquid droplets takes place. In point 9, liquid air is stored in a storage tank.

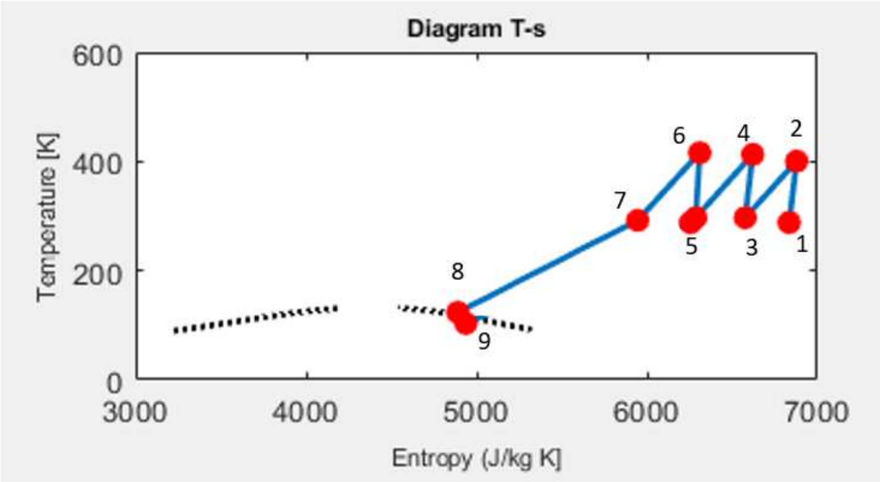

Figure 2.4.2: T-s diagram of Solvay air liquefaction cycle based on 3 compression stage

In 1902, George Claude proposed a system with two expansion mechanisms combining a JT valve expansion with a near-isentropic expansion through a turbine located along a portion of the stream. The Claude cycle has been reported in Figure 2.4.3. Claude cycle presents many advantages compared to LH cycle. According to Sciever (2012), the near-isentropic expansion makes the system potentially more efficient and additional work can be produced by the expansion device improving the overall efficiency.

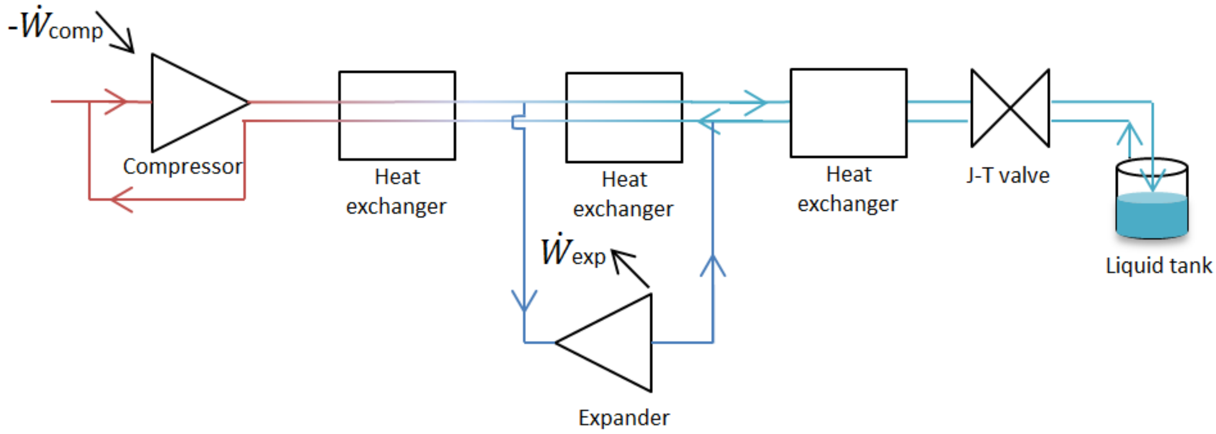

Figure 2.4.3: principle of Claude cycle

Improved version of Claude cycle was also developed by Highview Ltd, in order to manufacture the first LAES demonstrator without combustion. In their patents (Nelmes et al., 2015) they represent a liquefier with two or more cascading turbines. With this extended version of Claude cycle, more cold is provided within the heat exchanger, henceforth more liquid is produced and so the liquefier efficiency can be enhanced. Multiple configurations were proposed, as well, in patent (Alekseev, 2016) of air liquefaction unit based on Claude cycle. Regarding this fact, more complexity is added to the circuit and CapEx increases as well.

Despite the low values of exergy efficiency of Linde Hampson, many industrials refer to this system to produce liquid air, as in many patents LAES systems were based on the LH liquefier (Gatti et al., 2011; Sinatov and Afremov, 2015; Stiller et al., 2016; Vandor, 2011). This means that the Linde Hampson principle has been regarded for a long time as potential liquefier for industrial application and it is always the case nowadays mainly due to the cost benefit criterion. The cycle that may replace Linde Hampson because of low complexity and enhanced efficiency is Solvay. The replacement of JT valve by a Liquid turbine assures better efficiency with minimum investment.

A revival of the Solvay cycle was proposed in recent studies (Guizzi et al., 2015; Li, 2011; Li et al., 2014) of cryogen liquefaction that involves also some more sophisticated technologies using a Cryoturbine for providing the cooling capacity needed for liquefaction of the cryogen. It has been shown that the use of a Cryoturbine instead of a throttling device in a conventional setup improves considerably the efficiency of the liquefaction unit. For example, in particular conditions, Li (2011) obtained an optimal round trip efficiency of 48% using throttling valve while, this value increased to about 82% by using a Cryoturbine. Kanoğlu (2001) investigated and tested a Cryoturbine used for natural gas liquefaction and the analysis was made using data provided by the Cryoturbine test facility. The objective of the paper (Kanoğlu, 2001) was to compare the efficiency of a throttling valve and a Cryoturbine for cryogen production in order to assess isentropic, hydraulic and exergy efficiencies of the Cryoturbine in a Solvay liquefier. Another variant of Claude cycle is Heylandt cycle. A turbine is placed along the first heat exchanger and not the second one as it is the case for Kapitza. In a study of the exergy analysis of a CES (Hamdy et al., 2017), Heylandt cycle was used for liquefaction. The authors claimed that this cycle is commonly applied for CES regarding technical and economical reasons.

2.4.2 Cryogenic Energy Extraction Methods (CEEMs):

Thermo-mechanical exergy of liquid cryogens can be extracted after evaporation through turbines, while the remaining thermal exergy, in form of high-grade cold, can be recovered through heat exchangers and storage medium. This paragraph intends to provide details of some studies/patents of the CES/CEEM and to discuss their results.

In general, four basic methods for Cryogenic Energy Extraction Methods (CEEMs) are mentioned in literature (Hamdy et al., 2017; Li et al., 2010a) (Figure 2.4.4). The simplest one is the direct expansion method where the cryogen is pumped, heated by the ambient heat or waste heat and expanded into turbines to generate power (a). In the second method, cryogen is used as a secondary fluid instead of the main working fluid. It is whether used to condensate the working fluid in a Rankine cycle (b) or to cool down the working gas before compression in a Brayton cycle (c). For these two methods (b-c), the cryopump is kept to pump the cryogen in the secondary circuit (blue line) while the expander is used for the main circuit (green line). The fourth method is a combination of the three previous ones (d).

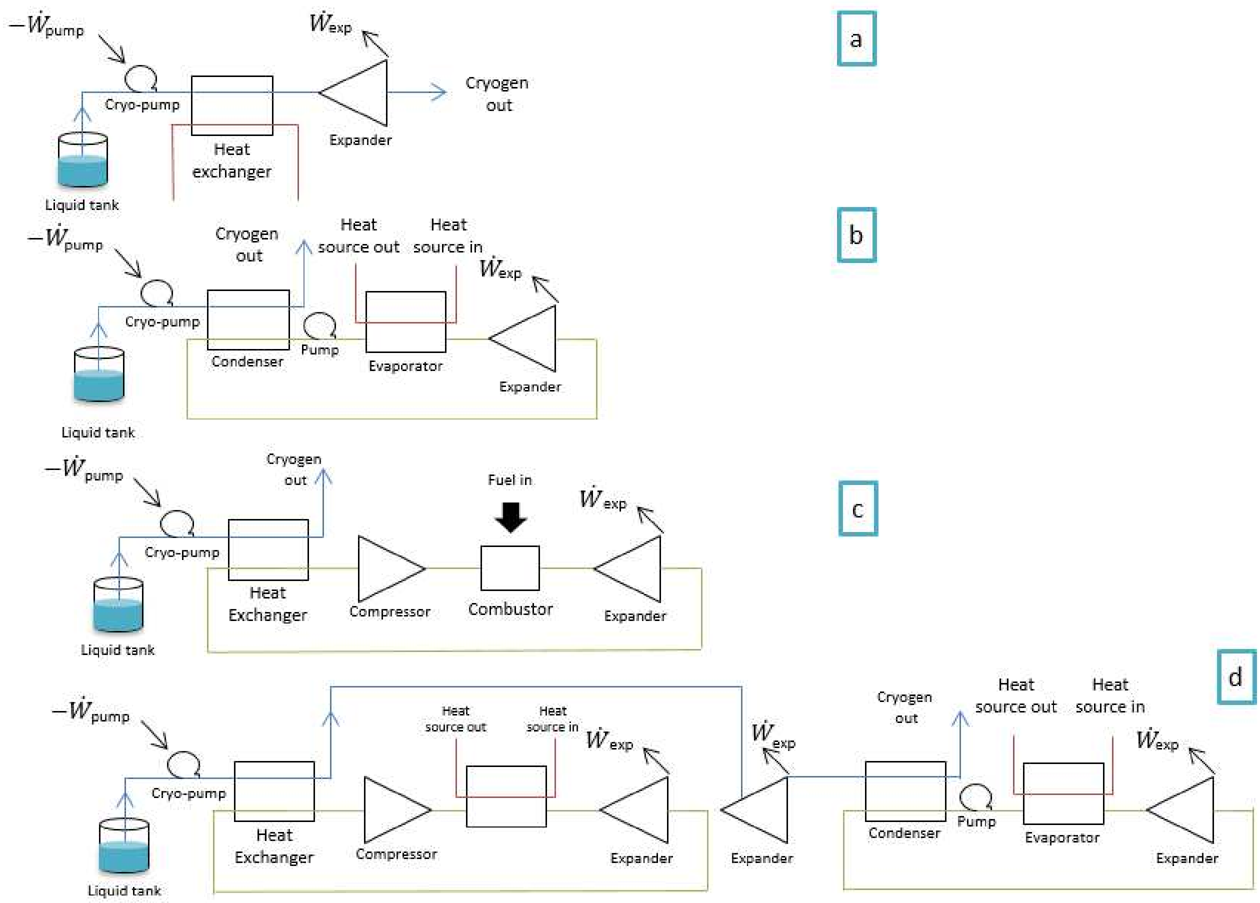

Figure 2.4.4: Cryogenic energy extraction, basic methods

In general, the cryogen is pumped, evaporated and expanded into turbines. T-s diagram for a three-stage expansion recovery cycle, with liquid air as working cryogen is represented in **Figure 2.4.5**. In this case, step 1-2 corresponds to the evaporation of liquid air, 2-3 is a small heat transfer with secondary fluid which exchanges with cold storage device, 3-4, 6-7 and 8-9: super-heating and 5-6, 7-8 and 9-10: expansion into turbines.

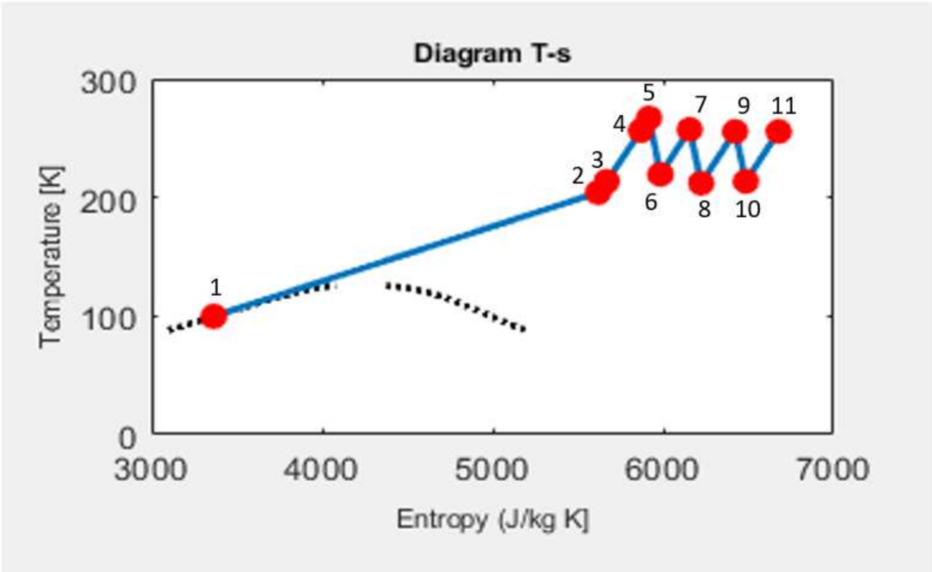

Figure 2.4.5: T-s diagram of recovery cycle

An alternative for the cryogenic energy extraction is the so-called "Dearman Engine" (Dearman et al., 2016). Cryogenic engine is extracted in piston engine system similarly to vehicle's engine. The cryogen is injected by small quantity into the engine cylinder where it is combined with a warm heat transfer fluid. The resulting sudden expansion of the cryogen drives the piston shaft, and therefore cryogenic energy is turned out to mechanical energy. As said in the beginning of this paragraph, one of the most important features of the cryogenic energy storage is that it can generate both mechanical/electrical energy and cold energy at the same time by the regasification process. Under this same approach, Dearman Company proposed a cogenerated system (Ayres et al., 2015). Therefore, in one of the embodiment proposed, mechanical energy and electrical energy could be extracted alternatively or simultaneously through mechanical coupling (by shaft rotating) or thermal coupling (Indirect Rankine cycle). Dearman vehicle engine cannot be considered as a direct application of the electric energy storage through cryogenic energy conversion, but in some aspects, it could also be considered as a CEEM.

A recovery system was also developed by Mitsubishi (Kishimoto et al., 1998). The generator is a combination of super-heating, combustion and direct expansion method with some modification, as showed by Figure 2.4.6. The cryogen is pressurized by a turbopump driven by expansion turbine, evaporated, heated and expanded. The power is produced by using a gas-turbine. The author calculated the thermal efficiency up to 77% (Eq.5) as an efficiency of the generation cycle.

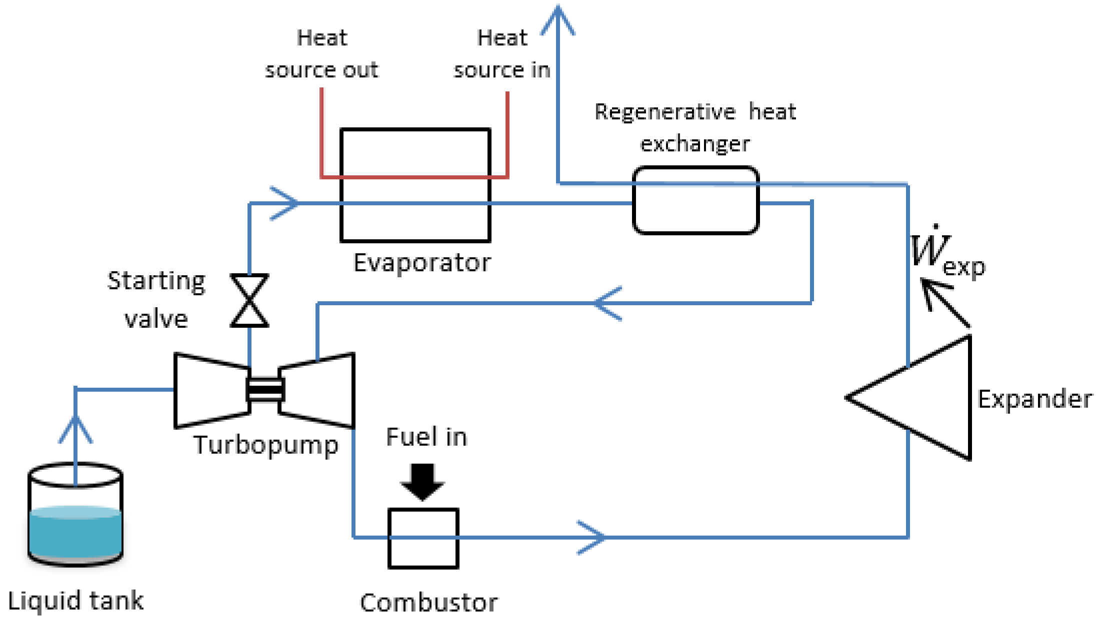

Figure 2.4.6: Mitsibushi LAES system

Expansion Energy's patent Vandor's Power Storage Cycle (called the VPS Cycle) of LAES includes natural gas fueled power generation as reported in (Vandor, 2011). In Vandor's patent (Vandor, 2011), a LAES that relies on combustion of natural gas with liquid air is presented. To limit CO2 emission, Vandor's proposed a CO2 adsorption chemical process. The final use of the CO2 captured was not mentioned in the patent. In a commercial document of the company that manufactures the system (Liebowitz et al., 2013) the round trip efficiency of the VPS cycle at a commercial scale is claimed to be greater than 95%. The VPS cycle is now subject to a feasibility study and a full scale system installation may be planned at a facility in New York City (Taylor et al., 2012).

2.4.3 Efficiency of LAES

CEEM and liquefaction system can be completely separated or thermally linked in the case of CES. Therefore, two major groups of LAES are distinguished in literature: "independent subsystems" and "thermally linked subsystems". In the liquefaction process, cold energy is needed and it can be recovered in the LA discharge process and recycled back. Additionally, in order to enhance the LA discharge process efficiency waste, heat is needed. This can be stored and recycled from the rejected heat coming from the compressors in the liquefaction plant. The following studies involve cold and hot energy reuse methods via different storage media which fill the gap between air liquefaction unit and recovery unit needs. High grade hot and cold storage and recycle is included in almost all recent studies related to cryogenic energy storage system for electrical storage applications (Abdo et al., 2015; Ameel et al., 2013; Chino and Araki, 2000; Li, 2011; Li et al., 2014; Morgan et al., 2015b; Sciacovelli et al., 2017) where mainly a super-heating based cycle is used for the generation process.

RTE, environmental impact and realization of the system are particularly factors of interest in this paper. In the following, two systems are distinguished the super-heating recovery process referred to with "S" letter and the combustion based recovery process referred by "C" as main Cryogenic Energy Extraction Methods. A comparison between these configurations is made in (*): thermal efficiency

Table 2.4.1 as they were studied in their corresponding mentioned references.

As for all energy storage technologies, the round-trip efficiency is the parameter that represents the ability of the LAES system to recover as much as possible of the input energy that it had initially consumed. The round trip efficiency for a LAES system is the ratio between the electric energy consumed for producing liquid air and the electric energy generated (or saved) during the discharge of LA and it is given by the following equation where $\dot{W}_{net.out}$ is the output energy and $\dot{W}_{net.in}$ is the input energy, both include all input and output energies throughout the system is given by :

$$RTE = \frac{\dot{W}_{net\ out}}{\dot{W}_{net\ in}} \tag{2}$$

Negro et al. (2018b) has defined a more detailed $\dot{W}_{net\ out}$ formulation and method of calculation for the heat/cold recovered as follows:

$$RTE = \frac{\sum ElectricalEnergyOutput + \sum ThermalEnergy/COP}{\sum ElectricalEnergyInput} \tag{3}$$

The Coefficient of Performance (COP) is an indicator for the refrigeration cycle as well as heat pump, it is defined on the basis of a level of valorization temperature of the cold recovered.

$$COP_C = \frac{T_C}{T_H - T_C} \tag{4}$$

Ref/System Peculiarities/Innovations	**Standalone recovery system**			**Integrated system**		**Round trip efficiency (%)**	**Calculation model**
	C	S	C+S	C	S		
Kishimoto et al. (1998) Rankine and Brayton combined			X			77*	Eq. 5
Chino and Araki (2000) Tank of liquid air placed inside a regenerator				X		87	Eq. 6
Vandor (2011)				X		>90	Not mentioned
Conlon (2016) combination of open Brayton air cycle with closed Rankine steam cycle	X					[47-87]	Not mentioned
Ameel et al. (2013) Linde liquefaction cycle and Rankine recovery cycle					X	43	
Li (2011) Superheaters supplied by heat from inter-coolers at the compression stage		X			X	[20-60] / 80	
Morgan et al. (2015b) packed bed for storage					X	8 demonstrator value [40-60] theoretical value	
Guizzi et al. (2015) cryoturbine included					X	50	
Sciacovelli et al. (2017) Packed bed for cold storage					X	50	
Antonelli et al. (2016)	X					70	

Natural gas combustion included				
Negro et al. (2018b) Cryo-Rankine cycle combined to refrigerated warehouse		X	[20-26]	Eq. 3
Hamdy et al. (2019) Exergy and economic analysis is carried out for 4 different circuits	X	X	[40-55]	Not mentioned

(*): thermal efficiency

Table 2.4.1: Main CEEMs in the literature

Two systems are distinguished: the super-heating recovery process referred to with "S" letter and the combustion based recovery process referred by "C" as main Cryogenic Energy Extraction Methods.

Negro et al. (2018b) investigated multiple possibilities of developing a demonstrator at an industrial site (food factory and refrigerated warehouses). From the parametric analysis, it was shown that 3 parameters can be controlled to enhance the RTE: discharge pressure, waste heat temperature at the expansion stage entrance and pressure in the storage tank. The cold recovered from the evaporation could either be recycled in the liquefaction cycle or used to supply refrigerated warehouse or food freezers. Depending on requirements of the industrial site, the round trip efficiency can be considered also as a variable parameter to the energy efficiency assessment in the refrigeration system. As practical turbomachinery efficiencies were considered, this study has presented lower RTE than other theoretical values obtained in other works.

A complete exergy analysis based on fuel and product approach was conducted by Hamdy et al. (2019) comparing 4 configurations including the combustion process. Waste heat/cold recovered was also investigated in order to evaluate the exergetic efficiency of the CES. Waste energy as defined by the authors is related to the energy that can be vented to the environment. An interesting point of the slight difference between exergetic and energy methods analysis was highlighted through different formula in each of the studied system. The exergy known to be « the true thermodynamic value » of the energy, is claimed to be the best approach for comparison purpose. Contrary to the results found in literature, exergy and energy analysis results of this study show that the use of waste heat of 450°C represents the highest exergetic efficiency of 55% comparing to 44% with combustion. Depending on the industrial site where the CES is implemented, availability of waste heat source is not certain, and therefore, the of the RTE changes consequently.

RTEs shown in this table are results of theoretical simulation. The only system that was fully built as LAES demonstrator has only 8% compared to the theoretical 49%. According to the author, this poor value is due to the small size of the plant. LAES would be more efficient when scaled-up. Nonetheless, more details and experimental data related to the subject are therefore required to investigate the main energy loss sources in the energy conversion process.

Almost all recent studies (Ameel et al., 2013; Guizzi et al., 2015; Hamdy et al., 2017; Sciacovelli et al., 2017) on the subject of LAES obtained approximate results of exergy efficiency and the round trip efficiency varies at a range of [43-50%]. Architectures studied of LAES are almost focused on Solvay or Claude liquefier cycle with the integration of Cryoturbine for charging phase and the super-heating process of energy extraction process for the discharging phase. Sciacovelli et al. (2017) has carried out a typical configuration of the LAES system based on super-heating process recovery. The proposed system shown in **Figure 2.4.7** includes a modified Claude cycle which includes multiple expansion stages and a JT valve. Packed bed filled with quartzite pebbles is integrated in order to store high-grade cold energy. Heat from multiple compressor stages is recovered, as it was the case in the work of Guizzi et al. (2015). Sensible heat is stored in a diathermic oil that acts both as heat transfer and storage medium. The author focused on the integration of the packed bed storage in a dynamic RTE analysis and the impact of this component on the system overall performances. According to the authors, the use of packed beds for cold thermal storage improves the efficiency of liquid air energy storage by around 50%.

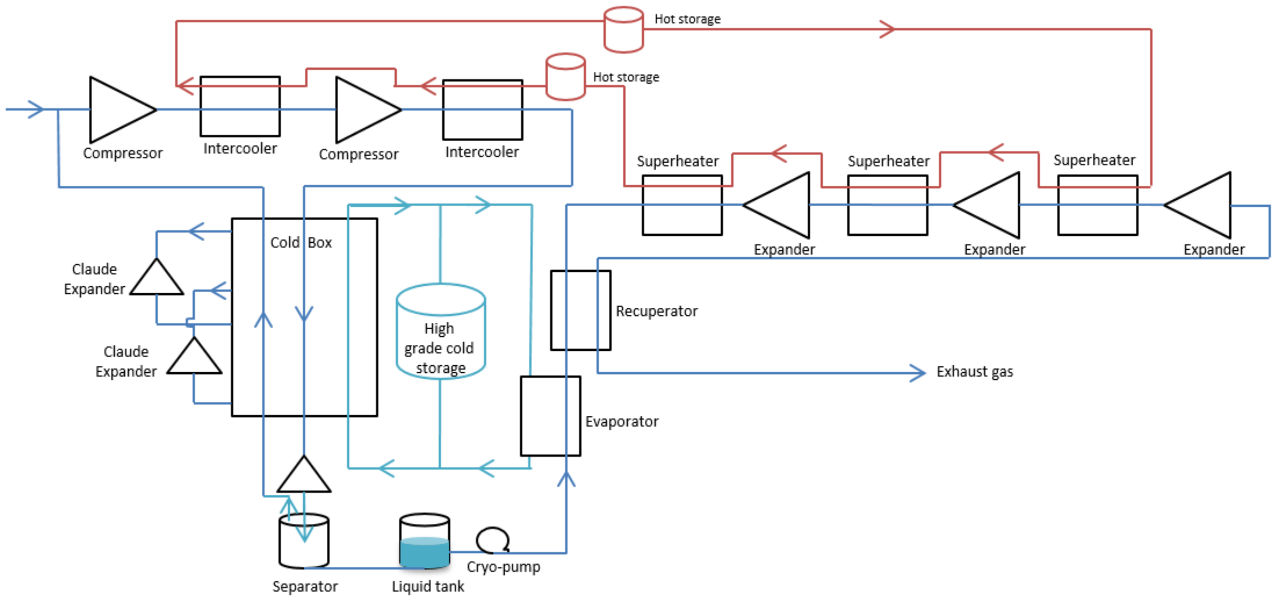

Figure 2.4.7: Sciacovelli's LAES process

According to (*): thermal efficiency

Table 2.4.1, LAES with combustion methods have the highest RTE comparing to super-heating cycle whether in independent or in coupled cycle. Values of theoretical RTE are generally higher than 70%, while those of super-heating are limited 40 to 50%. This can be explained by the high chemical exergy (Fyke et al., 1997) contained in the fuel and provided to the system as an extra source of energy in addition to liquid air energy. Besides, combustion leads to high temperature at the turbine inlet before expansion and this provides more work to be recovered from the expansion process. But combustion also includes CO_2 emissions. Carbon capture is a frequent proposed solution (Conlon, 2016). This can be done by use of cryogenic cold energy so as in Li et al. (2011). Nevertheless, combustion still rejects many others toxic particles like CO or NO, O_3, etc which require additional combustion post treatment processes and could lead to more complexity and expensiveness of the system.

RTE can be higher when using combustion process; however, efforts of recent theoretical research on energy storage methods aim at conserving the environmental friendly aspect of LAES especially when applied to green energy management in the grid. In the following, details of combustion based recovery cycles based on combustion and ways proposed to guarantee environmental aspects are discussed.

2.5 Pilot plant demonstrators in the history of LAES

The use of liquid air energy storage, as a large-scale energy storage technology, has attracted more and more attention with the increased share of intermittent renewable energy sources connected to the electricity grid. Consequently, some commercial companies got involved in the development of this technology beginning with Mitsubishi and Hitachi (Kishimoto et al., 1998; Wakana et al., 2005) at the end of the nineties and more recently Highview Power Ltd. Tests and performance of the deployed systems did not match theoretical expectations because of technical limitations and real world efficiencies of the equipment.

The first prototype was designed and demonstrated by Mitsubishi Heavy Industry in 1998 (Kishimoto et al., 1998), with no information published about the design of the liquefaction unit. Liquid air was directly pumped from a liquid air storage tank. The only reported performance indicator was the efficiency of the LA discharge system which could reach 77%, without taking into account the energy consumed by the air liquefaction plant, but only accounting for the chemical energy of the fuel burnt in the combustor.

In a second trial of this technology, Wakana et al. (2005) designed a generation circuit that combined combustion with the integration between liquefaction and generation units. As previously described, this design included a form of cold storage unit which is conceived in specifically designed regenerator. The R&D activities were conducted by the Japanese company Hitachi, Ltd. According to the Center for Low Carbon Futures (Taylor et al., 2012), Hitachi made experimental works on the regenerator, and claimed that the system could exceed 70% of storage efficiency depending on the regenerator performance. However there was no full scale pilot plant demonstrator.

Working with the University of Birmingham (UK), Highview Power Storage has built the world's first fully integrated 350kWh/2.5MWh liquid air energy storage system Highview Power Storage designed and assembled this LAES pilot (Highviewpower, 2017). It was initially operative in 2011 at Scottish and Southern Energy's 80MW biomass plant in Slough, UK. A self-developed cold storage (Morgan and Dearman, 2013) was used for the full integration of liquefaction and energy generation units. Various tests to assess the system response to load variations were carried out. Results were reported by Morgan et al. (2015b). The round trip efficiency obtained was in the range of 8%. But, according to the authors, this low value is due to the small size of the plant and the inefficient cold recycle design. A 100MW/600MWh "best built" configuration was proposed by the same authors in another paper (Morgan et al., 2014) and a round trip efficiency of 60% was claimed as achievable with current technology.

In February 2014, the UK government awarded Highview Ltd. of a £8 million grant for the realization of a 5MW/15MWh demonstration plant alongside Viridor's landfill gas generation plant at Pilsworth Landfill facility in Greater Manchester (Highviewpower, 2017; Luo et al., 2015). The waste-heat provided by the adjacent piston engines generators will be used to increase the discharge system power output and it will enhance the overall efficiency of the system. The plant is now in operation and it is providing power for around 200,000 homes during a day (Highviewpower, 2019).

2.6 Methods of hybridization of cryogenic energy storage

As described in this paper, initial research activities on energy storage and recovery via cryogens had begun with simplified systems using independent liquefaction/recovery subsystems. Then, the overall RTE had been greatly enhanced with the integration of the hot and cold energy storage and recycle. In the following paragraphs, some studies are presented where the CES is hybridized with a second system. The idea is to maximize the cryogenic energy recovery by using additional systems, and secondly to integrate a CES system with another process.

In two papers, Li (Li et al., 2014; Li et al., 2012) suggested to co-locate cryogenic energy storage near an existing electrical plant and make use of waste heat recovery in the cryogenic plant, instead of rejecting it to ambient. In fact, the waste heat recovery has a large impact on the increase of the net power output. In the first study from Li (Li et al., 2014), he suggested the integration with a nuclear power plant. The round trip efficiency of this system could be higher than 70%. Li et al. (2012) studied the hybridization of a CES and a solar thermal power plant in the form of a solar-cryogen hybrid power system. Results of simulation in this study show that the system delivers power 30% greater than the sum of the power outputs of each system individually.

The power generation sector is the main source of CO_2 emissions worldwide. Consequently, several technologies of carbon capture emerged in recent years as a way to limit emissions. Cryogenic Carbon Capture (CCC) is a viable approach to achieve the target of CO_2 emission level (Safdarnejad et al., 2016). A hybrid system of CCC and a CES based on combustion process is studied within three reference papers by Safdarnejad and Li (Li et al., 2011; Li et al., 2013; Safdarnejad et al., 2016). The process then, separates solid CO_2 in the form of dry ice (Li et al., 2013). To further increase the efficiency of the LA discharge, waste heat from the exhaust gas is recovered to superheat the gaseous nitrogen at the turbine entrance (Li et al., 2013). In the latter study by Li (Li et al., 2013), the air would be separated into liquid oxygen (for the oxy-fuel combustion of the gas turbines), and liquid nitrogen (the working fluid in the circuit and the medium of CO_2 removal). The overall efficiency of the proposed system was claimed to reach 70%.

Antonelli et al. (2017) presented several ways of LAES integration with existing processes. The first suggestion was to include an Organic Rankine Cycle (ORC) where cryogenic temperatures of released liquid air could be used as the lower temperature sink of the ORC. According to the author, the ORC contributes to negligible improvements in the efficiency of LAES, since the energy exploitable is lower compared to that provided in the combustion. A second proposition consisted of a combustion based cycle, where air cooled by cryogen entered the compressor. The advantage of this cycle would be that the compression would be less energy intensive since the working fluid is at a lower absolute inlet temperature. The authors' analysis of this configuration yielded the highest power output and the best round trip efficiency (68%).

According to Fikiin et al. (2017), refrigerated warehouses are an ideal industrial environment to the integration of renewable energy source by switching 'passive' and 'active' modes of the LAES and using both cold and electrical energy of the LAES. A recent innovative European project - CryoHub (CryoHub, 2019) investigates and extends the potential of large-scale LAES by recovering the stored energy in two forms cold and electrical energy. By employing RES to liquefy and store cryogens, CryoHub balances the power grid, while meeting the cooling demand of a refrigerated food warehouse and recovering the waste heat from its equipment and components. The project is, yet under study and a demonstrator might be deployed in order to supply a refrigerated warehouse.

2.7 Discussion and perspectives

The cryogen contains high-grade cold as a valuable energy, and we may call it "cold exergy". For this reason, as we could see through paragraphs of this paper, some authors gave a special focus on the recovery of this extra source of energy. Almost all hybrid systems discussed include the integration and recycle of the cold exergy released by the cryogen, i.e. the capture of CO_2, the condensing in an ORC or cooling the fluid in a Brayton cycle.

Aside from capturing and storing the cold exergy of the released liquid air for the liquefaction process, the stored cold energy might also be used in refrigerated warehouses or food/pharmaceutical plants. This idea was first introduced by Fikiin et al. (2017). This is currently under investigation and would be demonstrated as part of a European project (CryoHub 2019). Integrating the LAES system would enable demand-side energy management and supply of cooling to refrigerated warehouses at the same time. The main objective of this project is to enhance the sustainability of both the power grid and the cold chain.

Using the same approach, but in a different application, Tafone et al. (2017) presented a techno-economic analysis of a LAES providing for daily air conditioning of an existing office building in Singapore (hot climate conditions throughout the year). Results of simulation gave ideally a round trip efficiency of 45% with some assumptions.

Both previous applications explored the concept of a sustainable cold economy, defined in Tafone et al. (2017). The objective would be to make sites requiring refrigeration energetically self-sufficient and increase the share of “green” energy sources used. As main results of the study conducted by Negro et al. (2018b), the efficiency of the cold energy recovery sub-system can reach the value of 88%: « this will constitute a key technological enabler for any LAES technology to be commercially viable in the future ».

Many studies and configurations have already been considered theoretically, but, the lack of experimental validation of the simulated LAES systems should be addressed first. LAES technology needs an important investment regarding the size of machinery required (number of compressors and turbines and engineering/conception study price). This explains somehow the lack of experimental validation and industrials reluctance.

In CEEM section (0), recovery methods with combustion are proven to be more efficient in terms of RTE than with super-heating. However, due to the environmental damage that can occur from the combustion of natural gas with liquid air. Oxy-fuel combustion should be considered since it presents reduced NO_x emission than the usual air-firing. Besides carbon capture operation has lower complexity in the oxy-fuel due to the higher CO2 density in the flue gas (Buhre et al., 2005). Oxy-fuel combustion with CO2 capture has been investigated by companies like Air Liquide (Châtel-Pélage et al., 2003) and Alstom (Nsakala et al., 2001) in the case of coal-fired power plant. In our vision, oxy-fuel combustion could represent a way to maintain good electrical efficiency and reasonable environmental impact.

2.8 Conclusion

This paper provides a review of the current development of LAES technology from both a scientific and technical perspective. CAES and PHS are technologies currently deployed for large-scale energy storage which are constrained by geographical features. LAES, as a particular sub-set of LAES, is a novel EES technology that could respond to grid-scale requirements.

One advantage of this technology is the energy storage density and, secondly, its independence from location constraints like the presence of a gravitational potential (PHS) or underground caves (CAES). A difficulty of using liquid air used as cryogen is that a particular attention should be given to the problem of stratification and oxygen enrichment during storage. Some measures are necessary to avoid the risk of ignition in presence of hydrocarbons.

Linde-Hampson, Claude and Collins cycles were mentioned in previous works to be the most appropriate for cryogen liquefaction. Super-heating and combustion methods combined to direct expansion are the most popular energy recovery methods in studies related to CES or LAES. Many authors confirmed that the integration between liquefaction and energy recovery units through cold and hot storage considerably enhances the system performance. Potential round-trip efficiency has been claimed to be more than 80% when using combustion for LA discharge cycle. Combustion process has undeniably negative impact on the environment and this goes against the environmentally friendly characteristic of LAES as a solution for the green energy global transition. Environmental issue should be carefully assessed and solution like oxy-combustion process with biogas as fuel may represent a potential solution, at the expense of the Operating Expenditure (Opex) of the entire system.

More and more integration possibilities can emerge from LAES in the form of by-products of liquid air production/use. As discussed previously, carbon capture and storage using liquid nitrogen is one of many options already investigated by some authors. In fact, hybridization of LAES is open to multiple opportunities when considering that cryogenics have been used in superconductivity, rocketry, cryosurgery, cooled electronics since the 60’s. The possibility to increase the energy recovery and so the energy efficiency of the system, and to respect the environmental issues in the context of renewable energy integration, makes of the CES a potential method for the large scale EES.

Based on results of mentioned studies in this review, LAES represents an excellent candidate for the energy transition in terms of energy storage technology, regarding theoretical thermodynamic performances. Studies have shown attractive results of thermodynamic efficiency as well as possibilities of cogeneration of cold energy or/and hot energy depending on the industrial site needs where the plant is implemented. The cryogenic energy can also be used for CO_2 carbon capture and for sequestration or more recently for turning it into coal (Cockburn, 2019). Despite the maturity of machinery used for LAES (compressors, expanders, heat exchangers), the lack of experimental validation of theoretical performances is clearly undeniable. This is due to huge investment related to the project, even at a demonstration level. LAES economic viability for investors is not yet virtuous of millions of euros investments. Economic solutions to shorten payback duration are, therefore, required to attract investors. A part of liquefied oxygen or nitrogen can be sold on the market or provided for local use as sub-products, without diverting from the main purpose of storing energy.

Acknowledgement

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2.9 Conclusion of the scientific background chapter

Studies have shown attractive results of thermodynamic efficiency as well as possibilities of cogeneration of cold energy or/and hot energy depending on the needs of the industrial site where the plant is implemented. The cryogenic energy can also be used for CO_2 carbon capture and for sequestration if needed, for example. The coupling to a refrigerated warehouse with cold energy recovery from the liquid air evaporation is also another way to enhance the energy efficiency and to involve more investors. Based on results of mentioned studies in this review, two main energy recovery methods were identified: Super-heating and combustion based systems.

Therefore, in the following papers, these two systems will be under studies including thermodynamic, environmental and economic aspects.

CHAPTER 3

ENERGY ASPECT

Introduction to the energy aspect of LAES

The LAES energy and exergy performance paper

Conclusion and transition towards next chapter

3.1 Introduction to the energy aspect:

Recovery methods with combustion are proven to be more efficient in terms of Round Trip Efficiency than super-heating according to data found in the literature. The difference between both lays on the component before expansion into the turbine, whether it is a combustor or a simple heat exchanger with an important amount of hot thermal energy.

Therefore, in this part of the work, thermodynamics of a LAES based on three combustion methods will be studied and compared to a more usual process of LAES using only evaporation and super-heating processes. Oxy-biogas combustion, oxy-natural gas combustion and air-biogas combustion are investigated as innovative LAES systems in this work. Besides, a small difference in the charging part will be studied in order to highlight the impact of recycling cold from the evaporation to the liquefier. Figure 3.1.1 represents the combination of the compared systems in terms of cold recovered in the liquefaction unit. A focus on the combustion modelling and simulation results will be underlined in order to highlight the importance of thermodynamic and environmental impact of this component.

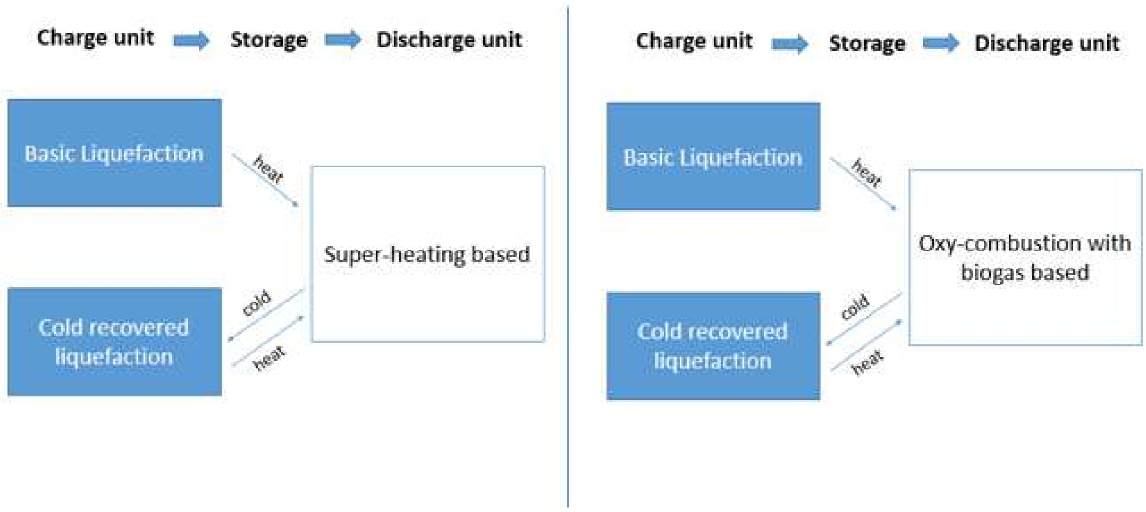

Figure 3.1.1: Diagram of LAES studied combinations with the recycled cold represented by the blue arrow and details of combustion methods

Energy and exergy analysis will be conducted in order to evaluate real efficiencies and to point out irreversibilities and most exergy destructive components. Due to the harmful consequences to environment that can occur from combustion, a preliminary environmental analysis related to pollutants emission is here represented by the evaluation of GHG, NO_x and CO emission after combustion. The objective of the energy analysis combined to emissions evaluation is the determination of the optimum operating conditions with the lowest harmful emissions for the environment for each studied system. Figure 3.1.2 summarizes the above discussion in a schematic diagram.

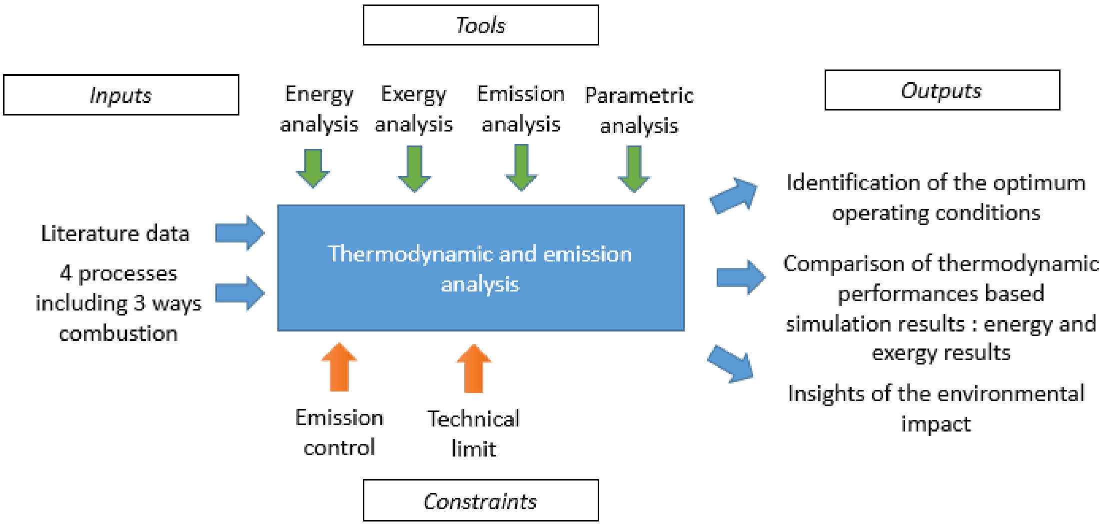

Figure 3.1.2: Schematic representation of comparison of thermodynamic performance and emissions analysis paper

3.2 The LAES energy and exergy performance paper: Energy and Exergy performance investigation associated to emission analysis of innovative Liquid Air Energy Storage (LAES) systems including oxy-fuel combustion process

This paper is subject to ongoing publication

Energy and Exergy performance investigation associated to emission analysis of innovative Liquid Air Energy Storage (LAES) systems including oxy-fuel combustion process

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ABSTRACT

Liquid Air Energy Storage (LAES) is recently considered as a potential large scale Electrical Energy Storage (EES) for the renewable energy integration. This work investigates the energy and exergy efficiency of different LAES configurations the LAES. The particularity of this work is that it is presented as a comparison of the usual super-heating based discharge cycle of the LAES to an innovative system proposed within this work. An environmental analysis is also carried out due to the combustion process integration within the developed configurations.

A thermodynamic analysis is carried out with a focus on three combustion methods: oxy-biogas, oxy-natural gas and air-biogas fueled combustion processes. GRIMECH 3.0 mechanism was adopted as the reaction scheme. A comparison of energy efficiencies of two LAES methods with different cold energy recovery is presented: direct expansion of Liquid Air in a super-heating based cycle and the combustion-based cycle. The environmental impact of both systems is evaluated thanks to the emission analysis of the combustion furnace gases as results of the combustor modelling method.

Energy recovery in the combustion-based cycle is greater than super-heating-based cycle, but it is necessary to consider the environmental impact of these cycles which is a crucial criterion. The use of biogas in oxy-fuel combustion and carbon capture are suggested solutions for energy efficient, commercially viable and environmental friendly LAES.

Acronyms

CEEMs Cryogenic Energy Extraction Methods
COP Coefficient of Performance
GHG Greenhouse Gas
GWP Global Warming Potential
JT Joule Thomson
LA Liquid Air
LAES Liquid Air Energy Storage
LHV Low Heat Value
RTE Round Trip Efficiency

Nomenclature

Cp Heat capacity ($J.K^{-1}$)
Comp mixture composition
EmNOx NOx emission ($g.kg^{-1}$)
EmGHG Greenhouse Gas emission ($g.kg^{-1}$)
Ex Exergy ($kJ.kg^{-1}$)
h enthalpy ($kJ.kg^{-1}$)
H Total enthalpy (kJ)
LHV Low heat value ($J.kg^{-1}$)
L Latent Heat ($J.kg^{-1}$)
p potential
P pressure (pa)
s entropy ($kJ.kg^{-1}$ K^{-1})
t time
T Temperature (K)
Y mass fraction (kg/s)
Z chemical equilibrium coefficients
$\dot{m}$ mass flow rate ($kg.s^{-1}$)
h° formation enthalpy ($J.mole^{-1}$)
$\hat{h}$ surenthalpy ($J.mole^{-1}$)
$\dot{W}$ Power (kW)
$\dot{V}$ Volume flow rate ($m^3.s^{-1}$)
$\dot{Q}$ heat rate (kW)
$\bar{y}$ mass fraction
υ mole fraction
η efficiency

Subscripts

a oxidizer
c fuel
CO2 carbon dioxide
COLD/cold cold
comp compressor
cond condenser
cons consumed
conv converted
cop coefficient of performance

d diluent
discharge related to discharge unit
elec electrical
f fuel
freeze freezer
gene generation
hot hot
i reactant number
in input
j product number
l loss
liq related to liquefier unit
mech mechanical
out   output
p product (exergy product)
P product (product of combustion)
produced liquid produced
R Reactants
RTE Round Trip Efficiency
spec specific
t turbine
pump pump
th thermal
w water

3.3 Introduction

Liquid Air Energy Storage (LAES) has been recently reconsidered for grid-scale energy storage whereby air is liquefied at around -195 °C and stored in insulated tanks. This energy storage principle was classified by Morgan (Morgan et al., 2015a) as thermo-electric energy storage that utilizes liquid air as an energy storage medium. At off-peak times, energy produced by renewable sources supplies an air liquefaction unit to charge the LAES. When electrical energy is needed, discharge cycle is activated and Liquid Air (LA) is released (Gareth Brett and Matthew Barnett, 2014).

Multiple configurations were proposed for both parts of the LAES: charge and discharge units. More precisely, for the charge unit (i.e. air liquefaction unit), improved version of Claude cycle or a revival of the Solvay cycle were proposed in recent studies (Guizzi et al., 2015; Li, 2011; Li et al., 2014) which involves also some more sophisticated technologies using a Cryoturbine. Besides, concerning the discharge unit, at least four basic methods for Cryogenic Energy Extraction Methods (CEEMs) are mentioned in literature (Hamdy et al., 2017; Li, 2011). The simplest one is the direct expansion method where the cryogen is pumped, heated by the ambient heat or waste heat and expanded into turbines to generate power. In the second method, cryogen is used as a second fluid instead of the main working fluid. It is whether used to condensate the working fluid in a Rankine cycle or to cool down the working gas before compression in a Brayton cycle. The fourth method is a combination of the three previous ones.

Recent studies (Ameel et al., 2013; Guizzi et al., 2015; Hamdy et al., 2017; Sciacovelli et al., 2017) on LAES have shown an exergy efficiency and a round trip efficiency in a range of [43-50%]. These studies are almost all based on the direct expansion method where liquid air is directly evaporated and expanded within turbines to produce electric energy. This type of generation unit is the so-called super-heating based generation method. Nonetheless, some authors investigated the effect of natural gas combustion in enhancing the efficiency of this system. For example, a recovery system was studied by Mitsubishi (Kenji Kishimoto, 1998), where the power is produced by a gas-turbine. The author calculated an efficiency up to 77%. Meanwhile, in a commercial document of the same company that manufactures a combustion-based recovery system (Barry Liebowitz et al., 2013), the round trip efficiency of the cycle at a commercial scale is claimed to be greater than 95%. Clearly, combustion enhances the round trip efficiency, but the environmental aspect of the flue gas composition should be carefully evaluated so that this branch of LAES development could be granted as an eco-friendly solution for renewable energy integration.

In the present work, a process of LAES storage is developed and investigated as innovative solution to meet all the energy and environmental requirements. The oxy-combustion technology is suggested, as a way to guarantee a good efficiencies regarding important outlet combustion temperature and less pollutants considering the absence of nitrogen in the mixture. Besides, carbon capture could be technically possible employing the cryogenic carbon capture within the system itself. Significant energy and exergy performance results are expected while maintaining reasonable environmental impact.

Therefore, an environmental – thermodynamic comparison will be theoretically investigated for both recovery cycles: super-heating and combustion method including a post-treatment combustion system. Three combustion methods are investigated and compared by choosing different mixture conditons: oxy-biogas combustion, oxy-natural gas combustion and air-biogas combustion for a deeper discussion on the thermodynamic and environmental performances.

The aim of the work is on the recovery cycle optimization where significant changes are brought. Charging cycle is chosen as a combination of Claude and Solvay Liquefier with a small difference related to the addition of a thermal cold energy recovery device. With the configuration of the by-pass turbine, Claude liquefier is likely to represent a more energy efficient process with reduced energy consumed by liquid mass fraction.

This cold energy is recovered from the evaporation of Liquid Air (LA) in the discharge unit. In this study, cold recovery is not the only possibility to connect the charging and discharging circuits, since hot thermal energy recovered from the compressors of the liquefaction device is also captured and stored to boost energy generation unit. The present work presents new LAES configurations integrating combustion processes as oxy-fuel combustion and biogas as green source of energy. A combustion post-treatment block has been added to the system to diminish the environmental impact in case it exists. It consists on the formation of carbon dioxide and condensed water from thanks to cryogenic energy. First, an energy and exergy analysis will be carried out to evaluate the energy efficiency of those systems. Then, the calculation of combustion performance is provided adopting GRIMECH 3.0 mechanism. This part requires a particular algorithm for both thermodynamic results and emissions quantification. It leads to the second part of the work, which concerns the evaluation of the environmental impact based on the determination of flue gases composition. Three combustion methods with varying input parameters in each method are considered.

3.4 Process flow diagrams

3.4.1 General definition: Liquefaction for charge and direct expansion for discharge

The principle of using this type of energy storage is based on 3 main steps : (i) liquefaction of gaseous air when energy is available at off-peak times, (ii) storing liquid air in insulated tanks and (iii) expansion of pumped liquid air through steam turbines or gas turbines to generate power at peak demand period (Abdo et al., 2015; Ameel et al., 2013; Antonelli et al., 2016; Guizzi et al., 2015; Kishimoto et al., 1998; Li et al., 2014; Morgan et al., 2015b; Sciacovelli et al., 2017; Smith, 1977).

3.4.1.1 Liquefaction subsystems

The selection of the liquefier is crucial for the whole system efficiency regarding the fact that the global efficiency of the system is tightly influenced by the liquefaction energy consumption.

Claude cycle appears to be the best approach for the air liquefaction unit, since, flow temperature is reduced at the Joule Thomson (JT) valve inlet and therefore liquid yield of the throttling device (JT) is considerably increased because of the additional cooling provided by the by-pass turbine (Claude turbine). Therefore, specific energy consumption is found to be considerably reduced. Moreover, the use of a Claude turbine allows electric energy recovery. Nonetheless, fluid at the turbine outlet should not be at liquid state to prevent turbine blades damage.

Recent technology replaces the non-isenthalpic expansion of the JT valve by a cryoturbine (Kanoğlu, 2001), since it enhances the liquefier performance. A cryoturbine allows the production of liquid droplets and electric energy recovery at the same time. Simulations have shown that the replacement of the cryoturbine does not necessarily add a great performance value considering the system operating temperature range (-150°C). Therefore, in the current paper, a JT valve is selected based on these energy efficiency and economic criteria since that the cryoturbine represents a heavy investment cost for a small enhancement.

The basic process is shown in Figure 3.4.1. A small difference in the liquefaction cycle due to the addition of the cold recovery device is presented in Figure 3.4.2.

The working principle is as follows: air enters the system at ambient conditions; it then undergoes a double-stage compression with inter-cooling. Air exits the compression step to go through different blocks of cooling, first chilling with ambient ventilation.

Secondly it enters the cold box where it is cooled down by the by-pass Claude turbine mixed with cold non-liquefied air vapor portion at very low temperature. In the second configuration (Figure 3.4.2), an additional cooling effect exists after the by-pass turbine. The stored cold energyused here has been recovered from the evaporation process of the liquid air during the discharge process.

In those systems, hot storages have two roles. The first is to cool down the compressed air and the second role is to superheat the released liquid air in the super-heating based discharge system.

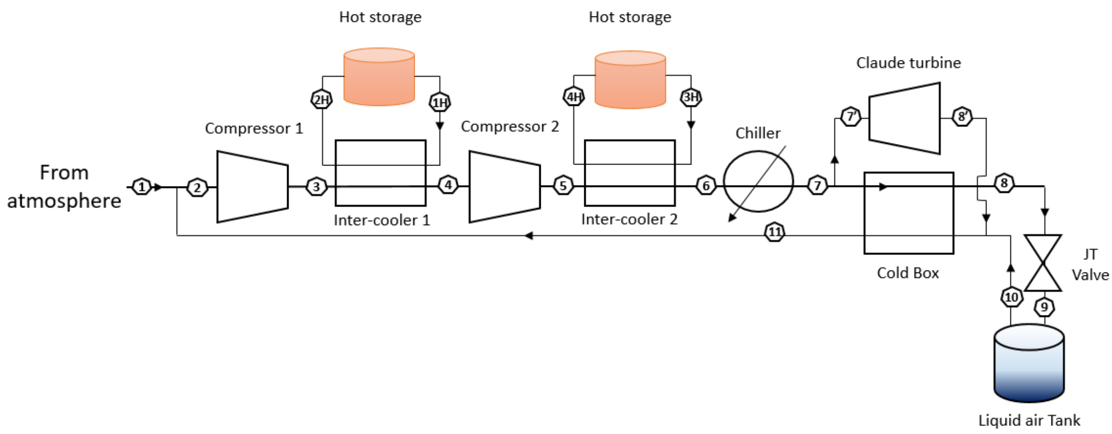

Figure 3.4.1: Process Flow Diagram of Claude liquefier: basic configuration

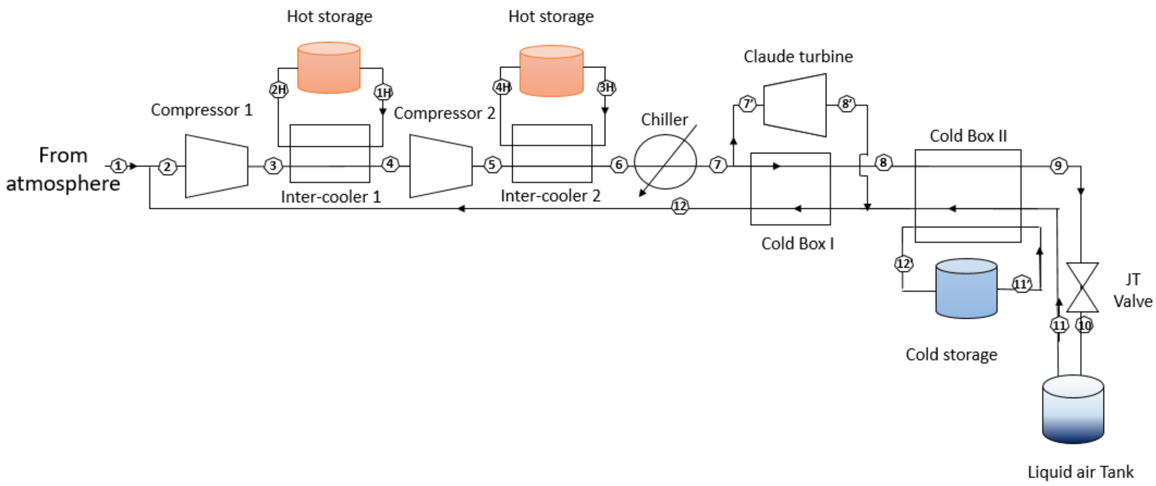

Figure 3.4.2: Process flow diagram of Claude liquefier with the addition of cold recovery

3.4.1.2 Discharge cycle 1: superheating-based cycle

Superheating-based discharge cycle as shown in Figure 3.4.3 is based on direct expansion of liquid air after evaporation and superheating in an open cycle. Liquid air is first pumped from the liquid air tank. Then, it evaporates and then expands through multi-stage turbines with super-heaters to recover both thermal and electrical energy, using steam turbines. It is noticeable that an important cooling load is produced by the first step of evaporation in this cycle. The low temperature thermal energy can be provided to the liquefier and the medium temperature to a refrigerated warehouses or freezers as previously described (3.4.1.1). Super-heaters are supplied by hot thermal energy stored during liquefaction within the inter-coolers in the compression stage.

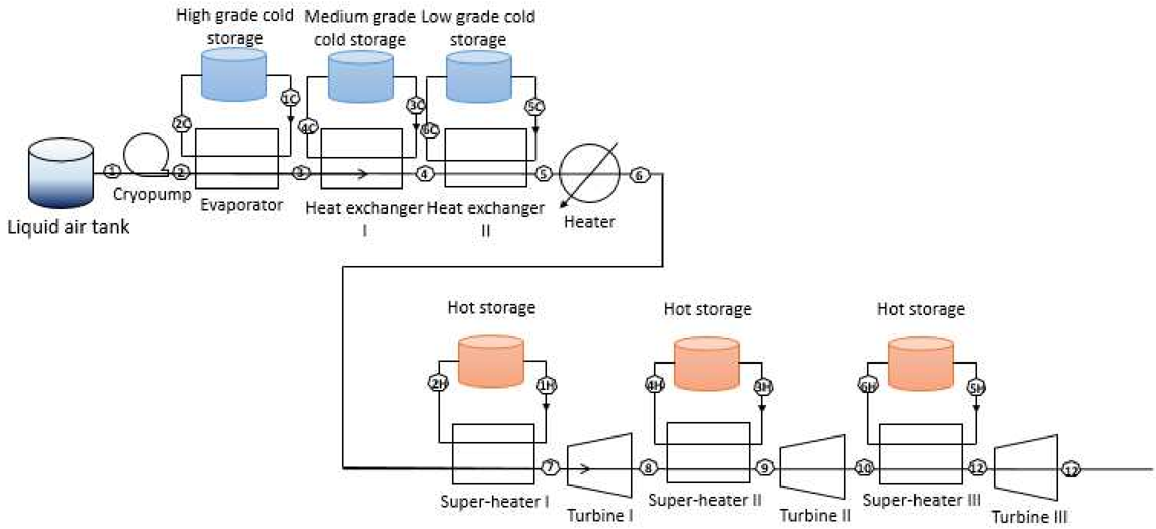

Figure 3.4.3: Process Flow Diagram of super-heating based recovery open-cycle

3.4.1.3 Discharge cycle 2- combustion-based cycle

The discharge cycle with combustion as shown in Figure 3.4.4 represents air-biogas combustion (*case study 1*). Besides, in Figure 3.4.5, energy generation with oxy-combustion is presented. The combustion may be fueled by natural gas (*case study 2*) or by biogas (*case study 3*).

The discharge cycle of *case study 1*, as shown in Figure 3.4.3, begins with the same evaporation and cold energy recovery blocks as for the discharge unit with superheating-based cycle. The difference lies in the expansion block where the superheaters are replaced by a combustor and a gas turbine instead of steam turbines.

For *case studies 2* and *3*, in order to allow oxy-fuel combustion, the system includes an air separation unit after liquefaction which is not presented in this figure. Initially, liquid oxygen and liquid nitrogen are stored in two different tanks. Then, both liquids go through evaporation and heaters to get their cold energy recovered before entering to the expansion block. In the oxygen loop, oxygen goes in the burner and flue gases are expanded in gas turbine, after a biogas-fueled or natural gas-fueled combustion process.

The heat exchanger after the combustion chamber has a double role. The first one is to cool down the flue gases from the combustion chamber and the second is for the heat recovery. Heat recovered from the combustion will be used in the super-heating process of the nitrogen loop.

Meanwhile, the nitrogen loop stays the same as that of the previous discharge circuit of super-heated liquid air. Cold from the evaporation of liquid nitrogen is captured and stored for later use (for use in liquefaction cold storage and industrial refrigeration). Before entering to the multi-stage expansion block, nitrogen is used in the post-treatment process of the oxy-fuel combustion. Cryogenic thermal energy from nitrogen is still available to freeze the carbon dioxide and condense water, two major components of the flue gases.

Furnace gases are treated in both *case study 2* and *case study 3*, in oxy-fuel combustion method. Density of carbon dioxide in the flue gases is higher than in air-firing and therefore post-treatment is less complex than in the basic air-combustion process. In the *case study 1* of air-biogas combustion, post-treatment process is not included. Oxy-fuel combustion method results in high combustion temperature. One solution for this issue is to control the fuel-to-air ratio and the diluent rate. Diluent chosen in this study is CO_2 which is captured and recirculated from the post-treatment process or issued from an external source. As it will be further developed (3.5.3), these two criteria play a major role in determining the gaseous pollutant emissions.

Despite the additional complexity in the discharge system, oxy-combustion is chosen because of its advantages related to environmental issues as carbon capture possibility, water producing and low NO_x emission.

In this work, air is used as hot/cold energy storage and heat transfer fluid.

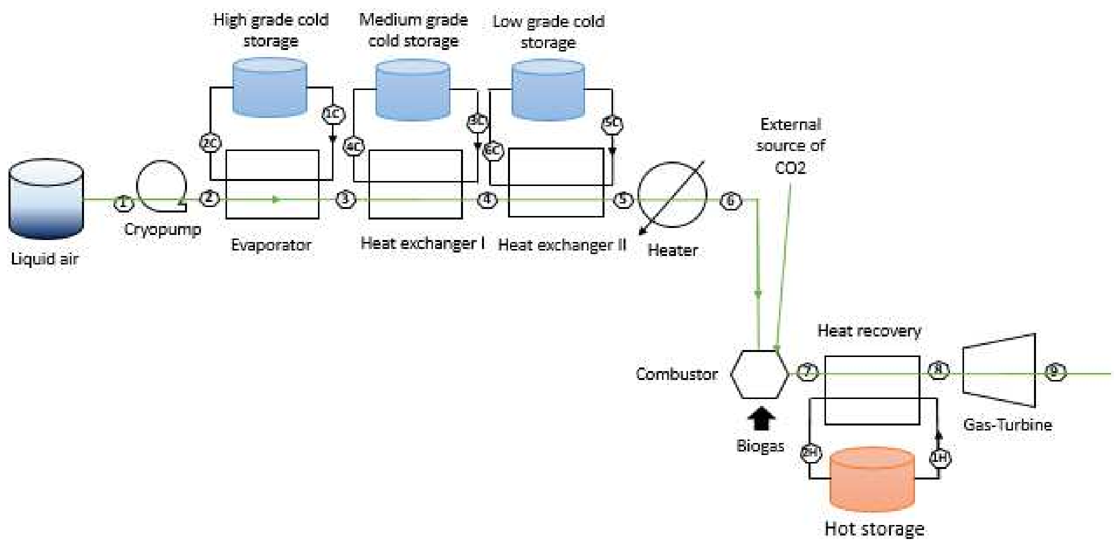

Figure 3.4.4: Recovery cycle with conventional combustion biogas fueled

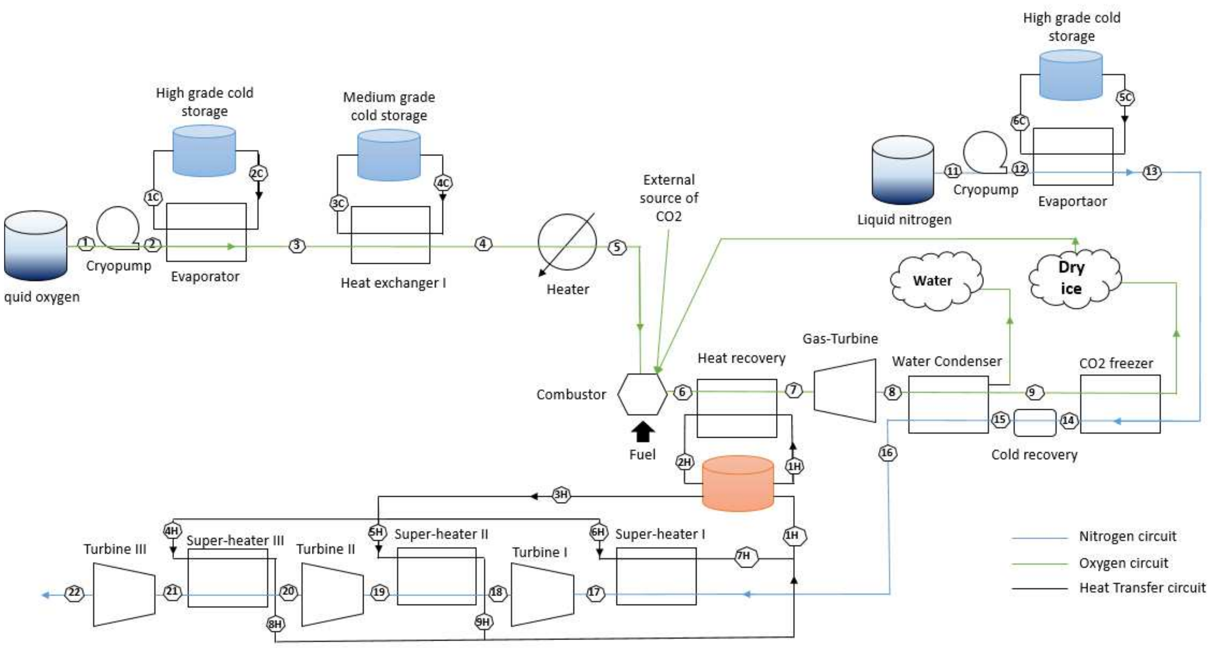

Figure 3.4.5: Process Flow Diagram of oxy-fuel combustion

3.5 Methodology

3.5.1 Assumptions and modelling methods

In this modeling work, NIST REFPROP 9.1 database (Lemmon, 2018) is used for the physical properties calculation at each state point of the circuit. Efficiency values are assumed and given in **Table 3.5.1** corresponding to their equivalent in some references found in literature (Guizzi et al., 2015; Li, 2011). The calculation assumptions are presented as follows:

(1) Steady-state condition
(2) Pressure drops are neglected in heat exchangers, evaporators, condenser freezer, combustor, pipes and tubes.
(3) In all components, no heat losses are considered.
(4) For water condensation and CO_2 freezing calculation the flow gas is supposed as a mixture of only water and CO_2 proportion.
(5) Maximum allowed temperature turbine inlet is 1400K ~ 1126.85 °C (after combustion) (Antonelli et al., 2016).
(6) Thermal behavior variation of fluid during storage is not considered; therefore, outlet temperatures can be estimated and given in **Table 3.5.1**.

Parameters	**Value**	**Unit**
Isentropic efficiency of compressors, turbines and pumps $\eta_{comp}, \eta_t, \eta_{pump}$	0.8	none
Electrical and mechanical efficiency of turbo-alternator $\eta_{elec-mech}$	0.67	none
Fuel potential conversion $\eta_{fuel,conv}$	0,6	none
Heat exchanger efficiency	0.9	none
Ambient pressure	1	bar
Ambient temperature	25	°C
Hot storage outlet	50	°C
High-grade cold storage outlet	-50	°C
Medium-grade cold storage outlet	-20	°C
Low-grade hot storage outlet (for chillers)	0	°C

Table 3.5.1 : Design parameters and initial condition

3.5.2 Energy calculation

Compressor power demand:

$$\dot{W}_{comp} = \dot{m}\frac{\Delta h}{\eta_{comp}} \quad (1)$$

Pump power demand:

$$\dot{W}_{pump} = \dot{V}\frac{(P_{out} - P_{in})}{\eta_{pump}} \quad (2)$$

The power generated by turbine:

$$\dot{W}_t = \dot{m}\Delta h \eta_t \quad (3)$$

Temperatures of fluids through heat exchangers (super-heaters, inter-coolers, evaporators, chiller, heater and cold boxes) are calculated using NTU (Number of Transfer Units) method. This method computes the effectiveness of a heat exchanger, and applies this efficiency to the maximum possible heat transfer rate that could be reached by a heat exchanger of infinite length.

Water condensation demand power:

$$\dot{W}_{cond} = \dot{m}_w \times (h_{in} - h_{out}) \quad (4)$$

Where $\dot{m}_w$ is the mass fraction of water contained in the flue gas mixture.

CO_2 freezing demand power:

$$\dot{W}_{freeze} = \dot{m}_{CO2} \times (h_{in} - h_{out}) + \dot{m}_{CO2} \times L_{CO2} \quad (5)$$

Where $\dot{m}_{CO2}$ is the mass fraction of carbon dioxide in the flue gas mixture.

Conversion of thermal energy to electrical energy:

$$\dot{Q}_{elec} = \frac{\dot{Q}_{th}}{COP} \quad (6)$$

Where $\dot{Q}_{th}$ is the power exchanged in each thermal storage (High grade cold storage, medium grade cold storage, heat recovery, hot storage).

Calculation of cold COP for refrigerant cycle and hot COP for heat pump are based on a valorization temperature of the exchanged thermal power.

Specific electrical consumption of liquefaction in kWh/kg:

$$\dot{E}_{spec,cons} = \frac{(\dot{E}_{cons} - \dot{E}_{gene})}{Y_{produced}} \quad (7)$$

$\dot{E}_{gene}$ is the electrical power generated by Claude turbine and $Y_{produced}$ is the mass fraction in kg/s of liquid air produced.

Specific electrical generation in kWh/kg:

$$\dot{E}_{spec,gene} = \frac{(\dot{E}_{gene,discharge} + \dot{Q}_{elec} - \dot{E}_{fuel} - \dot{E}_{cons})}{Y_{discharged}} \quad (8)$$

Where :

$\dot{Q}_{elec}$ is thermal power recovered converted by means of COP to its equivalent in terms of electrical energy;

$\dot{E}_{fuel}$ fuel potential as calculated in Eq. 11

$\dot{E}_{gene,discharge}$ refers to the electrical power generated by the turbine considering isentropic efficiency and electro-mechanical efficiency as calcutated in Eq. 10

$Y_{discharged}$ is the mass fraction of liquid air being discharged

$$\dot{E}_{gene} = \dot{E}_{turb} \times \eta_{turb} \times \eta_{elec-mech} \quad (10)$$

Fuel potential:

$$\dot{E}_{fuel} = \dot{m}_{fuel} \times LHV_{fuel} \times \eta_{fuel,conv} \quad (11)$$

where LHV_{fuel} is the Low Heating Value of the considered fuel.

Recovered thermal power and electrical power are counted as output of the system. On the other hand, the energy consumption in the system is the chemical energy of the fuel and the energy consumed by the liquefaction unit. The chemical energy of the fuel converted to thermal energy and then to electrical form by means of $\eta_{fuel,conv}$.

The general form of specific generated energy is given in Eq. 8. It could have different forms depending on the discharge process type. In the super-heating case, $\dot{E}_{gene,discharge}$ and $\dot{Q}_{elec}$ are counted as recovered power. For the combustion process, $\dot{E}_{fuel}$ is subtracted to the numerator as a consumed power.

RTE calculation in case of simple Claude liquefaction:

$$\eta_{RTE} = \frac{\dot{E}_{spec,gene}}{\dot{E}_{spec,cons}} \quad (12)$$

RTE calculation in case of Claude liquefaction with cold storage addition:

$$\eta_{RTE} = \frac{\eta_{RTE_{COLD}} \times t_{cold} + \eta_{RTE_{COLD}} \times (t_{total} - t_{cold})}{t_{total}} \quad (13)$$

Where t_{cold} is the time required to fully discharge the liquid air tank (cold recovered from evaporation being available) and t_{total} refers to the total duration if the liquefaction. $\eta_{RTE_{COLD}}$ corresponds to the round trip efficiency when cold is being added to the liquefaction circuit.

3.5.3 Combustion and emission calculation

The combustion model aims at calculating the outlet temperature and the pollutants emissions in the furnace gases while varying the composition corresponding to each of three combustion cases, the fuel-air ratio and diluent rate (CO_2 rate). A GRIMECH 3.0 mechanism, including 53 species with 325 reactions, was adopted as the reaction scheme to determine the temperature profile regarding all species interacting in the combustion reaction including the polluting ones in adiabatic equilibrium state.

Hypothesis:

(1) Combustion is considered as ideal adiabatic and isobaric

(2) Biogas and natural gas are at gaseous state

(3) In this work, biogas is considered as a composition of 70% of methane and 30% of CO_2 regarding the complexity and energy and economical cost of biogas total purification (Ullah Khan et al., 2017).

(4) Natural gas composition : 97,5% of CH_4 and 2,5% of C_2H_6

The first step consists in computing the chemical equilibrium of the combustion reaction written in its generalized form as in Eq. 16 using the CANTERA open-source software (David G. Goodwin, 2018):

$$Z_c(\vartheta c_{CH4}CH_4 + \vartheta c_{CO2}CO_2) + Z_a(\vartheta a_{O2}O_2 + \vartheta a_{N2}N_2) + Z_d \vartheta d_{CO2}CO_2 \rightarrow product\ of\ 53\ Species\ [GRIMECH] \quad (14)$$

Where Z_c, Z_a and Z_d are coefficients related to the fuel, the oxidizer and diluent mole fraction. The mass equilibrium of the chemical reaction gives:

$$Z_c = \frac{\emptyset}{\vartheta c_{CH4}} \quad (15)$$

where $\emptyset$ is the fuel – air ratio

$$Z_a = \frac{Z_c \vartheta c_{CH4}}{0{,}5\emptyset \vartheta a_{O2}} \quad (16)$$

$$T_d = \frac{Z_d \vartheta d_{CO2} + Z_d \vartheta d_{N2} + Z_c \vartheta c_{CO2}}{Z_c + Z_a + Z_d} \Rightarrow Z_d = \frac{(Z_c + Z_a)T_d - Z_c \vartheta_c CO_2}{1 - T_d} \quad (17)$$

T_d is the dilutant rate

Supposing that all the heat released from combustion is produced by chemical reaction, the thermodynamic equilibrium is represented by Eq. 20, kinetic and potential energy are neglected:

$$\Delta H = 0 \leftrightarrow \left(\sum_j n_j h_j\right)_p - \left(\sum_i n_i h_i\right)_R = 0 \quad \text{where } h_i(T) = h_f^0 + \hat{h}(T)$$

(18)

$$\vartheta_P \sum_{J=1}^{53} y_j \left(\boldsymbol{h_f^0} + \hat{h}(T2)\right)_P - \vartheta_R \sum_{i=1}^{53} x_i \left(\boldsymbol{h_f^0} + \hat{h}(T1)\right)_R = 0$$

(19)

If temperature and pressure at the combustor inlet of the mixture are different from the standard temperature and pressure, a term noted $\hat{h}(T)$ appears called « surenthalpy ». It indicates the sensible enthalpy between the enthalpy of formation of each reactant and their enthalpy corresponding to the inlet conditions.

CO, CO_2, NO, NO_2 and N_2O are the species considered for the emission analysis, NO_x are determined by Eq. 22 and greenhouse gas by Eq.23:

$$EmNO_x = \bar{y}_{NO} + \bar{y}_{NO2} \quad (20)$$

$$EmGHG = \bar{y}_{CO2} + 25\bar{y}_{CH4} + 298\bar{y}_{N2O} \quad (21)$$

where the coefficient 1, 25 and 298 Global Warming Potential (GWP) values for a lifespan of 100 years.

3.5.4 Exergy calculation

Exergy analysis is one of the best tools for the performance evaluation of systems operating at different temperatures and integrating different energy sources (Hamdy et al., 2019). The exergy analysis applied in this paper is followed the fuel and product” approach.

Exergy at each point (in Figures 1 to 5) is calculated as in Eq. 22.

$$Ex = (H - H_0) - T_0(S - S_0) \quad (22)$$

$$\Delta E = \sum_i \dot{m}_i \dot{Ex}_{in}^i - \sum_i \dot{m}_i \dot{Ex}_{out}^i \pm \sum_i \dot{Q}_i \left(1 - \frac{T_0}{T_i}\right) \pm \sum_j \dot{W}_j \quad (23)$$

The exergy calculation at each component is summarized in Table 3.5.2.

Component	**Exergy destruction calculation**
Compresseur / cryopump	$\Delta E = \dot{m}(Ex_{in} - Ex_{out}) + \dot{W}_{in}$
Turbine	$\Delta E = \dot{m}(Ex_{in} - Ex_{out}) - \dot{W}_{out}$
Heat Exchanger/ Evaporator	$\Delta E = \dot{m}(Ex_{in} - Ex_{out}) \pm \dot{Q}\left(1 - \frac{T_0}{T}\right)$
Multi-stream exchanger	$\Delta E = \sum_i \dot{m}_i\left(Ex_{in}^i - Ex_{out}^i\right)$

Table 3.5.2: Exergy calculation for each component

Where subscripts: “in”: inlet operating conditions; “out”: outlet operating condition, “ex” : Designation of exergy terms. “Fuel”, “product” and “dest” refer to exergy fuel, exergy product and exergy destructed or lost respectively. Subscripts “hot” and “cold” refer to hot fluid and cold fluid. “Rev” and “irr” refer to reversible and irreversible work.

The exergy destructed related to the combustion reaction can be written as follow:

$$\Delta \dot{ex}_{dest} = \dot{ex}_{reactants} - \dot{ex}_{products} \quad (24)$$

Where :

$$\dot{ex}_{reactants} = \sum_{i=1}^{53} h_i(T_i) - T_0 S_i(T_i) \quad (25)$$

And

$$\dot{ex}_{products} = \sum_{j=1}^{53} h_j(T_j) - T_0 S_j(T_j) \quad (26)$$

3.5.5 Structure of the results and discussion part:

The results and discussion section will be presented in accordance with the following steps:

- Combustion : temperature, emissions and exergy analysis
- Integration of optimum combustion temperature to the entire circuits
- Results and discussion of parametric analysis depending on pressure : stream data (mass flow, temperature, pressure) of the presented layouts and RTE variation
- Exergy results

In the combustion section, an optimum operating point is evaluated for each case study by taking into account simultaneously thermodynamic aspect and environmental constraints. Then, outlet temperature of combustion is integrated as key element in the process to the global thermodynamic analysis of the entire system.

The effect of variation of the Fuel-Air Ratio (Ø) and Diluent Ratio (Td) is considered for each mixture composition in this study with a constant mass flow rate at steady-state condition. Diagram depicted in Figure 3.5.1 illustrates the methodology adopted in the combustion analysis part. The Td and Ø are chosen from the profiles of temperature allowing the maximum combustion temperature with the lowest pollutant emissions possible.

The studied composition values for each of the mixtures are shown in Table 3.5.3. Environmental performance is evaluated from pollutant emissions: Greenhouse Gas (GHG), nitrogen oxide (NO_x) and carbon monoxide (CO). Thermodynamic performance is analysed using the outlet temperature and exergy loss within the combustor. All cases were computed with inlet conditions of 35 bar as pressure and 300K as initial temperature of the mixture.

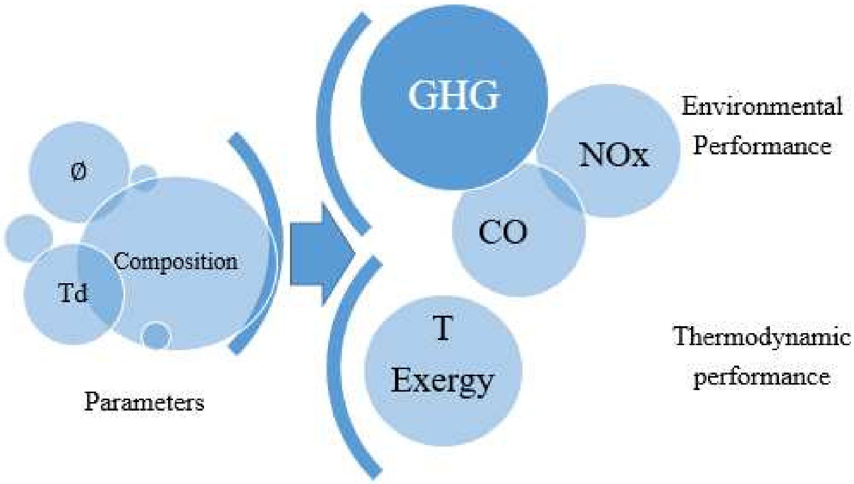

Figure 3.5.1: Diagram depicting the parametric analysis conducted for the combustion study

Case study 1 - Reactants of air-biogas combustion		
Fuel (CH_4, C_2H_6, CO_2)	Oxidizer (O_2, N_2)	Diluent (CO_2)
0.70, 0.00, 0.30	0.21, 0.79	1.00
Case study 2 - Reactants of oxy-natural gas combustion		
Fuel (CH_4, C_2H_6, CO_2)	Oxidizer (O_2, N_2)	Diluent (CO_2)
0.975, 0.025, 0.00	1.00, 0.00	1.00
Case study 3 - Reactants of oxy-biogas combustion		
Fuel (CH_4, C_2H_6, CO_2)	Oxidizer (O_2, N_2)	Diluent (CO_2)
0.70, 0.00, 0.30	1.00, 0.00	1.00

Table 3.5.3: Reactants composition for the studied cases

In the second part of the study, a parametric analysis on the basis of pumping discharge pressure will be conducted to determine the optimum operating pressure corresponding to a maximum

RTE. As shown in the diagram in Figure 3.5.2 the following combinations will be considered for this part:

- LAES super-heating based discharge in combination with simple Claude liquefier and cold recovery Claude liquefier.
- LAES oxy-biogas fueled combustion as discharge cycle in combination with simple Claude liquefier and cold recovery Claude liquefier.

In all cases, the heat from inter-coolers in the liquefaction subsystem is recovered in the discharging part. Cold from the evaporation of the cryogen is recovered in case of cold recovered liquefaction and not in the simple Claude liquefier.

Depending on results from the parametric analysis, the best configuration will be retained for the second part (RTE, Exergy).

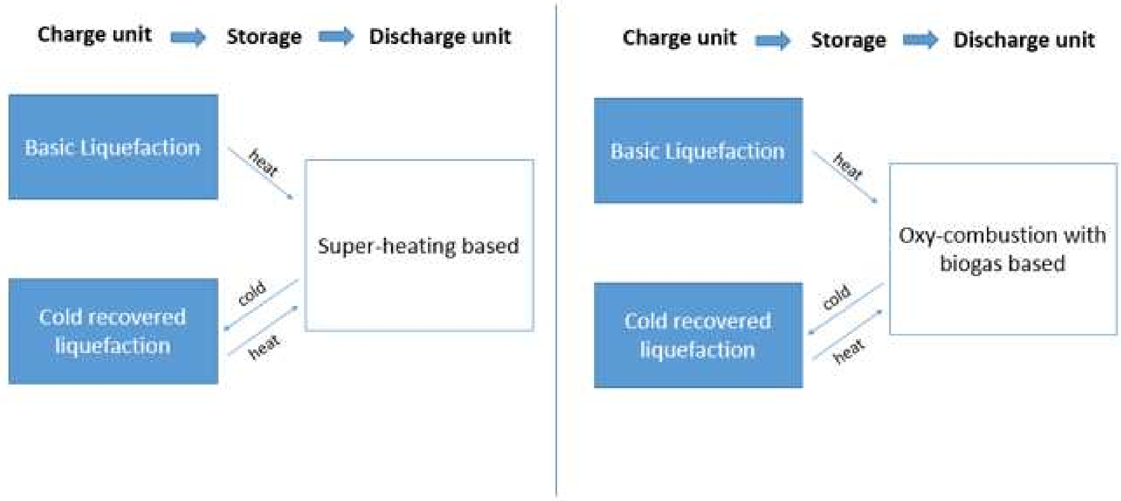

Figure 3.5.2: Diagram of LAES studied combinations with the recycled cold represented by the blue arrow and details of combustion methods

3.6 Results and discussion

3.6.1 Combustion exergy and emissions results and analysis:

3.6.1.1 Temperature and pollutant profiles:

As shown in Figure 3.6.1, temperature in every case reaches its maximum value at Ø=1 and has the highest value when there is no diluent added. A noticeable gap in temperatures values between oxy–combustion and air – combustion can be observed in Figure 3.6.1. The temperature profiles are affected by the removal of nitrogen fraction in the oxidizer. However, these high temperatures lead to higher CO emissions, products of the CO_2 dissociation reaction, as well as

NO_x production, even at very low ∅ values as it will be discussed later. Pollutant emissions are calculated and represented on the basis of one kg of fuel unit.

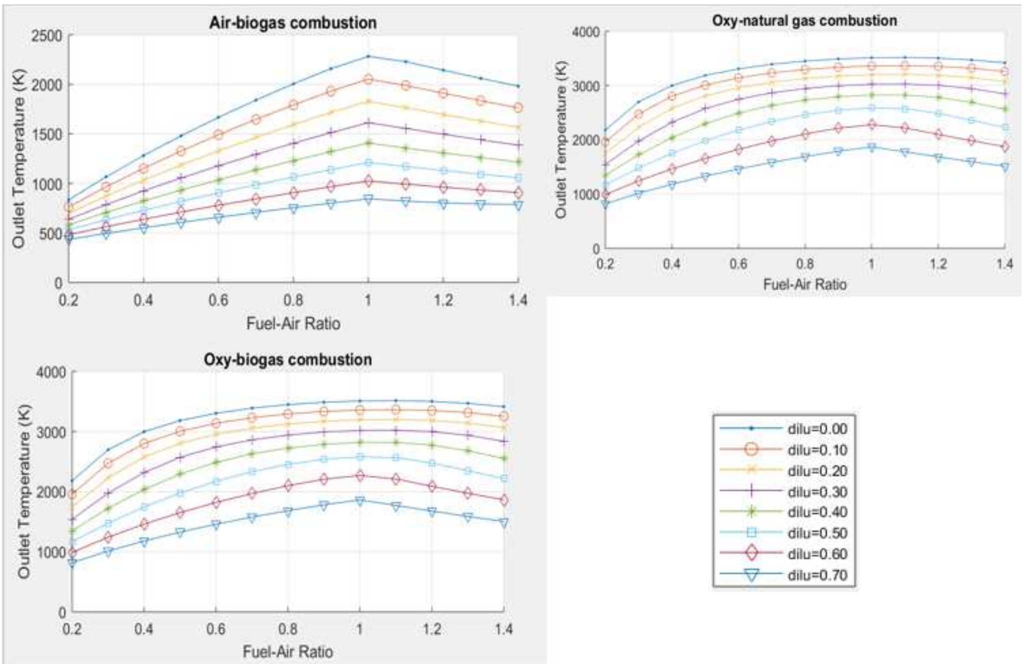

Figure 3.6.1: Temperature profile depending on the Fuel-Air ratio and dilution rate for three mixtures

Figure 3.6.2 presents pollutant emissions results (GHG, CO, NO_x) for the combustion case study 1: Air-biogas combustion.

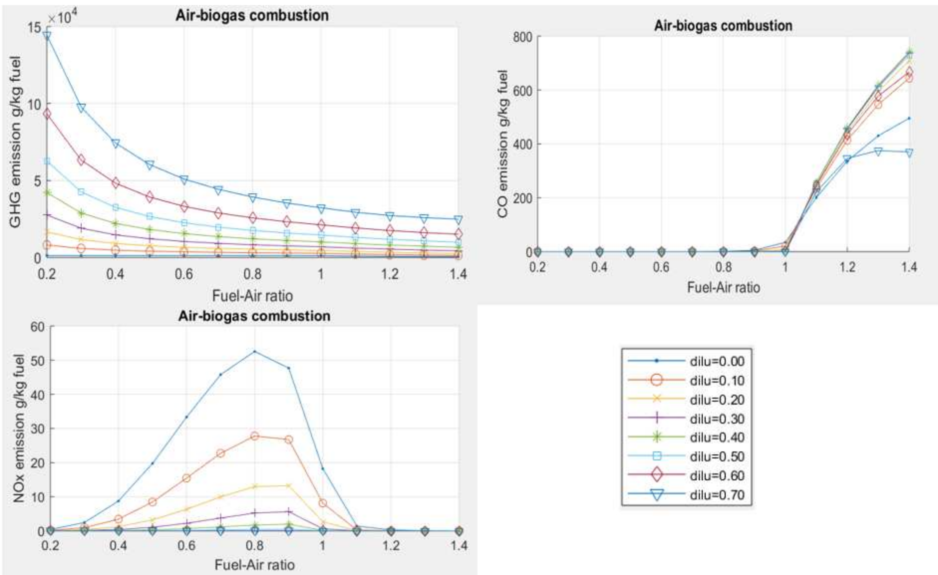

Figure 3.6.2: Pollutants emissions profiles (GHG, NOx, CO) for Air-biogas (case study 1) as a function of ∅ and Td

There is a significant drop in the GHG/kg fuel emissions as the ∅ increases until ∅=1 from where the decrease becomes more slow as all GHG agents disappeared with high temperature.

The GHG emission increases as the amount of diluent increases. The CO_2 as a diluent contributes to the GHG emissions with more CO_2 in the mixture and unburnt CH_4. A Ø value higher than 1 has a significant impact on the CO apparition, clearly the stoichiometric condition is a favorable for the CO emission due to high temperature and dissociated CO_2 onto carbon monoxide and oxygen consequently. NO_x profile presents a classical bell shape centered in a Ø range of 0.8 to 0.9 depending on the Td. Zero dilution presents a peak of NO_x emission corresponding to 0.8 Ø, a part of O_2 is unburnt at this Ø value and temperature is sufficiently high for NO production.

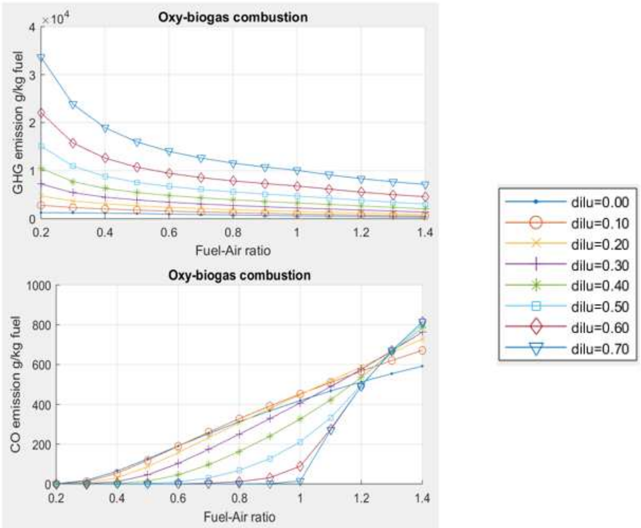

Figure 3.6.3: GHG and CO emission for oxy-biogas combustion (case study 3) as a function of Ø and Td

From a qualitative point of view, same remarks can be done in both *case studies 2* and *3* since curves of temperature and polluting emissions follow the same tendency (**Figure 3.6.3** and **Figure 3.6.4**). Nonetheless, values of GHG emissions are higher for the same combination in oxy-natural gas than in oxy-biogas combustion for almost the same temperature variation. This difference is due to the important mass fraction of CH_4 in one mole of fuel corresponding to almost 100% in natural gas compared to 70% in biogas. These values get even higher for the air-biogas combustion because of the presence of N_2 in the air composition. In the GHG equation, the GWP of N_2O counts for 298 for a lifespan of 100 years. The production of CO in any combustion case reflects an inefficient combustion because part of the heat released by the combustion is consumed for endothermal CO_2 dissociation rather than the combustion reaction itself. CO production for the oxy-natural gas combustion is the highest among other combustion mixtures and almost the double of oxy-biogas combustion case at the same range of temperature despite the fact that in biogas there is a fraction of CO_2. CO emission are not proportional to the presence of CO_2 in the mixture, since the lowest Td leads to the highest CO emission in all cases, and therefore, it is only a matter of temperature. CO_2 dissociation is very sensitive to temperature, since there is a slight difference in temperature (oxy-natural gas slightly higher than oxy-biogas temperature), this is the only apparent explanation of the big difference in CO profiles.

In general, at ∅ values lower than 1, the presence of CO is due to the reaction of dissociation of CO_2. When ∅ exceeds the stoichiometric conditions, the CO apparition reflects the degradation of the fuel due to incomplete combustion.

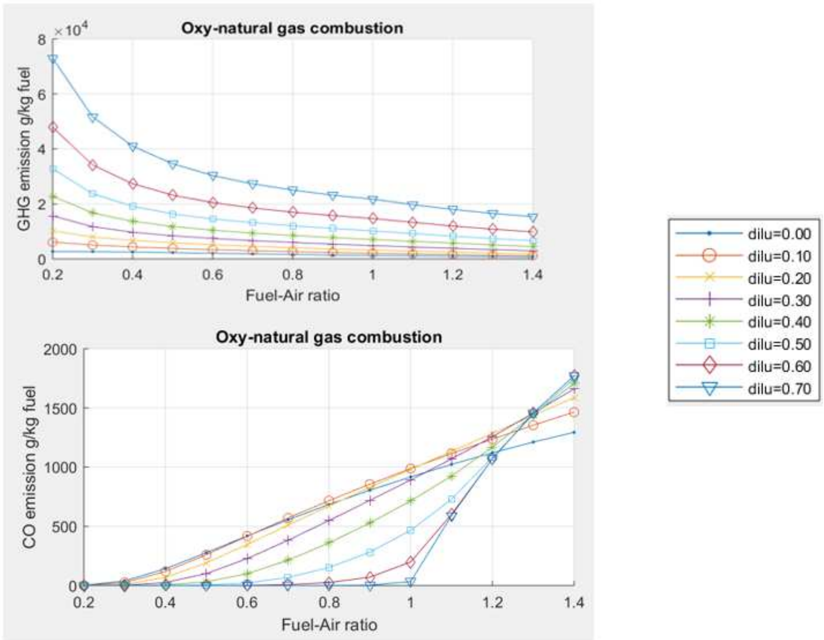

Figure 3.6.4: GHG and CO emission for oxy-natural gas combustion (case study 2) as a function of ∅ and Td

3.6.2 Identification of optimal operating parameters

Figure 3.6.2 shows that optimal operating parameters for the air-biogas combustion case (case study 1) could be around 1 for ∅ and with no additional of the diluent rate. Outlet temperature is still technologically acceptable (around 2300K) without additional diluent. NO_x emissions are of 18g/kg fuel. At these conditions, gas treatment methods for the control of NO_x emissions could be integrated to the Air-biogas combustion methods especially that this circuit does not include a post-treatment process as in *case study 2* and *3* as described in 3.4.1. Besides, it represents the lightest system in terms of complexity and components number of all the circuits presented herein.

In Figure 3.6.3, from one side, high diluent rates induce important GHG and low outlet temperature and from another, it has the positive impact on low CO emission. To assure the best thermodynamic performance, it is essential to choose the highest temperature possible according to the process configuration investigated herein as it will be discussed in paragraph 3.6.3.3. The compromise found for this *case study 2* seems to be Ø=0.4 and a diluent rate of 0 with almost 0 GHG emission and 54g/kg fuel of CO and a temperature of 3000K. In this case, the outlet temperature is controlled by the Ø and not by the diluent as it was conceived for.

Based on Figure 3.6.1 and Figure 3.6.4, the optimal operating point for this case study appears to be 3000K and approximately 0 GHG emissions for *case study 3*. Unfortunately, this compromise in terms of temperature and GHG emissions results in 119g/kg fuel of CO emission.

Figure 3.6.5 summarizes all the exergy losses in three combustions ways. In general, in the combustion process, three types of irreversibilities exist: chemical and thermal irreversibilities as well as the mixture irreversibility. The important temperature gradient is responsible for the exergy destruction. The mixture composition presents inert species that consumes heat released from the combustion. The dissociation of CH_4 represents an exergy destruction due to the degradation of the chemical potential within the fuel. Exergy loss follows the same tendency for three cases. Ø increase has a positive impact on the exergy efficiency on the contrary of Td which increases the exergy loss. Indeed, for the same fuel quantity, the dilution of CO_2, as inert specie, would only absorb heat from the combustion and therefore, reduce the exergetic efficiency of the combustion reaction.

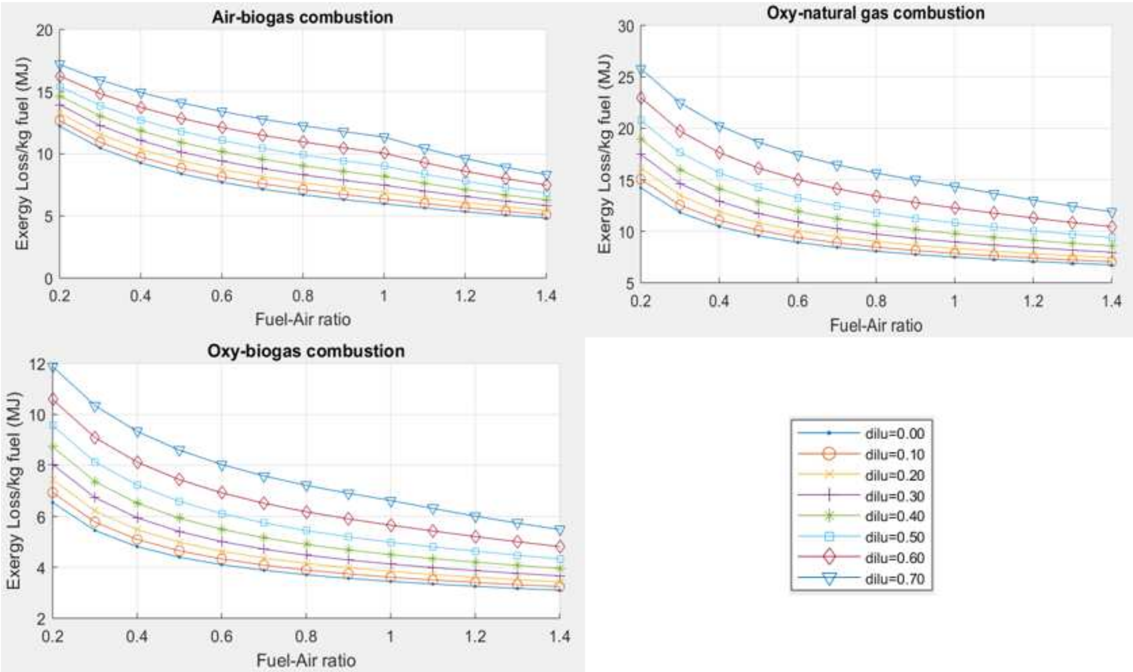

Figure 3.6.5: Exergy Loss/kg fuel variation as a function of ∅ and Td for three mixtures

Table 3.6.1 summarizes one solution considered as optimum-operating points for three cases, as it will be integrated in the second part of the analysis 3.6.3. Selected values of ∅ and Td in this given solution, prioritizes the low GHG emissions at the expense of relatively high CO emission. As previously explained, the CO production means inefficient combustion chemical reaction (fuel degradation or endothermal reaction of dissociation). In other words, it is a waste of energy and money.

Another configuration with ∅=0,6 and Td=0,5 for the case of oxy-natural gas could be possible to produce almost 0 CO, but a GHG value of almost 2g/kg of fuel is calcuted as well as a reduced combustion temperature (2200K). These values represent almost same tendency for the oxy-biogas case, too. Due to the temperature decrease, the global efficiency of the LAES will be also reduced. (Cf. 3.6.3.3).

As a conclusion of this part, the selected values shown in table Table 3.6.1 lead to a relatively “optimal” solution, there is no absolute optimality in this case, since, it strongly depends on the analysis approach (Environment, energy, exergy, etc.)

Case Study	Parameters		Temperature (K)	GHG (g/kg fuel)	CO (g/kg fuel)	NO_x (g/kg fuel)	Exergy Loss (MJ/kg fuel)
	Ø	Td					
Air-biogas	1	0	2282	≈0	≈0	18.24	6.36
Oxy-natural gas	0.4	0	3000	≈0	54	≈0	5.19
Oxy - biogas	0.4	0	3000	≈0	119	≈0	11.07

Table 3.6.1: Possible optimal combustion outlet conditions for each combustion case

3.6.3 Parametric analysis and process improvements

This section is based on RTE results and data stream in appendix. The optimization parameters considered in this study are the pumping pressure and the recovered cold energy to the liquefaction circuit. Other process improvements related to the use of waste heat and combustion post treatment are also discussed. Figure 3.6.6 presents how the round trip efficiency (RTE) changes with the pumping pressure of liquid air, liquid oxygen and liquid nitrogen in both cases: simple and cold recovered for the 2 configurations, superheating and combustion based cycle.

3.6.3.1 Cold recovery

Valuable energies calculated in this study are thermal energy of cold and hot energy from successive steps of heat exchanges and storing whether in cold or hot stores. Clearly, when cold energy is recycled to the liquefier the system efficiency is enhanced. Electrical consumption by Claude cycle per liquid fraction is less important when cold recovery is added. An RTE of 60% is calculated in the combustion case when no cold is recycled comparing to almost 80% when thermal cold energy is used to cool down fluid in Claude liquefier. With an optimal operating pressure of 100 bar in the case of super-heating cycle, RTE is respectively 22% and 30%. One advantage of oxy-fuel combustion method is that liquid nitrogen and liquid oxygen are 2 separated circuits, in this way, cold energy from the evaporation of liquid nitrogen can be used for the liquefaction and cold energy from the oxygen evaporation can be addressed to another external facility.

The consumption of the liquefaction sub-system decreases from 0.66kWh/kg to 0.26kWh/kg when integrating the cold load from the evaporation of liquid cryogen, but this concerns only during the discharge phase. The compression pressure in the liquefier (40 bar) is obtained from double compression stage with inter-cooler. A quick parametric analysis allowed the identification of this pressure as optimal pressure for this specific configuration.

Temperature at the JT valve inlet without cold added is -153°C and with the integration of cold its value is -185°C. The importance of the decrease of temperature has also the benefit of less exergy losses in the throttling device. In the simple case the exergy loss at the JT valve is 48.7 kJ/kg and when cold is recovered this value decreases significantly to 12.14 kJ/kg.

3.6.3.2 Optimal pressure of liquid air

It can be observed that the RTE increases linearly with the pressure of liquid air in the case of recovery with superheating process. The pressure should be then chosen regarding technical feasibility and efficiencies of heat transfer, especially when cold recovery is needed for refrigeration purpose or Claude liquefier. Hot and cold thermal energy recoveries are converted by means of COP to electrical energy form (Eq. 6). Temperature for cold recovery is set to -80°C as in freezers application for high grade cold usage, medium grade cold is supposed to be utilized at chillers temperature (-20°C). Heat source is valuable energy regarding important temperature level of combustion and this valorization level is set at 150°C, even if temperatures reach higher values. The industrial site where the system could be implemented (food refrigeration) is not demanding in terms of heat requirements. Recovery of the oxy-combustion heat has a double role. The first one is to reduce flue gas temperature to meet turbine inlet temperature limit (max. 1400-1500K), and, the second role is to allow high-grade heat recovery to increase power recovered from the expanded nitrogen as explained.

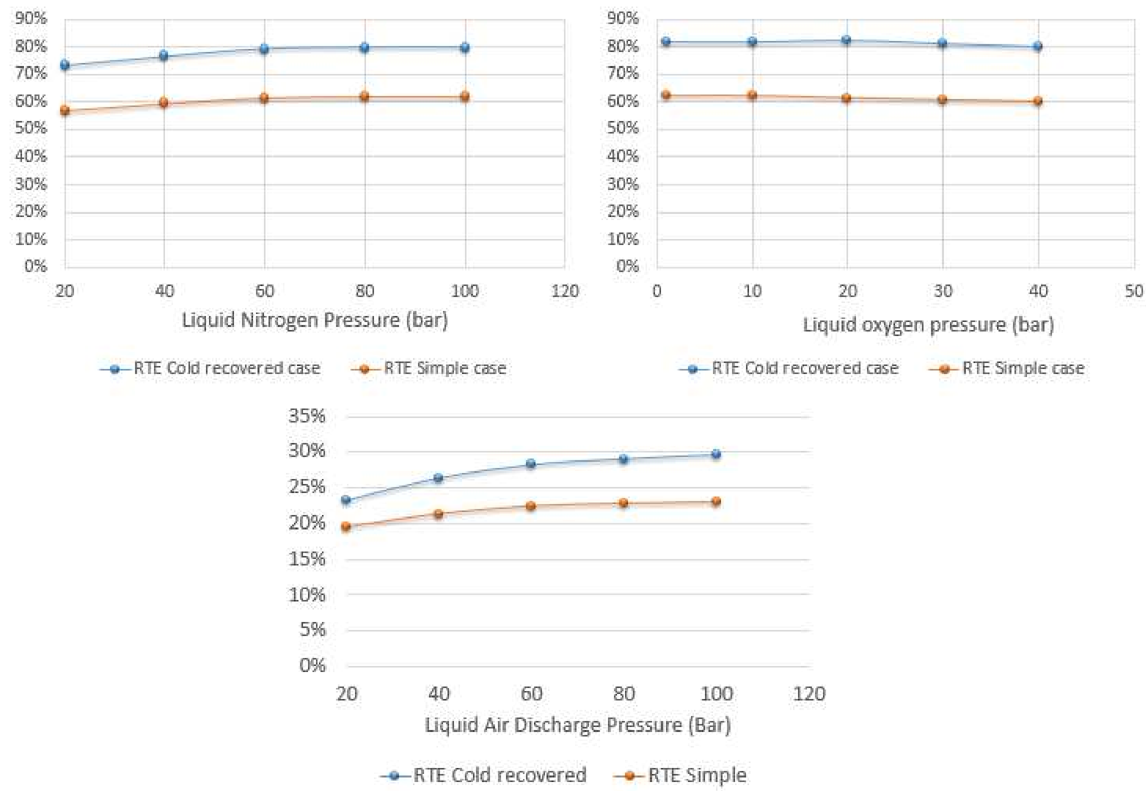

Figure 3.6.6: RTE variation depending on the pressure of pumping of liquid air, liquid oxygen and liquid nitrogen

RTE has an optimal value for the case of combustion and it is set at 80 bars for liquid nitrogen and at 35 bars for liquid oxygen. The very slight decrease of the RTE profile after 35 bar in oxygen pressure is due to the less effective heat transfer required in the combustion case. When the pressure of liquid oxygen increases, heat is less efficiently transferred from furnaces gases to the hot store. The heat released after the combustion serves for the nitrogen super-heating process and therefore electrical generation. At high pressures of oxygen, heat recovery from oxy-combustion valuable for the nitrogen circuit diminishes and consequently electrical generation from nitrogen expansion is reduced. For example, at 35 bar, heat recovered from the flue gases is 4400 kW instead, this value decreases to 4290 kW at the same mass flow.

80 bar seems to be the optimal discharge pressure since any further increase in pressure does not yield any benefit. Apart from the electrical energy recovery, cold energy is recovered in the evaporation steps before entering to the post-treatment process. Cold energy recovered from the evaporation of liquid nitrogen is more important than electrical energy recovered from its expansion into turbines at a certain pressure. It is a point where the cold energy recovered gets over the electrical energy recovered in terms of valuable energy.

In case study 2 and 3, an Air Separation Unit (ASU) should be included in between the liquefaction and the discharge sections. The consumption of the ASU is 30% of the liquefier consumption. Schematically it is not represented, but it is considered as a percentage in the calculation of global efficiency.

3.6.3.3 Waste heat

Total of works from expansion block in the super-heating based cycle is equal to 287kW. Super-heating reaches 243°C at its highest value in this configuration. On the contrary, works recovered from turbines in the expansion block of nitrogen are 418, 556 and 750kW, with a temperature of 996°C in super-heaters. The highest is Turbine I where the pressure drop is the most important. So the waste heat in super-heaters is very important factor in enhancing the electrical recovery. Recovery of the oxy-combustion heat has a double role. The first one is to reduce flue gas temperature to meet turbine inlet temperature limit (max. 1400-1500K), and, the second role is to allow high-grade heat recovery to increase power recovered from the expanded nitrogen as explained.

Heat recovered after the combustion process is a major parameter in improving the overall performance of the system. Using the same processes in terms of properties and geometric dimension, the rise of the combustion temperature from 2000K (2727°C) to 3000K (2727°C) as shown in Figure 3.6.7 increases the RTE from 68% to 80%. Therefore, the waste heat or the heat recovery in the discharge process is a key parameter in obtaining the highest performances.

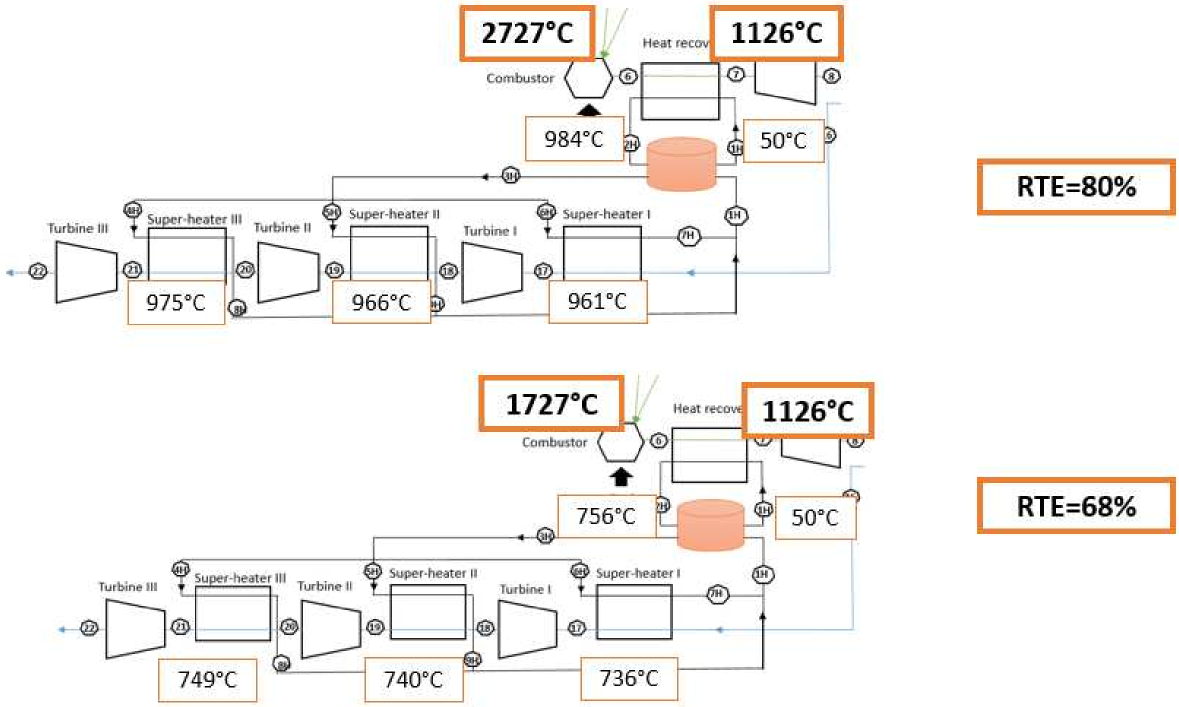

Figure 3.6.7: Heat recovery as a key factor for the RTE enhancement

3.6.3.4 Post – treatment

After evaporation, cold from nitrogen is used for the CO_2 freezing and water condensing in the combustion post treatment. Nitrogen enters the post treatment at a temperature of -128°C which is more than enough for freezing CO_2 at adequate mass fraction (1kg/s). This carbon capture method is one among multiple possibilities for energy use and reuse offered by cryogenic process (Damak et al., 2020).

Air-combustion with biogas requires less components comparing to oxy-fuel methods. From an economic point of view; it represents the most advantageous system regarding its significantly lower investment cost than those with oxy-biogas. Process of post-treatment of the combustion is not integrated in this case study because of the complexity that it might generate, in oxy-fuel combustion in particular where concentration in CO_2 and H_2O of furnace gases is higher than in air-firing method.

3.6.4 Exergy results:

The exergy analysis is a powerful tool to compare systems where electrical, thermal or fuel chemical energy sources are interacting, and to identify the source of irreversibilities. Exergy can be seen as the more valuable part of the energy, so evaluating the exergy production and exergy loss in each component is a method to estimate the energy efficiency of industrial processes. Based on this analysis, ways of enhancement can be proposed. In this study, exergy is defined as unit of energy per unit of mass (kJ/kg).

In this part of the results and discussion section, the exergy analysis will be performed only for the optimum combustion scenario. This part also concerns only the machinery, heat exchangers and thermal storage of the process. It does not include the exergy analysis related to the combustion process. This part of the analysis is detailed and discussed in 3.6.2. The exergy product is the amount of exergy left after subtracting all the exergy losses. It represents the exergy efficiency of the system.

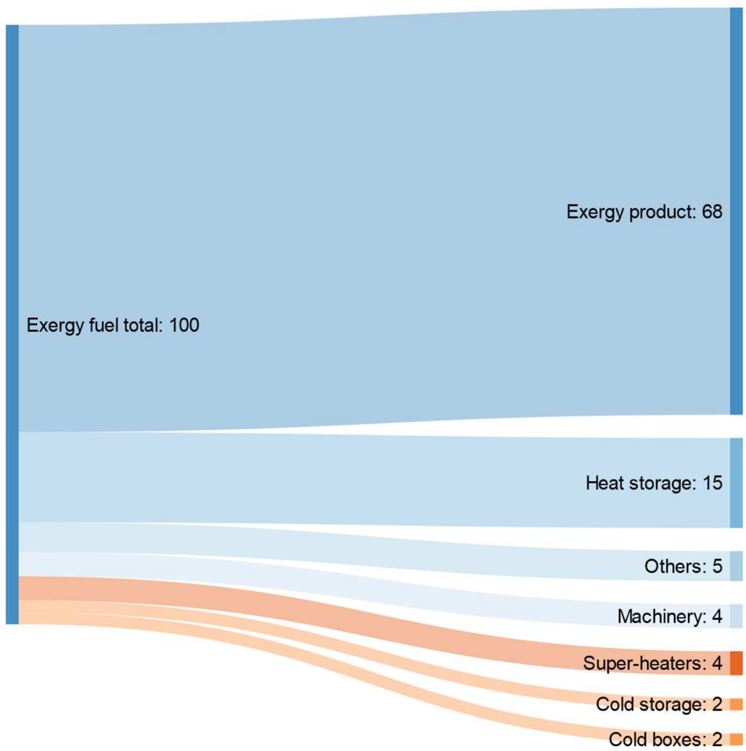

Figure 3.6.8: Exergy results of the LAES system: Liquefaction with cold recovery and combustion discharge units as *case study 2*

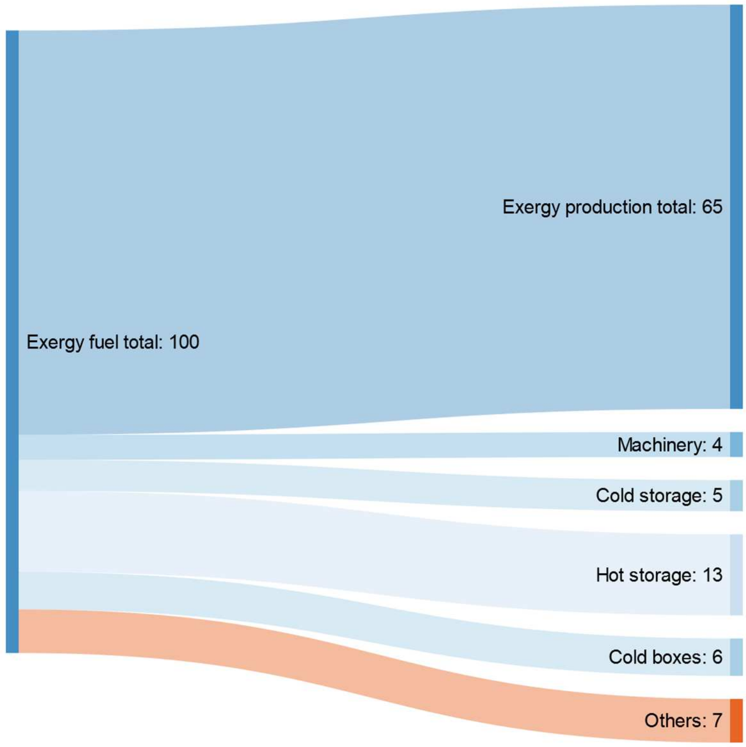

Figure 3.6.9: Exergy results of the LAES system: Liquefaction with cold recovery and combustion based discharge units as *case study 1*

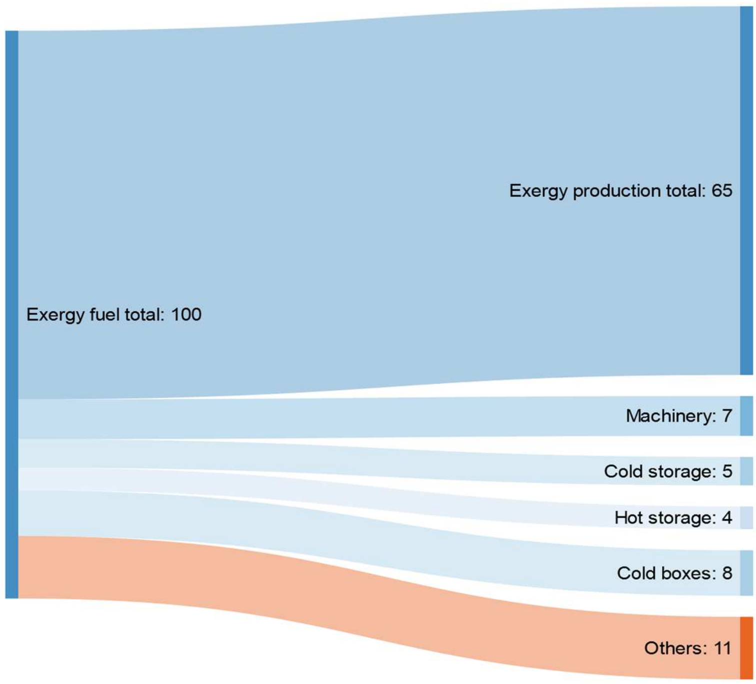

Figure 3.6.10: Exergy results of the LAES system: Liquefaction with cold recovery and super-heating based discharge units

Figure 3.6.8, Figure 3.6.9 and Figure 3.6.10 present an overview of the exergy production and exergy loss in each process. Components of similar processes are gathered in one family type of process, i.e, cold storage for example includes “evaporators” and “heat exchanger I” as defined in the recovery unit of *case study 2*. Looking at those figures, hot storages in *case study 1* and *2* represents the highest exergy losses. This is due to the important temperatures mismatch in the heat exchanger where the recovery takes place. Outlet combustion temperature is higher than 2000°C in every case and the fluid input is supposed to be at 50°C.

Concerning the losses due to machinery part, it is still not important even gathered comparing to the heat recovery section. For example, the most destructive component in this zone is the gas turbine in the oxy-biogas combustion, where calculation of the exergy loss gives 157 kJ/kg compared to the heat recovery loss which is about 1417 kJ/kg. This is also the reason why the combustor exergy calculation is not included in this section, the magnitude being considerably different. In the case of oxy-biogas combustion, the exergy fuel is estimated at 2 MJ/kg. Two types of exergy are contained in the biogas: chemical and physical exergy.

Despite this very important exergy loss in heat recovery, exergy efficiency remains quite reasonable thanks to the multiple energy recoveries (co and tri recoveries) and also to the tight components layout in terms of temperature matching in thermal processes and multi-stage compression/expansion.

One way to reduce the exergy destruction in the heat recovery section is to create a multi-stage heat exchanger process where temperature of the working fluid would gradually decrease throughout the process. But, this solution represents a more important costs investment. It is worth to mention also that the hot store dynamic study is not included in this work, so, the supposed 50°C as the fluid temperature outlet from the store might be changed to a higher value inducing the reduction of irreversibility.

Regarding the machinery part, it is difficult to take into consideration significant improvements, because design parameters and configuration are set considering almost ideal assumptions. Actually, these values are complex, depending on the rotation speed, the fluid physical properties and of turbomachinery design. These parameters should be experimentally characterized.

3.7 Concluding remarks and perspectives

CASE STUDY	RTE (%)	Exergy efficiency (%)	CO emission (g/kg of mixture)	GHG (g/kg of mixture)	NOx (g/kg of mixture)	Fossil fuel
Super-heating based cycle	37	65	0	0	0	No
Oxy-biogas combustion	81	68	54	≈0	0	No
Oxy- natural gas combustion	72	68	119	≈0	0	Yes
Air-biogas combustion	52	65	0	≈0	18.24	No

Table 3.7.1: Summary of major results of comparison between 3 combustion cases study and super-heating method

Adding combustion to the recovery part of a LAES energy storage system increases by a large amount the efficiency of the storage process. The RTE can reach values until 80%, which is a very significant improvement of the super-heating based process.

Table 3.7.1 summarizes all the thermodynamic and environmental performances for every configuration. RTEs values are obtained at optimum operating conditions. Oxy-biogas and oxy-natural gas fueled combustion have really close RTE values due to similar configurations. RTE of oxy-natural gas is a bit lower than the oxy-biogas one, since the electric potential of fuel is converted in the calculation of RTE equation in the denominator. LHV of natural gas is almost double times higher than LHV of biogas.

RTE of air-biogas combustion is relatively low because the system does not include as many components as in the case of oxy-fuel combustion system. It does not include a multi-stage expansion block, and therefore, the RTE calculated is reasonable regarding economic cost and technical operability (component number and configuration complexity).

RTE is only a theoretic calculated value of a storage system simulation. It includes the cold thermal energy recovered and the electrical one. However, the system should produce whether cold or electrical energy, but depending on the instant industrial needs, the system can switch easily by regulating the pumping pressure.

Combustion results showed that the dilution with CO_2 intended for the temperature control has a negative impact on the pollutant emissions as well as the exergy efficiency of combustion. This is due to the increase of GHG emission and CO_2 dissociation reaction. Fuel-to-Air ratio is preferable in limiting the outlet temperature value as well as the polluting emissions. In the air-biogas combustion process, a NOx treatment process could be integrated, and therefore, this system could represent the lowest emission amongst the other cases with the lowest investment cost.

Three major conclusions can be made from the energy analysis:

- Combustion process is obviously more efficient than the super-heating one. This is due to the chemical potential of added fuel. This is obtained at the price of a higher environmental impact which has to be taken into account
- High-grade cold recovered from evaporation is more valuable when added to the liquefier than when used in freezers and refrigerated warehouses. It greatly reduces the liquefier consumption and thus increases the RTE;
- Pressure of pumping as well as waste heat in super-heaters is a key factor in determining the optimal RTE. It should be chosen regarding the system theoretical performance as well as the practical operability.

Three stages compression instead of two could be explored to further diminish the energy consumption induced by the Claude cycle. Compression ratio should not exceed 4,5 to allow the lowest compression work. The air separation unit could also represent an energy consuming process and therefore, in future calculations, this energy cost should be included.

Valorisation of the various energies provided by the system (electrical, thermal cold/hot energy) as well as sub-products (oxygen, nitrogen, carbon dioxide, etc.) of the LAES depends on the industrial site, i.e; the liquid oxygen/nitrogen could be also of some use apart from the LAES system. Heat from the combustion has also a high value, but it is not fully exploited in the present work. Depending on the industrial site where the LAES is implemented, it could be of a much greater value.

A Life Cycle Analysis should be carried out to have a better idea of the environmental impact due to combustion. An economic analysis is also required to evaluate the profitability of such a technology. All these criteria should be included in a decision making process to develop a more global analysis.

3.8 Conclusion of the energy aspect chapter

Calculations have shown that LAES efficiencies are obviously higher for systems including energy recovery system by combustion than those with only evaporating and super-heating. This is due to the chemical potential of added fuel which is whether biogas or natural gas in the suggested system. Oxy-biogas fueled combustion has great potential from the energy and emissions performance point of view with the highest round trip efficiency among other studied systems and lowest CO emission. However, deeper environmental impact assessment is needed to evaluate better the environmental performance of different LAES configurations.

CHAPTER 4

ENVIRONMENTAL ASPECT

Introduction to the environmental aspect of LAES

The LAES environmental analysis paper

Conclusion and transition towards next chapter

4.1 Introduction to the environmental performance analysis:

After the detailed investigation on the thermodynamic performance and a short insight of the flue gas composition, a deeper consideration of the ecological aspect is needed in order to better quantify pollutants of combustion and to find ways to prevent possible damage. For this reason, a Life Cycle Assessment method is carried out within this paper. This approach consists in 4 phases: goal and scope definition, inventory analysis of the life cycle, impact assessment and interpretation and perspectives of enhancement (ISO14040, 2006). LCA method is herein used for evaluation of the operational phase and is not extended to the other phases (material extraction, construction and destruction/recycling processes). Three LAES configurations with a focus on the discharge unit are evaluated: oxy-biogas-fueled combustion, oxy-natural gas-fueled combustion and air-biogas fueled combustion. The input/output data are obtained from thermodynamic analysis (previous chapter). Figure 4.1.1 summarizes the above discussion in a schematic diagram.

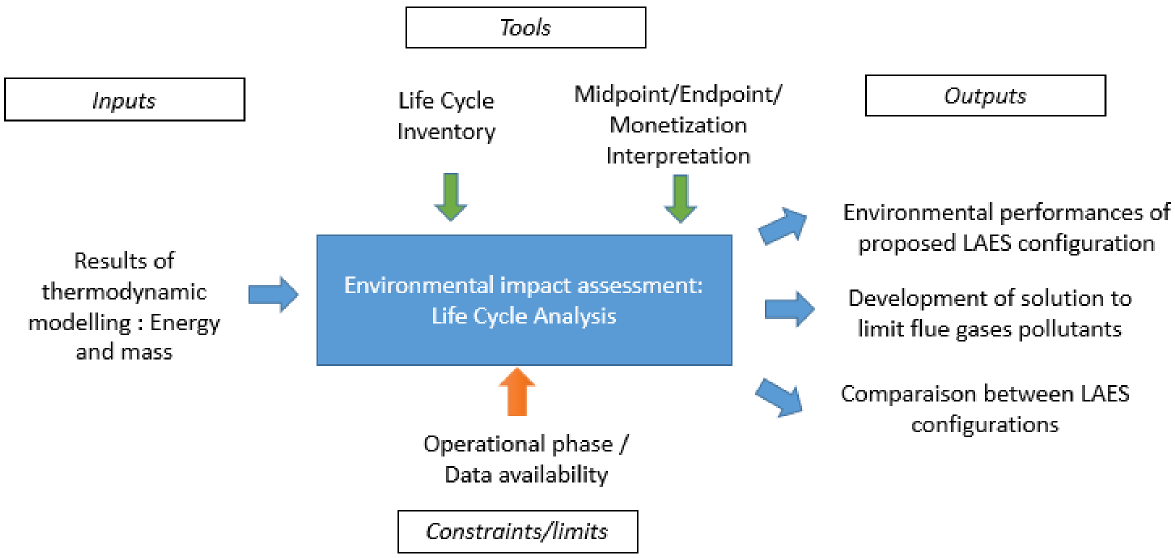

Figure 4.1.1: Schematic representation of environmental performance paper; a Life cycle approach

4.2 LAES environmental performance paper: Environmental performance analysis of Liquid Air Energy Storage (LAES) innovative systems: A life cycle approach

The environmental performance article is intended for an upcoming conference

Environmental performance analysis of Liquid Air Energy Storage (LAES) innovative systems: A life cycle approach

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Abstract

The estimated share of renewable energies in global electricity generation was more than 26% by the end of 2018 (21, 2019) comparing to 7% in 2016 (REN21, 2016). Nevertheless, power generation gets locally affected by this strongly intermittent renewable energy sources depending on weather patterns and day/night cycle. To limit this phenomena, Large-scale Energy Storage Systems (EES), are widely considered as a solution to the rapid transition of electricity generation towards green and sustainable electrical grids.

Liquid Air Energy Storage (LAES) which presents the lowest carbon footprint among other deployed EES could become a sustainable and environmental friendly technology. An LAES process consists in two parts: liquefaction unit (charging: cryogenic energy of air was stored) and discharging unit (energy recovery). In the present work, a newly developed oxy-fuel combustion method is considered and compared, to the conventional air-fueled combustion process in terms of environmental impacts using LCA.

The results show that the oxy-biogas combustion might be the cleanest and even beneficial for the environment comparing to other studied configurations. Air-biogas and oxy-natural combustions have high impacts on human health by nitrous oxide, carbon monoxide and Greenhouse gas emission besides the use of fossil fuel.

Keywords: Liquid Air Energy Storage; Life Cycle Analysis; Oxy-fuel combustion; environmental performance

4.3 Introduction

The share of renewable energies in global electricity generation continues to increase rapidly: more than 26% by the end of 2018 (21, 2019) comparing to 7% in 2016 (REN21, 2016). Consequently, there is more and more impact of the intermittent nature of renewable energy sources on the electricity production. Large-scale Energy Storage Systems (EES) are widely considered as a solution to the rapid transition of electricity generation towards green and sustainable electrical grids.

EES is not a single technology, but rather refers to a portfolio of technologies. EES that could have significant contribution to the grid balancing are Pumped Hydro Storage (PHS), Compressed Air Energy System (CAES) and flyweels (IRENA, 2017). At the present moment, PHS is the most deployed EES and represented 96 % (mid-2017) of worldwide installed electrical storage capacity, followed by flywheels and Compressed Air Energy Storage technologies. Conventional PHS systems use two water reservoirs at different elevations. CAES technology requires underground storage cavities such as caverns or abandoned mines; it represents the most powerful and less expensive storage system. Environmental impact of these technologies is non negligible regarding the geographical/geological constraints. Moreover, combustion process needs to be considered in the case of the CAES. In the global context of sustainable energy transition, the environmental impact has become an important factor for the technology choice, which has led to an increasing research effort on storage technologies with lower environmental impact.

Air has been recently regarded as a Cryogenic Energy Storage (CES) medium, whereby air is liquefied at around -195 °C and stored in insulated tanks (Antonelli et al., 2017). Liquid Air Energy Storage (LAES) was described as sustainable and environmental friendly technology. LAES could be a potential candidate for this energy transition regarding the fact that it has the lowest carbon footprint among other deployed EES (Damak et al., 2020). The principle of this storage is divided onto two parts: liquefaction unit (charging) and discharging unit, which could have different configurations. The surplus of renewable sources generation is fed to an air liquefaction unit, while the liquid air could be pumped, heated and expanded into turbines to generate power when electrical energy is needed (Brett and Barnett, 2014).

In recent studies (Ameel et al., 2013; Guizzi et al., 2015; Hamdy et al., 2017; Sciacovelli et al., 2017), architectures studied of LAES are almost focused on Solvay or Claude liquefier cycle with the integration of Cryoturbine for charging phase and the super-heating process for the discharging phase. Nevertheless, in some other cases, the discharging part could include a combustion process followed by a gas turbine in order to enhance considerably the round trip efficiency of the storage system. However, the integration of the combustion is rarely considered for the LAES due to suspected environmental impact. In fact, combustion could be the main contributor to the environmental damages due to the rejection of pollutants contained in the flue gases into the atmosphere and the use of fossil energy resources. Consequently, the objective of the current study is to evaluate the environmental performance of the LAES with three combustion methods.

In order to assess the environmental impacts that are associated with EES processes, Life Cycle Assessment (LCA) can be applied (ISO14040, 2006). However, few LCA works have been dedicated to EES technologies. Abdon (Abdon et al., 2017) compared PHS, CAES, batteries and Power to gas to Power (gas electrolysis) to grid electricity in a techno-economic analysis including an environmental analysis using LCA. (Abdon et al., 2017) distinguished short, medium and long-term storage duration and considered an optimistic, pessimistic and expected case scenario depending on running parameters and round trip efficiency. Conclusion of this work is that most storage technologies can contribute to a reduction of overall system GHG emissions, if intermittent renewable electricity is stored and subsequently replaces conventional grid supply produced by fossil fuel. From results of LCA, Abdon (Abdon et al., 2017) discussed the contribution of the gravel and cement in the case of PHS contributes to about 60% of the GHG emissions and that of metals if of 23%. For the case of CAES, turbomachinery contributes more than 99% to the life cycle GHG emission. Bouman (Bouman et al., 2016) studied the life cycle environmental impacts associated with two types of CAES systems, conventional CAES and adiabatic CAES, which are coupled to an offshore wind power plant as well as the standalone wind farm. The authors concluded that for the CAES system the main contributors for most of the impact categories are the actual wind power generation and the natural gas combustion (95%). Plant construction contributes of 1-4% for most impact categories, except for land occupation to which construction contributes by 22%. Impacts related to machinery and equipment, and components transport are negligible in this case, on the contrary of the conclusion reached by Abdon (Abdon et al., 2017). An explanation could be the differences in the data inventory and system boundaries in those studies. Methodology employed for impact assessment is also different from one study to the other.

The present work is the first of its kind to study the environmental performance of the LAES through its operational life stage. The use of biogas as green fuel is compared to the use of natural gas. A post-treatment combustion process is also included in the oxy-fueled combustion cases to assess its effect. The super-heating based system is not considered in this comparison regarding the fact that the process does not include any component that could potentially generate harmful effect on the environment through its operational life stage. The environmental performance of three discharge units configurations for LAES is evaluated in this work: oxy-biogas-fueled combustion, oxy-natural gas-fueled combustion and air-biogas fueled combustion. The SimaPro 8.0.5.13 software was used for this analysis. Three different methods are used for impact assessment: ReCiPe Midpoint (E) V1.12, ReCiPe Endpoint (E) V1.12 and Ecocosts 2017 V1.5.

4.4 Methodology

4.4.1 Brief description of technology

This section presents the three case studies of discharge cycles; they are coupled with a liquefaction unit which is not shown in the following description.

The *case study 1*, as shown in Figure 4.4.1, uses air-biogas combustion. After the evaporation and cold recovery, the liquid air passes through a combustor where it gets mixed with the biogas as fuel and goes into a gas turbine to get expanded and to generate electricity.

Air combustion is replaced by oxy-combustion in *case studies 2* and *3* as shown in Figure 4.4.2; the system includes an air separation unit (not represented in this figure) after liquefaction. Initially, liquid oxygen and liquid nitrogen are stored in two different tanks. Then, both liquids go through an evaporator and heaters to get their cold energy stored in storage devices before entering to the expansion block. In the oxygen circuit, oxygen goes in the burner (combustor) and flue gases are expanded in gas turbine, it is whether a biogas-fueled (*case study 2*) or natural gas-fueled (*case study 3*) combustion process. Cold from the evaporation of liquid nitrogen is captured and stored for later use (additional liquefaction cold storage or industrial refrigeration requirements). Before entering to the multi-stage expansion block, nitrogen is used in the post-treatment process of the oxy-fuel combustion. Cold from nitrogen is still available to freeze the carbon dioxide and condense water, two major components of the flue gases.

Furnace gases can be treated in both *case study 2* and *case study 3*. In oxy-fuel combustion method, density of carbon dioxide in the flue gases is higher than in air-firing and therefore post-treatment is less complex than in the basic air-combustion process. In the *case study 1* of air-biogas combustion, post-treatment process is not included. Oxy-fuel combustion method results in high combustion temperature. One solution for this issue is to control the fuel-to-air ratio and the diluent rate. Diluent chosen in this study is CO_2 which is captured and recirculated from the post-treatment process or issued from an external source.

In in this work, air is used as hot/cold energy storage and heat transfer fluid.

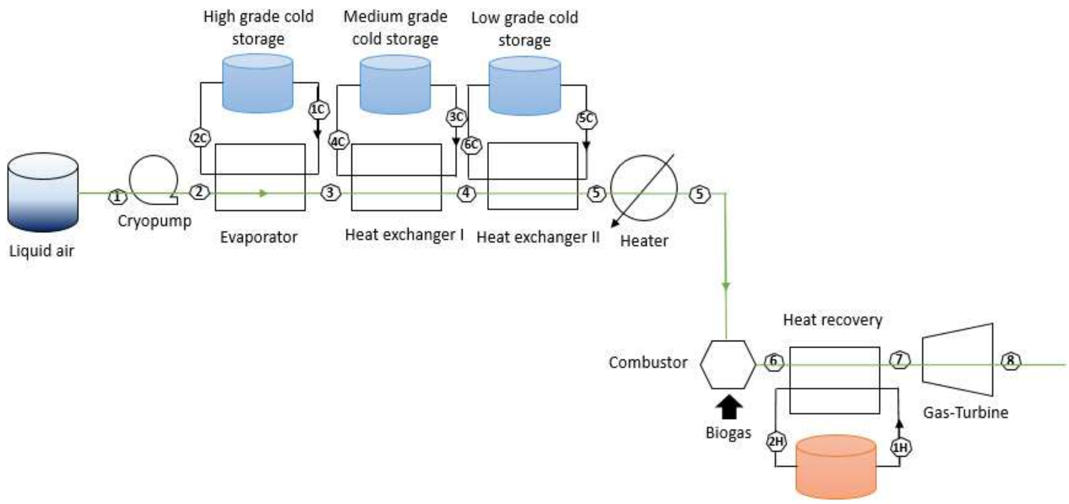

Figure 4.4.1: Process Flow Diagram of recovery cycle with conventional biogas fueled combustion

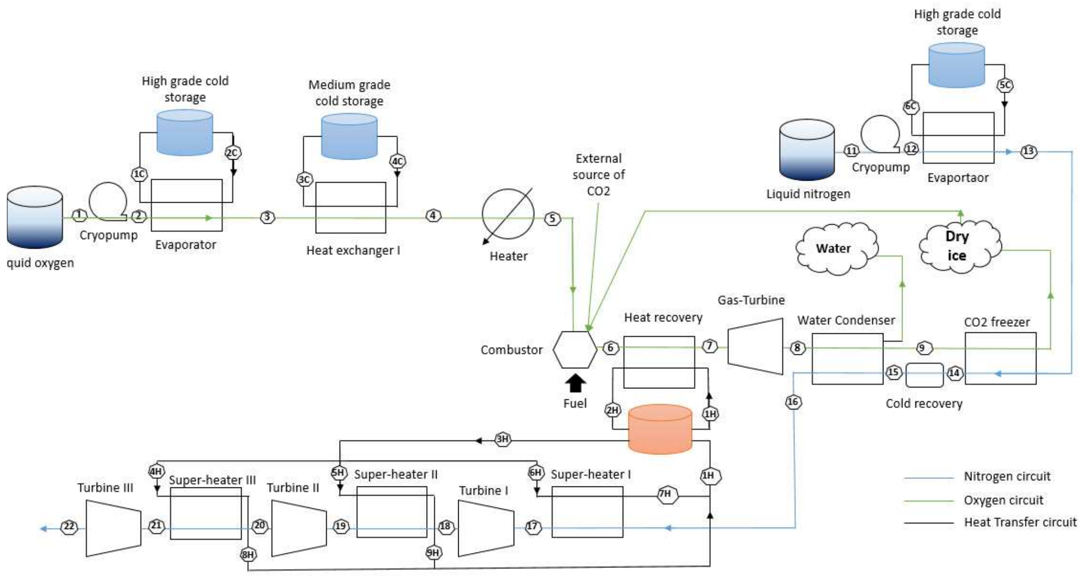

Figure 4.4.2: Process Flow Diagram of recovery cycle with oxy-fuel combustion

4.4.2 Life Cycle assessment methodology

In order to assess the environmental impact of electricity generation from different considered forms of LAES, an LCA approach was selected. According to ISO 14040 (ISO14040, 2006), LCA approach consists of 4 principal phases: goal and scope definition, inventory analysis of the life cycle, impact assessment and interpretation and axis of enhancement. The ISO 14040 defines LCA as the ‘‘compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle’’.

4.4.3 Scope definition, system boundaries and inventory

The current work focuses on the environmental impact of the recovery of electricity (discharging part) in LAES processes. The charging part (liquefier) is the same for three considered configurations. LCA concerns only the standalone LAES system and not the one combined with renewable sources. Thus, the environmental impact related to the use of renewable energy source is beyond the scope of the study. The Air Separation Unit (oxy-combustion cases) is also not considered in this analysis.

In the present study, LCA is applied for the operational phase in order to identify the impact of the choice of combustion method on the environmental performance of the three configurations. The other phases of a product system life cycle (extraction of raw materials and fabrication of the system, maintenance, end-life or recycling) are not considered.

For comparison purpose, the functional unit is defined as 1 kWh delivered from the storages to which all the impacts are referred.

The inventory analysis is a quantitative description of all materials and energy flows across the system boundary either into or out of the system itself (ISO14040, 2006). Input/output data inventory is obtained from the thermodynamic modeling work which was done using NIST REFPROP 9.1 database (Lemmon, 2018), for the physical property calculation at each state point of the circuit. Besides, a GRIMECH 3.0 mechanism was adopted as the reaction scheme to determine the masses of all species interacting in the combustion reaction including the polluting ones. The system boundaries and the input and output data of for the inventory analysis is shown in Figure 4.4.3 and data is given in appendix II.

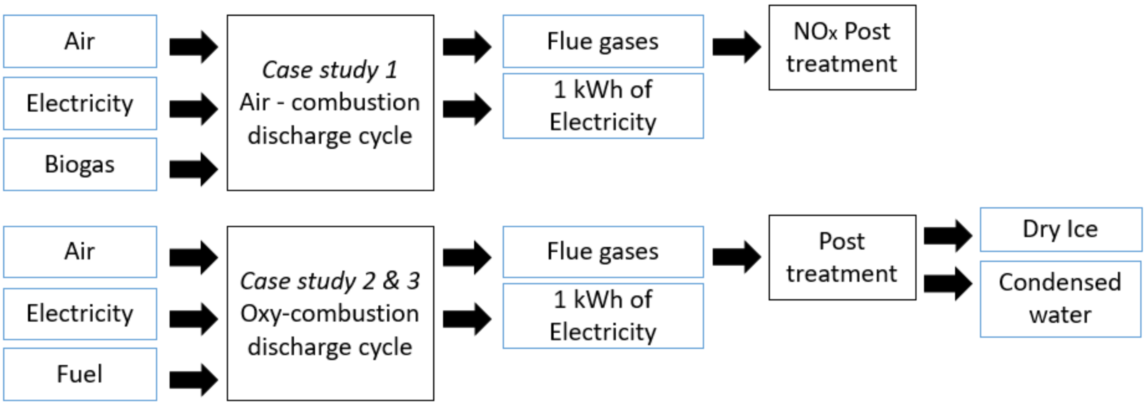

Figure 4.4.3: Schematic representation of the LAES discharge cases for the LCA inventory

In all cases, for the air liquefaction (charging unit), air and electricity are required. Fuel is whether biogas or natural gas in the oxy-combustion case. To assess the effect of the combustion cryogenic post-treatment in the oxy-fuel combustion, simulations of the process with and without post-treatment are considered. For the air-combustion case, 2 options, with and without NO_x post-treatment, were also tested.

The processes from ELCD and ecoinvent v3 databases used in this study are presented in the following table:

Process	Name of the process in the database	Note
Electricity	Electricity mix, AC, consumption mix, at consumer, 1kV - 60kV FR S	French electricity consumption mix provided by multiple energy carriers
Biogas	Biogas, from grass {RoW}| biogas production from grass | Alloc Def, S	process "grass to digestion" describing a bio-refinery (grass-refinery)
Fuel (Natural gas)	Natural gas, high pressure {FR}| market for | Alloc Def, S	energy requirements and the emissions of the high pressure distribution network in France

Table 4.4.1: Process used in current LCA (ELCD and ecoinvent v3 databases)

4.4.4 Impact assessment methods

Life cycle impact assessment examines the mass and energy inventory input and output data for a product system, to interpret these data and to identify their possible environmental impact (ISO14040, 2006). In this study, the impact assessment for the operational phase of the life cycle of 3 LAES configurations was performed using different methods: ReCiPe Midpoint (E) V1.12, ReCiPe Endpoint (E) V1.12 and Ecocosts 2017 V1.5. The aim of using three methods is to have different points of view of the cause-effect impact chain: from detailed to global interpretation.

Midpoint method evaluates the impact in various detailed 'midpoint' categories: ozone depletion; freshwater eutrophication; agricultural land occupation... From a global point of view, Endpoint method transforms the long list of midpoint indicators into a limited number of "endpoint" indicators: each of the "midpoint" categories is weighted and gathered with similar impacts to form a family of "endpoint" impact. Three indicators are considered for ReCiPe Endpoint (E) V1.12: human health, ecosystems and resources. A particular attention to the Human Health unit "DALY" (Disability-Adjusted Life Years) which is defined as "the years lost to premature death and expressing the reduced quality of life due to illness in years as well" (Golsteijn, 2016).

Finally, the eco-cost monetization method represents a way to convert all the ecological impacts of a system product (taking into account carbon costs, water usage, ecotoxicity and several other environmental values) into costs (Limited, 2020). As the environmental performance can now be represented by a single value (in euros), it becomes more and more a 'privileged' method for industrials.

4.5 Results and discussion

The final stage of LCA is the interpretation phase, where the inventory analysis and impact assessment results are summarized and discussed.

Figure 4.5.1 presented the environmental impacts for operating phase of 3 LAES configurations: air-biogas combustion, oxy-biogas combustion and oxy-natural gas combustion using ReCiPe Midpoint (E) V1.12. The post-treatment (dry ice, condensed water and NOx) are not considered in this simulation.

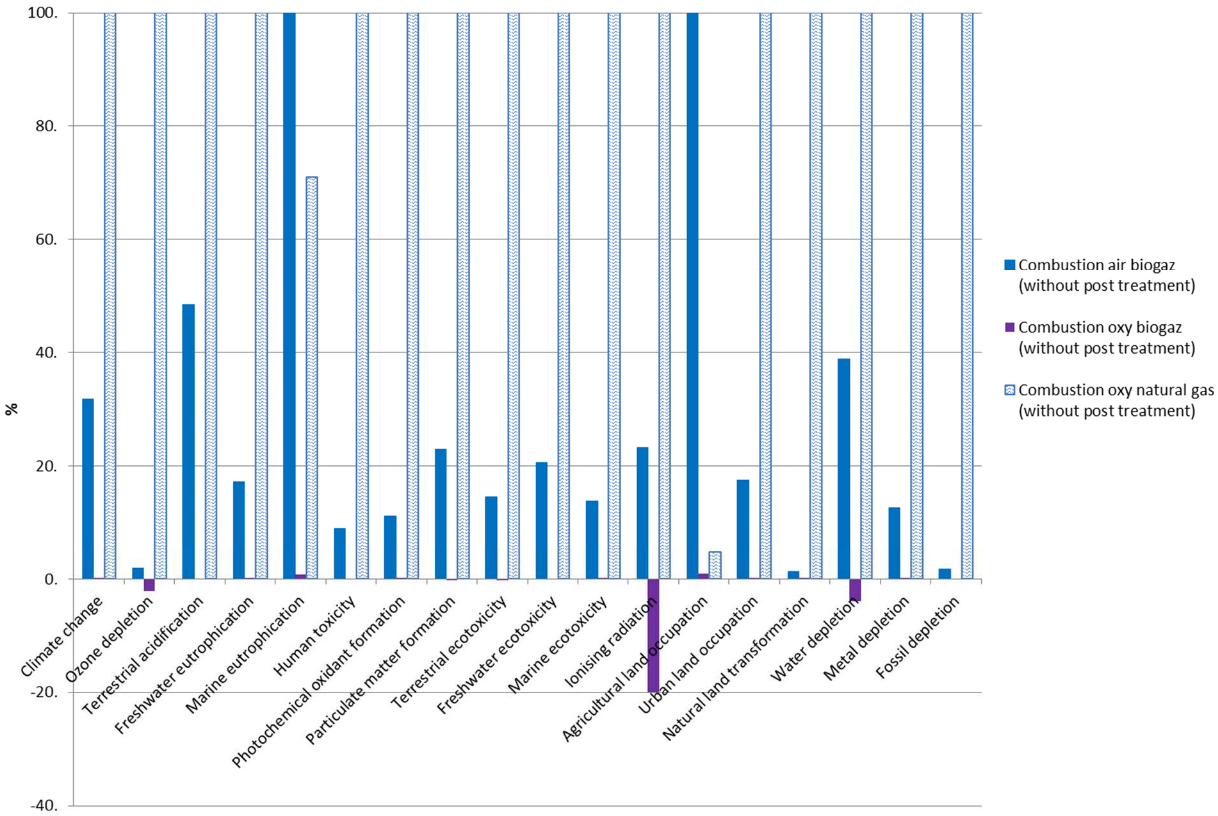

Figure 4.5.1: Comparison of environmental impacts of three LAES processes (operational phase) considering Midpoint ReCiPe method

Various ‘midpoint’ impact categories from the 3 processes are compared among them, the highest value is associated with 100 % and the two other values are calculated according to this value. In general, the oxy natural gas combustion (dotted bars) shows the highest impact, followed by air biogas combustion (blue bars). The best performance (lowest impacts) is obtained by oxy biogas combustion (purple bars) Negative contributions of the oxy-biogas combustion can be noted to some impact categories (ozone depletion, ionizing radiation and water depletion). A negative impact means a possible positive and beneficial effect on the considered impact. For the oxy biogas process, the negative impact is due to the fact that the quantity of generated electricity (1 kWh) is more important than the consumed one (0.15 kWh, see appendix II).

Although the oxy natural gas combustion also has the advantage of generating more electricity than its consumption, it has significant impact on many categories due to the use of natural gas as fossil fuel and related extraction process.

For the air-biogas combustion, its impacts are less important than the oxy-natural gas case thanks to the use of biogas. Its impacts are produced mainly by its electricity consumption (1.36 kWh) which is more important than the output quantity (1 kWh).

The ReCiPe Endpoint method has been used to transform the long list of the impact categories of "midpoint" into a limited number of indicators: human health, ecosystems and resources. The Figure 4.5.2 presents the Endpoint results obtained for the three case studies.

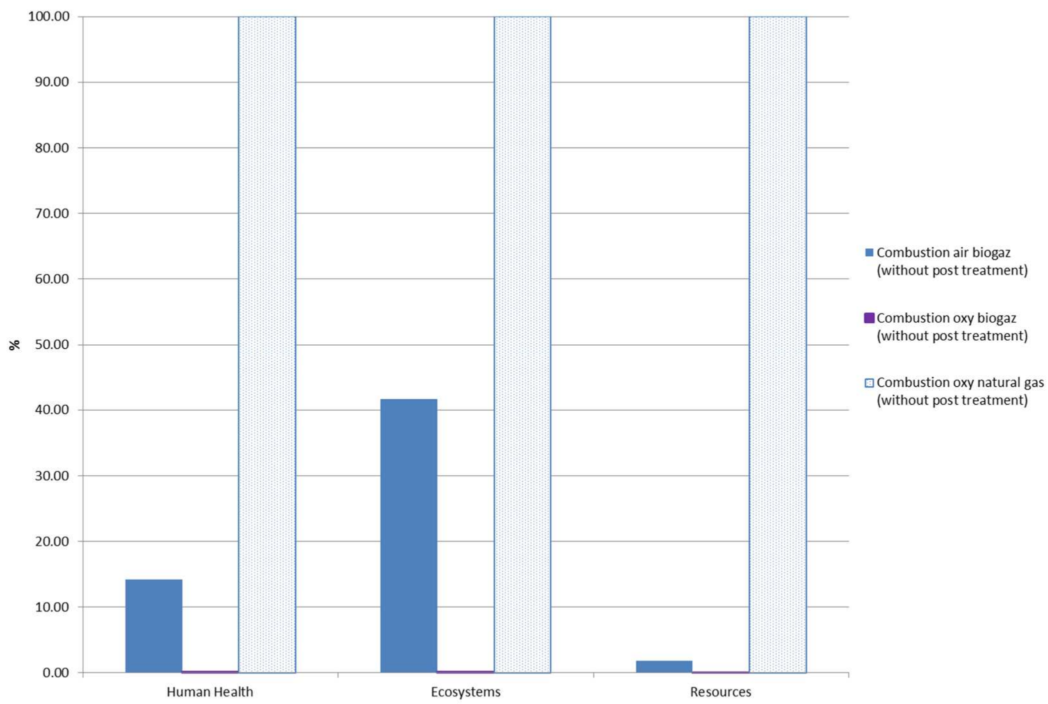

Figure 4.5.2: Comparison of environmental impacts of three LAES processes (with and without combustion post-treatment) considering Endpoint ReCiPe method

In accordance with results obtained by "midpoint" method, the oxy – biogas combustion case has the highest environmental performance with little impact, followed by the air biogas combustion. The oxy natural gas combustion presents the greatest environmental impacts in the 3 categories.

In addition, the EcoCost method was applied to the three studied configurations. It represents a tool to assess the economic value of the environmental impact of these processes by evaluating the prevention cost to reach the "no level effect" regarding the norm of sustainability. 4 categories were considered: climate change, human health, ecosystems and resource depletion as shown in Table 4.5.; climate change impact reflects, somehow the carbon taxes as it may be represented by the GHG including CO_2 emission.

Damage category	Unit	Combustion-air-biogas	Combustion-oxy-biogaz	Combustion-oxy-natural gas
climate change	euro	0.482	0.000	2.050
human health	euro	0.057	0.002	0.628
ecosystems	euro	0.397	0.000	1.061
resource depletion	euro	0.043	0.000	0.245

Table 4.5.2: Comparison of Ecocost data for three LAES processes for the recovery of 1kWh of electrical energy

Although insignificant values of the damage impact can be observed in **Table 4.5.**. The recovery of 1kWh of electricity represents the highest environmental cost in case of oxy-natural combustion, followed by the air biogas case while little cost is associated with oxy biogas combustion.

Finally, the integration of the post-treatment was considered: NOx for air-biogas combustion process and generation of dry ice and condensed water for oxy-biogas and oxy-natural gas combustion processes. For each configuration, the process impacts obtained with and without post treatment are compared. For the oxy combustion processes, the integration of the post treatment allows reducing the climate change impact due to CO_2 capture in dry ice. However the NOx and condensed water treatments have shown no impacts on the results.

4.6 Conclusion & perspectives:

In this study, a LCA was conducted on novel LAES systems. The environmental performance of three types of combustion based discharge cycle was discussed. One of the configurations considers a “clean” combustion process: oxy-fuel as oxidizer and biogas as green fuel. The other processes are: air-biogas and oxy-natural gas fueled combustion.

Main results of this work are:

- The oxy-biogas combustion is clean and might present beneficial impact for the environment
- The oxy-natural gas combustion has a lower environmental performance (higher impacts) than the oxy-biogas due to the use of fossil fuel.
- The air-biogas combustion presents the second lowest environmental performance despite the use of biogas as renewable energy source. On the contrary of the oxy-fuel combustion, the conventional air-combustion demands more electricity consumption

and leads to the formation of nitric oxides and higher GHG emissions which are harmful to the environment.

- The post-treatment of the CO_2 as dry ice added a beneficial value on climate change.

The present LCA has limited interpretation regarding the limits related to the system boundaries and data inventory: only the operational phase was considered.

As perspectives of this work, next steps could be a more complete LCA in which more phases of the process's Life Cycle are investigated: raw material, construction, maintenance. destruction or recycling. The turbomachinery used is non-negligible and is issued from heavy construction processing so it could generate high pollution and requires important amount of raw material.

In this study, electricity input is considered from the electrical grid. In future simulation, the electricity generated from renewable sources should be integrated to assess the potential of LAES development as EES facility.

4.7 Conclusion of the environmental aspect chapter

Oxy-fuel combustion is more likely to be the best candidate as a form of LAES in terms of energy efficiency and environmental impact. However, in terms of configuration complexity. it contains the double of components number than that of the super-heating or the air-biogas configuration. The Air Seperation Unit, the combustion chamber, turbines, thermal stores and heat exchangers are additional features with heavy investment. Consequently, the final chapter of the thesis proposes a preliminary techno - economic analysis of the LAES system.

CHAPTER 5

TECHNO-ECONOMIC ASPECT

Introduction to the techno-economic aspect of LAES

The LAES techno-economic paper

5.1 Introduction to the techno-economic analysis:

The objective of this chapter is to evaluate energy optimization control and economic benefit from the integration of LAES in an industrial site with needs of refrigeration load and electrical energy. As a preliminary work, a real case study is considered: CryoHub's partner "Frigologix", which is the demonstration site for CryoHub project, equipped with an important area of PV power panels (1 MW). For these first simulations, the LAES is settled under super-heating configuration and coupled to a refrigerated warehouse supplied by the PV power plant. In this work, an optimization is performed based on minimizing the electricity tariff consumption, with a range of equations and constraints to each component. Afterwards, as a key factor determining the optimum energy scenario, the solar irradiation is also studied by comparing a typical day of January and another day of July for the considered location. Then, optimum energy scenarios are analysed under significantly different solar irradiations to further investigate the profitability of LAES implemented in different climates.

Thereafter, results of scenarios' analysis will lead to investigate economic feasibility of the storage system. Techno-economic assessment of the LAES is carried out by a sensitivity analysis in which the annual savings achieved are evaluated. Four parameters are varied: energy efficiency of the LAES, PV plant parameters, a ratio of discharge to charge power (D/C) and the geographical location. Following the same logic, a second sensitivity analysis is performed to assess the variation of payback time for the reference system taking into account the electricity tariff variation. the capital cost, the annual economic savings and the effect of system maturity.

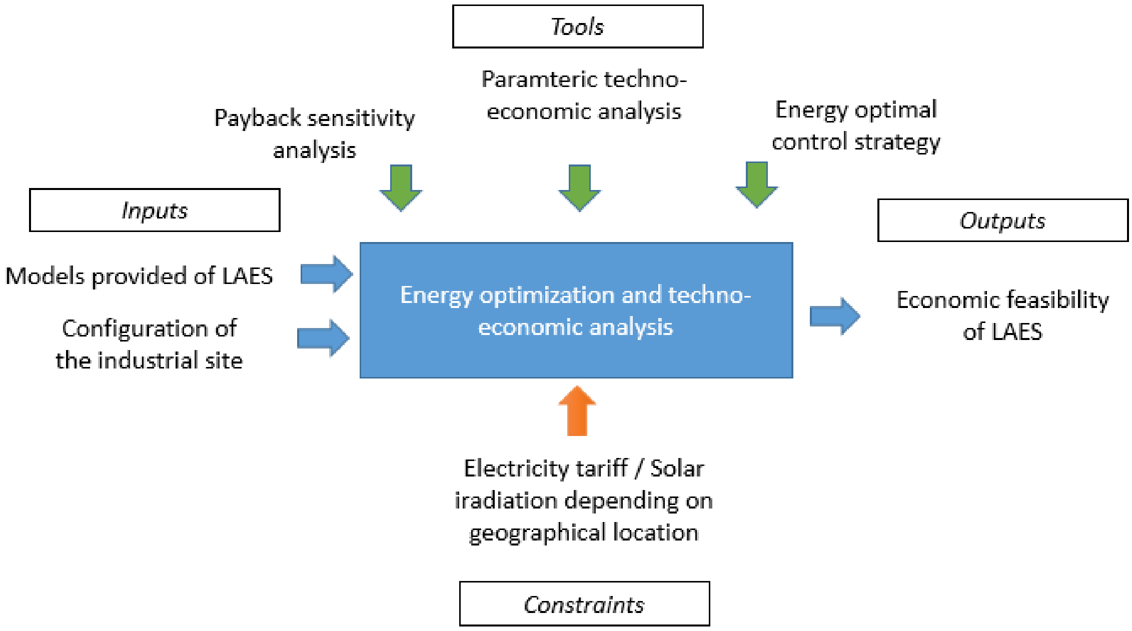

Figure 5.1.1: Schematic representation techno-economic analysis

5.2 The LAES techno-economic paper: Optimization of charge/discharge scenarios and economic analysis of a Liquid Air Energy Storage system used in combination with a photovoltaic power source and a cold storage warehouse

This paper has been subject to a presentation in the 25th edition of ICR: International Congress of Refrigeration in Montréal.

Optimization of charge/discharge scenarios and economic analysis of a Liquid Air Energy Storage system used in combination with a photovoltaic power source and a cold storage warehouse

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ABSTRACT

Intermittency of renewable energy generation and electricity tariff variation make necessary the analysis and optimization of different scenarios of charge/discharge cycle timing and duration of a Liquid Air Energy Storage (LAES) and the economics related to each case.

Solar irradiation and PhotoVoltaic (PV) power plant size, electricity prices, on-site electricity demand throughout the day/month/season and year are key factors here for the scenarios optimization in terms of cost of electrical energy consumed from the grid. These factors are also useful to determine the maximum allowed investment of the LAES and the payback time according to each case scenario.

Self-sufficiency and positive economics of the LAES combined to cold warehouse are reached when PV power plant surface and solar irradiation are high enough. Therefore, there are optimal PV dimensions depending on the round trip efficiency of the LAES, the power capacity discharge/charge ratio of the system and the geographic location of the site. Main results suggest that LAES can only be profitable when electricity from grid is expensive.

Keywords: Cryogenic storage, LAES, Optimization of energy scenarios, economical analysis

5.3 Introduction

Recently, cryogenic energy storage and more particularly Liquid Air Energy Storage LAES has drawn the attention of both academic and industry due to environmentally friendly grid-scale technology. LAES is adapted to large scale (grid scale) application, while refrigerant cycle system or ice storage system are limited to small storage size. Besides, the temperature reached in case of LAES is very low (-196°C) which makes the system very different from the refrigerant cyle system or ice storage system in terms of field of application. The idea of cryogenic energy storage was firstly proposed by E.M Smith, at university of New Castle in 1977 (Smith, 1977) using the energy of liquid air as the cryogenic energy. A particular configuration of LAES systems is to use excess cold energy from the electricity recovery process for food factory or refrigerated warehouse. This improves the profitability of the whole process. On one hand, this helps to reduce the electrical consumption of the warehouse refrigeration unit while maintaining adequate temperatures inside the warehouse. On the other hand, direct expansion of liquefied cryogen at high pressures (in this case liquid air) through multi-stage turbines allows electrical energy recovery.

This work investigates the economics related to this system based on the study of an Optimal Control (OC) strategy for charging/discharging/generation of cold enegy in the warehouse depending on the electricity tariff and the geographical location. Once the optimal strategy defined, a techno-economic study corresponding to the operating schedule can be conducted to evaluate the economic performance of the system. The OC strategy of this research work is developed for a cost function that aims to minimize the cost of electricity purchased from the grid and maximize the usage of the LAES. Thereafter, results of scenarios' analysis will lead to investigate economic feasibility of the storage system. The annual savings achieved, or losses generated are calculated to determine the investment threshold allowed for the LAES system as well as the CapEx and the payback period of the reference case.

In the current work, the case study is a refrigerated warehouse supplied by a PV power plant located in Belgium. The objective of the study is, therefore to evaluate energy optimization control and economic benefit from the integration of LAES in this site.

5.4 Energy management strategies methodology and simulations

This section describes the dynamic energy model of the whole system on-site for the OC strategy. First, the layout model is analyzed and the LAES storage system is described. Second, methodology of the OC strategy and economics is detailed. Finally, results of simulation are given in the final parts.

5.4.1 Schematic model layout

The proposed system analyzed in this work is composed of 4 sub-models: the power utility grid, PV modules, LAES and the warehouse with the power flow shown in Figure 5.4.1. The refrigeration load of the warehouse is mainly covered by the PV power plant. When energy delivered by the PV plant is in excess, surplus of generated energy is used for air liquefaction unit. When PV plant no longer produces electricity, air is being expanded through the turbine-generator set to meet the refrigeration load. The power grid is then used only in the case where neither the PV nor the storage system are able to supply the warehouse demand. The study is only focused on the excess renewable generation storing approach and not storing it from off-peak electricity grid. No resale to the grid is considered when the PV power plant produces energy excessively, only the profitability of the LAES integration is considered in the current study.

The following control variables to be optimized are represented by the arrows in Figure 5.4.1.

$P_{PV\ TO\ WAREHOUSE\ (t)}$ is the PV power used to directly supply the warehouse; $P_{PV\ TO\ LAES\ (t)}$ is the power for charging the LAES by the excess PV generation, $P_{LAES\ TO\ WAREHOUSE\ (t)}$ is the power generated from the turbine-generator set to supply the warehouse, $P_{GRID\ TO\ WAREHOUSE\ (t)}$ is the grid power used to supply the warehouse.

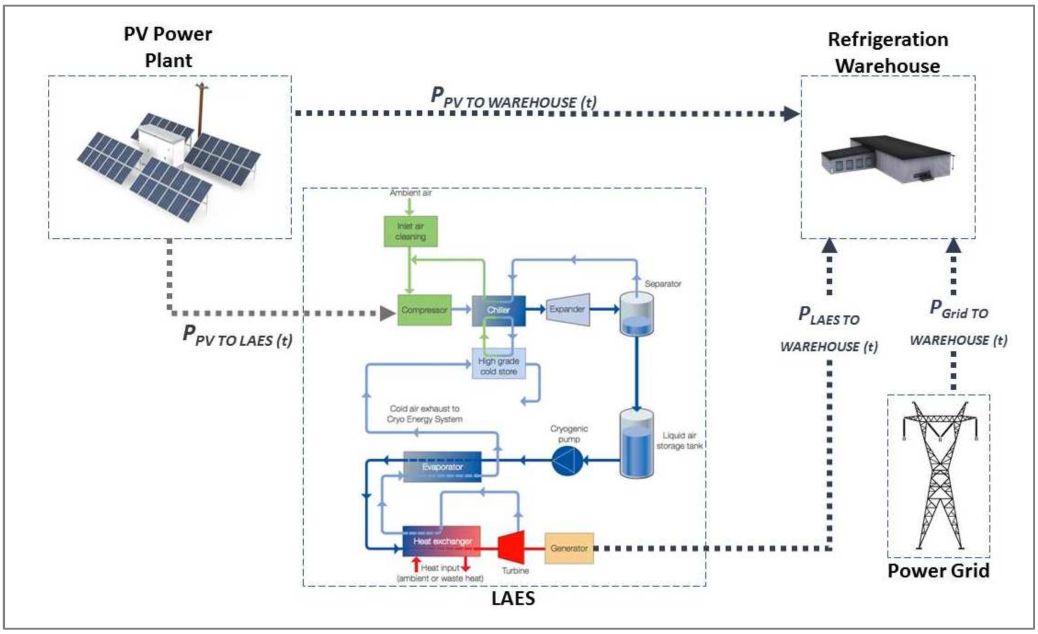

Figure 5.4.1: Schematic layout of the model (Negro et al., 2018a)

5.4.2 Presentation of the storage system

The LAES system comprises three main parts: the charging, storage and discharging processes. During charging phase, excess of renewable electricity is used for air liquefaction. Later at night when PV panels no longer produce electricity, the air is evaporated and expanded in turbines to generate electricity. Cold energy from the evaporation of liquid air is stored and used for liquefaction needs and also for refrigerated warehouse supply. Besides, hot storage captured from inter-coolers of the liquefaction part is used to “super-heat” air before expansion. More detail about the LAES process can be found in (Negro et al., 2018a).

5.5 Methodology of the optimization

The non-linear optimization problem can be solved using the Generalized Reduced Gradient Method as implemented in the standard Microsoft Excel Solver._Simulations are done for a duration 24 hours with a time lapse called “t” from 1 to 24 reflecting 1AM to 12PM.

Assumptions for each sub-model are given in Table 5.5.1 and they were made as follow:

Parameter	Unit	Value
Peak Rated power of PV panels* under a solar irradiation of 1kW/m²	MWp	1
Off-peak tariff**	€/kWh	0,0662
Peak tariff**	€/kWh	0,0842
Round Trip Efficiency***	-	0,25
Exergy efficiency *	-	0,3
Thermal energy load for refrigerated warehouse for winter case***	kWh/day	1500
Thermal energy load for refrigerated warehouse for summer case***	kWh/day	2000
LAES size***	kW/kW	180/60
Minimum power of PV panels*	kW	20
Maximum power of PV panels*	kW	80

(*) author assumption; (**) onsite data; (***) Thermodynamic simulation results (not included in the current work)

Table 5.5.1: Set parameters for the simulation

5.5.1 Sub-models

5.5.1.1 Power PV plant

The sum of the power delivered by the PV plant to charge the LAES and to supply the refrigeration load must be less than the power delivered by the PV panels at any instant *t*.

$$0 \leq P_{PV\ TO\ LAES\ (t)} + P_{PV\ TO\ WAREHOUSE\ (t)} \leq P_{PV,} \qquad \text{Eq. (1)}$$

5.5.1.2 Power grid

Night off-peak hours are set by the distribution system operator and are on average between 10 pm and 7 am. However, for the rest of the time, a peak hour tariff is applied:

$$p_{(t)} = \begin{cases} p_{0\ (t)} = 0{,}0662\ €/kWh & \text{if } t \in [22, 24] \cup [0, 7] \\ p_{1\ (t)} = 0{,}0842\ €/kWh & \text{if } t \in [7, 22] \end{cases} \qquad \text{Eq. (2)}$$

5.5.1.3 LAES

The LAES is charged with the excess of renewable energy from the PV panels $P_{PV\ TO\ LAES\ (t)}$. The recovered energy $P_{LAES\ TO\ WAREHOUSE\ (t)}$, consists of the electricity produced by the turbines during the system discharge stage and electricity saved by cooling the warehouse with liquid air from the LAES system. The State Of Energy $SOE_{(t)}$ of the LAES at any given time *t* and the flow of power from *t-1* to *t* is given in Eq. (3):

$$SOE_{(t)} = SOE_{(t-1)} + (RTE \times P_{PV\ TO\ LAES\ (t)} - P_{LAES\ TO\ WAREHOUSE\ (t)}) \times TP \qquad \text{Eq. (3)}$$

5.5.1.4 Refrigeration warehouse

The conversion of the thermal energy to its equivalent in terms of electrical energy is done by means of COP and it is expressed by Eq. (4) and Eq. (5):

$$COP = COP_{Carnot} \times \eta_{ex} = \left(\frac{T_c}{T_h - T_c}\right) \times \eta_{ex} \quad \text{Eq. (4)}$$

$$\sum_{t=1}^{N} COP_{(t)} \times P_{WAREHOUSE(t)} \times TP = Q_{f,tot} \quad (kWh) \quad \text{Eq. (5)}$$

5.5.1.5 Objective function:

The control strategy needs to identify the most beneficial periods in order to minimize the purchase of electricity in the grid. As described in the equation below the optimal system control strategy will be the one that minimizes the grid electricity purchased.

$$G = \sum_{t=1}^{N} TP \times p_{(t)} \times P_{GRID\ TO\ WAREHOUSE(t)} \quad \text{Eq. (6)}$$

5.5.1.6 Variable constraints:

At any instant *t*, the sum of the supplied power to the warehouse must be equal to the instantaneous refrigeration load.

$$P_{PV\ TO\ WAREHOUSE\ (t)} + P_{LAES\ TO\ WAREHOUSE\ (t)} + P_{GRID\ TO\ WAREHOUSE\ (t)} = P_{WAREHOUSE\ (t)} \quad \text{Eq. (7)}$$

The sum of the power delivered by the PV plant to charge the LAES and to supply the refrigeration load must be less than the power delivered by the PV panels at any instant *t*.

$$P_{PV\ TO\ LAES\ (t)} + P_{PV\ TO\ WAREHOUSE\ (t)} \leq P_{PV\ (t)} \quad \text{Eq. (8)}$$

5.5.1.7 Variable limits

The warehouse and the LAES are modelled as variable parameters which can be controlled from an upper to a lower set range for each sampling time period of the simulation horizon. These constraints can be expressed as:

$$20 \leq P_{WAREHOUSE(t)} \leq 80 \quad (kW) \quad \text{Eq. (9)}$$

$$0 \leq P_{PV\ TO\ LAES(t)} \leq 240 \quad (kW) \quad \text{Eq. (10)}$$

$$0 \leq P_{LAES\ TO\ WAREHOUSE(t)} \leq 60 \quad (kW) \quad \text{Eq. (11)}$$

$$0 \leq SOE_{t)} \leq 1704 \quad (kWh) \quad \text{Eq. (12)}$$

5.5.1.8 Proposed algorithm

The GRG algorithm solver is formulated as follows:

$$min_x f^T x \text{ Subject to } \begin{cases} A.x \leq b \\ A_{eq}.x = b_{eq} \\ lb \leq x \leq ub \\ c(x) \leq d \\ c_{eq}(x) = d_{eq} \\ x_i \in z \end{cases} \quad \textit{Eq. (13)}$$

- *Linear equalities*

A_{eq} is a $k \times n$ sparse matrix, b_{eq} is a $k \times 1$ vector.

- *Linear inequalities*

- A_{eq} is a $k \times n$ sparse matrix, b_{eq} is a $k \times 1$ vector
- *Decision variable bounds*

lb and ub are $n \times 1$ vectors indicating the lower and upper bounds respectively.

- *Nonlinear inequalities*

c is a $u \times 1$ vector of functions containing constraints, d is a $u \times 1$ vector.

- *Nonlinear equalities*

c_{eq} is a $v \times 1$ vector of functions containing nonlinear equality constraints, d_{eq} is a $v \times 1$ vector.

5.6 Simulation results and discussion

As a key factor determining the optimum energy scenario, the solar irradiation is herein studied by comparing a typical day of January and another day of July. According to solar irradiation of the location, the optimal schedule in January Figure 5.6.1.a shows the refrigeration load is assured by the grid during the night. The refrigeration load during this time remains at its minimal value so as to decrease the grid energy cost. At around 10:00 AM, the solar panels take over to supply the warehouse. In the meantime, the decision making of the OC is to maximize the refrigeration load (66 kW at 11:00) to take advantage of free photovoltaic electricity and also to turn on the charging of the LAES. The warehouse is only supplied by the LAES from 18 :00 to 22 :00 (almost 4 hours). A little pic of grid energy consumption appears between 16:00 and 18:00 it corresponds to the time adjustment required for the LAES to meet the load regarding decreasing PV energy production. The discharge time is below the LAES real discharge capacity due to unsufficient duration of charging (low PV panels production). A more optimistic scenario of July is represented by Figure 5.6.1.b where the site is entirely self-sufficient. LAES can supply the refrigerated warehouse during the night-time. The OC switches to LAES for the energy supply when PV panels can no longer produce electricity.

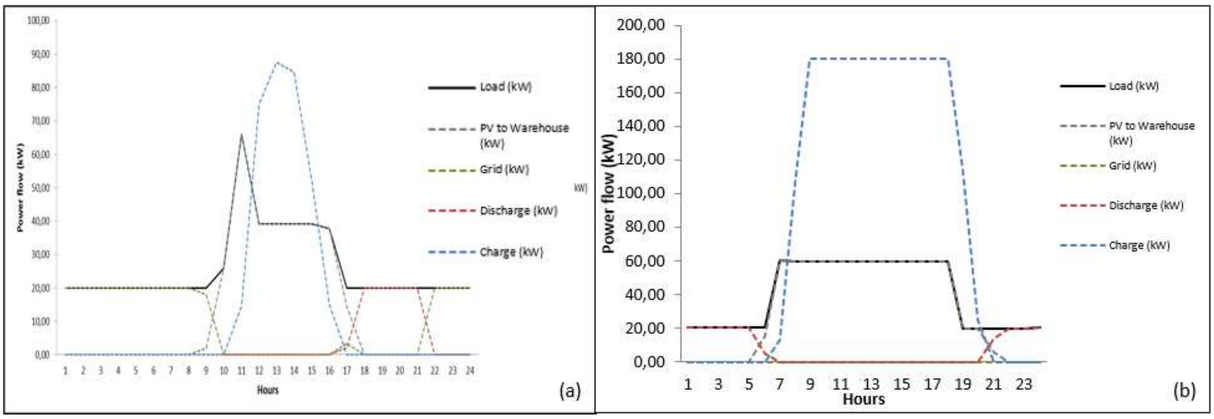

Figure 5.6.1: Optimal energy scenario in a typical winter day (January) (a) and in a typical summer day (July) (b)

Daily energy and cost savings of both cases are summarized in Table 5.6.1 and Table 5.6.2 for the winter case and the summer case respectively. Energy profiles and values of daily cost savings shows the evidence of the solar irradiation major impact on the energy distribution and cost savings from the LAES integration. Nonetheless, further investigations are needed to evaluate the representativeness of the 16 or 11€/day regarding the project CapEx.

Month	Baseline Energy (kWh)	Optimal Energy (kWh)	Baseline Cost (€)	Optimal Cost (€)	Saved Energy (%)	Saved Cost (%)
January	323,68	241,51	23,66	16,74	25,39	29,25

Table 5.6.1: Daily cost savings in January

Month	Baseline Energy (kWh)	Optimal Energy (kWh)	Baseline Cost (€)	Optimal Cost (€)	Saved Energy (%)	Saved Cost (%)
July	184,65	0	11,78	0	100	100

Table 5.6.2: Daily cost savings in July

The combination of the LAES to PV panels as renewable energy technology requires optimal meteorological conditions to be profitable. 4 cities representing different climates, both in winter and summer are chosen as subject for this study to investigate LAES profitability under different solar irradiation.

	Total Electricity Supplied (kWh)	PV Supply (%)	LAES Supply (%)	Grid Supply (%)
Riyadh - KSA	1776,95	54,57	34,11	11,32
Seville - Spain	1493,47	64,26	35,74	0
Helsinki	890,02	64,37	35,63	0
Québec	929,91	48,61	51,39	0
Belgium	966,59	80,90	19,10	0

Table 5.6.3: Total electricity supplied to the warehouse for the summer case

	Total Eletricity Supplied (kWh)	PV Supply (%)	LAES Supply (%)	Grid Supply (%)
Riyadh	841,00	50,40	49,60	0
Seville	855,57	50,74	41,88	7,38
Helsinki	646,68	37,11	0	62,89
Québec	603,57	37,01	47,06	15,93
Belgium	626,68	48,44	13,11	38,54

Table 5.6.4: Total Electricity Supplied to the warehouse for the winter case

The summer simulation for almost every city (Table 5.6.3) clearly shows that the warehouse load can be entirely assured without making use of the power grid, except for Saudi Arabia where the 1 MWp PV plant supported by the LAES plant seems unable to meet the high refrigeration load of the warehouse. In this case, a slight increase in the size of the PV plant or a more efficient storage system are needed to outweigh high ambient temperatures reflected in high-energy consumption.

On the other hand, in almost all cases of the winter model (Table 5.6.2), PV power plant is only responsible of the reduction of the energy drawn from the grid with differences from one city to another. Despite the low temperature in Helsinki, and therefore the low refrigeration demand, the low solar irradiation makes it hard for the PV power plant to supply both the warehouse and the storage system. The weather conditions allow the system to be self-sufficient by assuring both charging the LAES and supplying the refrigerated warehouse.

As a conclusion, the system represents the highest performance in areas characterized by a moderately warm climate and sunny throughout the year. Ideally, the system should be implemented in a Mediterranean region as southern Europe or North Africa.

5.7 Techno-economic analysis of the LAES

This section investigates technical and economic feasibility of the LAES powered by the PV power plant.

This study is presented in the form of a sensitivity analysis in which the annual savings achieved are evaluated varying 4 parameters: the RTE of the LAES, the PV plant peak power, the ratio of discharge to charge power (D/C) and the geographic location. When parameters are not under study, they are fixed as in the previous paragraph. The economic analysis is based on the annual economic savings calculated as the difference between the yearly energy costs before and after the integration of the energy storage. To achieve this purpose, 3 cases are studied:

Case 1: Only the grid supplies the warehouse; **Case 2:** Warehouse is supplied by both the PV plant and the grid; **Case 3:** The storage system is integrated.

The cost of energy is calculated on the basis of the cost of electricity drawn from the grid and the hourly cost of photovoltaic electricity estimated by Eq. (14).

$$Hourly\ PV\ Cost\ = \frac{1{,}2 \times Peak\ Power\ (Wp)}{Lifespan \times 365 \times 24} \qquad (€/h) \qquad \text{Eq. } (14)$$

5.7.1 Results and discussion

Profiles in Figure 5.7.1.a shows that the annual savings allow a maximum value of **9684,04 €**. The lower the DP/CP ratio, the lower this value is reached with low RTE values. The results show that the RTE must be increased by at least 5% to reach the maximum value of the savings achieved.

According to Figure 5.7.1.b, the values of the savings achieved remain constant for most cities from a RTE of 25%. For Brussels, the results show that the system can only be self-sufficient from a RTE of 30% (where the savings stabilize around a value of **9684,04 €**. In accordance with the results of the OC strategy carried out in the previous chapter, Seville represents in this analysis the ideal case for the integration of the storage system considering the interesting value of the realized savings of around **11 383 €**.

As illustrated by Figure 5.7.1.c, the results achieved show that for the various RTEs, the curves are increasing until they reach a maximum of savings corresponding to a certain PV plant size, and then decreasing slightly. This is because the larger the PV plant is, the more energy is stored, and the less electricity is drawn from the grid.

Table 5.7.1 shows for each RTE value the optimal PV plant size and the corresponding annual savings. Those savings are used to define an investment threshold not to be exceeded for the storage system. The investment threshold is calculated by multiplying the value of the annual savings achieved by the estimated life of the LAES estimated at 25 years.

Table 5.7.1: Optimal Size of PV Power Plant and Threshold Investment function of RTE

RTE (%)	PV Plant Peak Power (kWp)	Annual Savings (€/an)	Investment Threshold (€)
25%	154	3 429,17 €	**85 729,29 €**
30%	155	3 447,26 €	**86 181,61 €**
40%	155	3 484,41 €	**87 110,13 €**
50%	162	3 536,47 €	**88 411,77 €**
100%	395	6 968,56 €	**174 214,08 €**

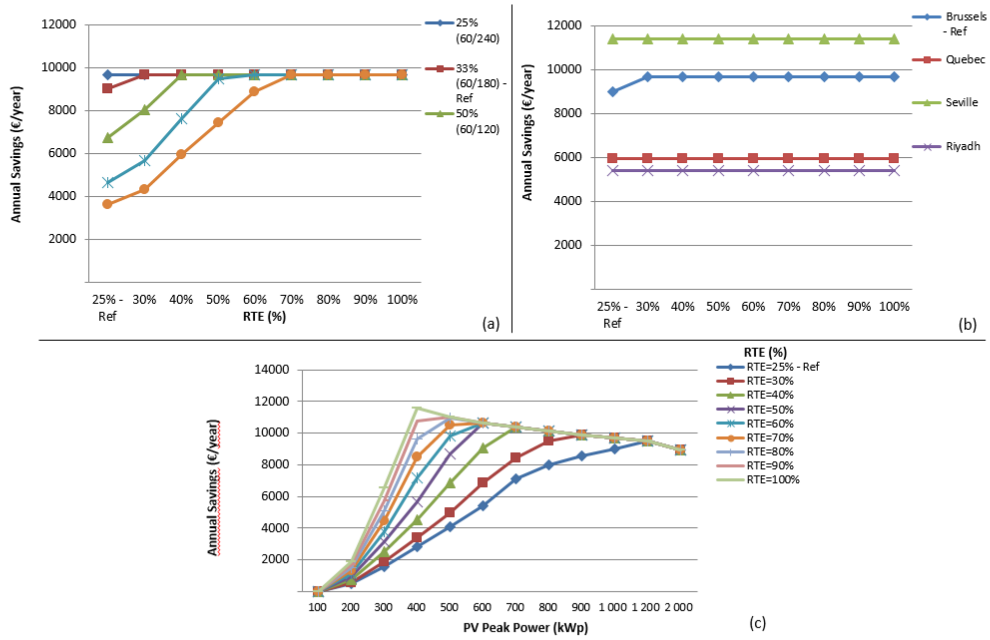

Figure 5.7.1: Sensitivity behavior of the annual savings of the LAES integration regarding 3 parameters : (a) D/C ratio of LAES; (b) geographical location of the system; (c) Peak rated power of PV panels

5.8 Concluding remarks and perspectives

It has been found that the LAES makes the refrigeration warehouse energy self-sufficient in summer while in winter, the storage system is only able to reduce the electricity drawn from the grid. Results of simulations showed that warm climate and sunshine throughout the year make the system more profitable than in regions where it is almost cloudy. This is due to the fact that the LAES is combined in this particular case to a PV power plant, and production of electrical energy is directly linked to solar irradiation. In other cases, if the LAES is connected to a wind farm for instance, results could be completely different from the present case. The techno-economic sensitivity analysis evaluated the annual savings achieved based on several key factors in the sizing of the LAES such as the LAES's RTE, the resale to purchase price ratio of electricity, the charge-to-discharge power ratio and the size of the PV plant. For the reference case, results showed that the system realized an annual savings of 8993,95 €. The capital investment cost computation shows that despite the significant annual savings achieved, LAES remains not very attractive given its high estimated payback period (higher than 25 years). In agreement with previously published research, this work has shown that, the economic profitability of the LAES system is very low given high CapEx values. The future of this technology could be even brighter if future research focuses on improving the technical performance of the system, so that the technology becomes accessible and mature, therefore more realizations could be made and the corresponding investment costs could decrease. In addition, under current market conditions, the system can have a large economic benefit if installed in a country where electricity prices are high.

CHAPTER 6

CONCLUSION

General conclusion and work summary

Perspectives

6.1 General conclusion and work summary

This work aimed at providing new knowledge to respond to scientific questions related to LAES in terms of energy efficiency and environmental impact. It also investigated and examined the mid-term to long-term techno-economic feasibility of LAES.

By analyzing various configurations of LAES, this thesis has highlighted the main factors to a very energy efficient storage unit, by an energy "co-recovery" and "tri-recovery". Based on a quantitative and qualitative analysis, the Life Cycle approach method has shown promising environmental impact results for the oxy-combustion process integrated in LAES. It also showed a clearer picture of the techno-economic aspect, of the payback period and economic profit, and gave a better look at the lack of LAES deployment up to this date.

The review paper, provided deep investigation on the current development of LAES technology from both scientific and technical perspectives. It highlighted the importance of developing such a novel storage facility by comparing it to the currently deployed technologies for grid-scale electrical storage purposes: PHS and CAES. It appeared that from an environmental point of view, the LAES presents advantages comparing to other EES technologies. Besides, depending on the technologies involved in the energy recovery unit, LAES may also represent higher electrical efficiencies, regarding different form of energy generation, as we may call it a "co-recovery" and "tri-recovery" of cryogenic energy in case of combustion process integration. Apart from the energy storing and restituting main functionalities, different possibilities can emerge from the LAES in the form of by-products of liquid air. In fact, hybridization of LAES is open to multiple opportunities when considering that cryogenics have been used in multiple industry fields. Recently, it has been conditioned for Cryogenic Carbon Capture (CCC) within the LAES system itself. This functionality was considered and used for a cleaner combustion in the studied system as a novel suggested LAES within this work.

A global comparative study has been made including: a thermodynamic performance analysis, environmental impact assessment and economic benefit evaluation on a newly proposed LAES system including several combustion cases to the usual LAES configuration. Oxy-biogas combustion, oxy-natural gas combustion and air-biogas combustion are investigated in this work and compared to the configuration with only evaporation and super-heating process.

The first part of the study concerned the energy analysis of four LAES systems and a parametric analysis, a focus on the combustion simulation results (temperature, emissions) and an exergy analysis. According to these results, and in accordance with the literature outcome, the combustion leads to higher electrical efficiencies. For oxy-fuel combustion, a range of [70-80%] RTE is obtained, while the calculated RTE of super-heating based cycle is 37%. Main reasons of this gap are, first, the waste heat in the discharge cycle before the expansion stage temperature is considerably higher in the combustion than in super-heating (heat of combustion). Moreover, in the oxy-fuel combustion, an air separation process allows the recovery of cryogenic energy in two different circuits. Liquid oxygen and liquid nitrogen have different pathways, and energy recovery is somehow done in double times through liquid nitrogen and liquid oxygen circuit.

Energy recovered after storage is not only electrical energy but thermal and electrical energy. Since these thermal energies are mostly converted in electricity, the efficiency of the global process is usually captured through a simple indicator: the RTE. However, a discussion was made within chapters to highlight the importance of the thermal energy especially when the pumping pressure exceeds a threshold value. In such a LAES configuration, energy flow recovery can be selected by regulating the pumping pressure, depending on the time, the instant industrial requirements: electricity, cold for freezers/cold store/refrigeration load or hot stores and thermal machine.

In the oxy-fuel combustion, a particular parameter has been added to the circuit which is the carbon dioxide as diluent to control the combustion temperature. The addition of carbon dioxide in the proposed circuit is issued from the carbon capture component included as a post-treatment process or from an external source. The choice of the carbon capture was made to avoid the emission of nitrous oxides, but calculation of combustion showed that this idea leads to other harmful emissions due to the increase of GHG emission and CO_2 dissociation reaction. Fuel-to-Air ratio is preferable in limiting the outlet temperature value as well as the polluting emissions. The link between emission profiles and temperatures profiles within this chapter was for determining the maximum temperature regarding the lowest emissions.

The environmental assessment of LAES through a Life Cycle Analysis method (LCA) has been performed to complete the investigation on the emission analysis and to perform the environmental impact assessment. Environmental aspect of this report concerns the LCA of the operational life phase of the LAES as preliminary estimation. The difference between this part of the work and the emission analysis is on the methodology employed. The LCA is a more appropriate and concise method for the environmental assessment, using SimaPro software as calculation and simulation tool for various impact categories. It takes into account qualitative and quantitative input and output data through the studied system boundaries. For example, biogas is considered as a mixture of 70% of methane and 30% of carbon dioxide in the combustion modelling, on the contrary in SimaPro, a type of biogas is considered for the case studies depending on its production process.

Results of comparison between three types of combustion based discharge cycle of the LCA study has led to the conclusion that the oxy-biogas combustion is clean and even beneficial for the environment compared to air-biogas and oxy-natural gas combustion cases. Post-treatment of combustion added a beneficial value on human health and ecosystems impact in case of oxy-natural gas and air-biogas combustion. Harmful emissions caused by the air-biogas and oxy-natural gas are mostly GHG, CO and NOx emissions, in accordance with previous combustion flue gases analysis. Regarding EcoCost results, the cost of ecological tax is of 21,6 € per complete discharge cycle for the air-biogas combustion. LAES is expected to run two times in a normal operating day, a dramatic increase in the operating expenditure is therefore possible, especially that, daily savings of the LAES should not exceed 20€/day as it was calculated within economic analysis chapter.

As discussed in the review chapter, one explanation of the lack of experimental validation is the investment cost related to the LAES machinery. The techno-economic study carried out in this chapter, was presented in the form of a sensitivity analysis in which the annual savings achieved are evaluated throughout the seasons, and varying the geographical location, the size of the PV power plant and the size and performance of LAES. Main conclusions of the study is that in the particular case of Belgium location, the LAES makes the industrial site self-sufficient in summer season, but it only reduces the grid electricity consumption in winter making a relatively low daily cost savings. The sensitivity analysis showed that in region where it is almost sunny and warm this system is likely to be the most profitable. Calculation of the payback period based on annual savings has shown a threshold of 174 214.08 € not to be exceed even at a maximum RTE of 100% to get a payback of 25 years (estimated PV power plant lifespan). Approximate theoretical calculation based on cost functions and assumptions provided by (Hamdy et al., 2019) has shown that the CapEx of the LAES is 10 times higher than this threshold value, so payback period is estimated to be very high.

6.2 Perspectives:

6.2.1 Perspectives on the energy aspect chapter:

Modelling strategy of the cryogenic energy storage within this thesis has its own limits. Therefore, we could recommend some perspectives to completely perform thermodynamic simulation of the LAES for future work:

- A more precise calculation for the turbomachinery in order to get as real efficiencies as possible, including physical properties of the fluid (velocity, density, heat capcity) as well as turbomachinery calculation.
- A dynamic simulation including the behavior of thermal storages regarding their major role in determining exergetic and energetic efficiencies of the system. (cold box, inter-cooler, super-heaters).
- The integration of liquid air leakage from the tank is also an important parameter not to be neglected in the dynamic simulation. It is evaluated to 0.5% (Chen et al., 2009)).
- A three-stage compression should replace double-stage compressor in the liquefaction, compression ratio should not exceed 4.5 to allow the minimum work consumption in the charging unit.
- An experimental validation would hopefully enrich the simulation work. The construction of a LAES demonstrator as ultimate objective of CryoHub project, would certainly help get validation for this theoretical work.

6.2.2 Perspectives on the environmental aspect chapter:

The LCA performed in this work was limited to the operational stage in the lifetime of a product system. As perspectives for this part of the work, we suggest to develop the following points:

- A "cradle-to-crave" analysis is more precise and takes into account different stages of life from the raw material to the recycling or destruction and all the impact related to the system.
- Preliminary results of the operational phase showed that the use of carbon dioxide as diluent in the oxy-fuel combustion have negative effect on the environment, but a gas completely inert like helium is more likely to be a preferable solution
- In the current simulation for LCA, the electrical energy consumed is the grid electricity, which is not always the real case, as the LAES is supposed to store electricity from renewables. Consequently, in future simulation, a more realistic input data should be selected in a complete LCA study to evaluate closer results to reality.

- A comparison to LCA study of existing storage technology is also required as an approach to data validation after performing a LCA “from cradle to grave”.

6.2.3 Perspectives on the economic aspect chapter:

The capital investment cost computation shows that despite the significant annual savings achieved, LAES remains not very attractive given its high estimated payback period under current market conditions. Nonetheless, some of the following ideas could be perspectives of the LAES economics.

- The system could have larger economic benefit if installed in a country where electricity prices are high.
- Investigation of the combination of the LAES with a wind farm could represent more advantageous payback period regarding more renewable energy production.
- Finally like any new technology, the first realizations tend to have very high costs; however as the technology becomes more mature, its technical performances are improved and its investment cost could be reduced.

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Appendix I

Cold recovered liquefaction

Points	Mass fraction (k□/s)	Temperature (°C)	Pressure (bar)
1	0.60	25.00	1.00
2	1.00	24.27	1.00
3	1.00	278.52	6.32
4	1.00	74.96	6.32
5	1.00	280.77	40.00
6	1.00	76.73	40.00
7	1.00	25.02	40.00
7'	0.40	25.02	40.00
8	0.60	-86.72	40.00
8'	0.40	-152.66	1.00
9	0.60	-185.20	40.00
10	0.60	-194.20	1.00
11	0.10	-191.51	1.00
11'	1.00	-173.20	1.00
12	0.40	23.17	1.00
12'	1.1	-129.20	1.00

Points	Mass fraction (kg/s)	Temperature (°C)	Pressure (bar)
1H	1.00	323.15	0.10
2H	1.00	533.78	0.10
3H	1.00	323.15	0.10
4H	1.00	536.86	0.10

Superheating based cycle

Points	Mass fraction (kg/s)	Temperature (°C)	Pressure (bar)
1	1	-194.33	1.00
2	1	-189.05	100.00
3	1	-124.70	100.00
4	1	-91.04	100.00
5	1	-51.53	100.00
6	1	-9.62	100.00
7	1	134.47	100.00
8	1	98.03	21.54
9	1	231.01	21.54
10	1	88.70	4.64
12	1	243.05	4.64
13	1	98.03	1.00

Points	Mass fraction (kg/s)	Temperature (°C)	Pressure (bar)
1C	1	-50.00	1
2C	1	-170.41	1
3C	1	-20.00	1
4C	1	-114.26	1
5C	1	0.00	1
6C	1	-79.55	1
1H	1	181.43	1
2H	1	7.56	1
3H	1	263.71	1
4H	1	46.85	1
5H	1	263.71	1
6H	1	112.85	1

Oxy combustion with biogas based cycle

Points	Fluid	Mass fraction (kg/s)	Temperature (°C)	Pressure (bar)
1	Oxygen	0.27	-183.09	1.00
2	Oxygen	0.27	-183.09	1.00
3	Oxygen	0.27	-50.00	1.00
4	Oxygen	0.27	-20.63	1.00
5	Oxygen	0.27	9.99	1.00

Points	Fluid	Mass fraction (kg/s)	Temperature (°C)	Pressure (bar)
6	Furnace gas	0.33	2726.85	1.00
7	Furnace gas	0.33	1126.85	1.00
8	Furnace gas	0.33	493.17	1.00
9	CO2	0.18	99.61	1.00
10	CO2	0.18	-56.00	1.00

Points	Fluid	Mass fraction (kg/s)	Temperature (°C)	Pressure (bar)
11	Nitrogen	1.00	-195.91	1.00
12	Nitrogen	1.00	-191.38	80.00
13	Nitrogen	1.00	-128.74	80.00
14	Nitrogen	1.00	-111.45	80.00
15	Nitrogen	1.00	9.71	80.00
16	Nitrogen	1.00	45.06	80.00
17	Nitrogen	1.00	987.06	80.00
18	Nitrogen	1.00	-46.26	18.57
19	Nitrogen	1.00	991.11	18.57
20	Nitrogen	1.00	433.76	4.31
21	Nitrogen	1.00	998.98	4.31
22	Nitrogen	1.00	246.42	1.00

Points	Mass fraction (kg/s)	Temperature (°C)	Pressure (bar)
1C	1	-50.00	1
2C	1	-84.13	1
3C	3	253.15	1
4C	3	250.78	1
5C	1	223.15	1
6C	1	99.95	1
1H	4.2	323.15	1
2H	4.2	1281.44	1
3H	4.2	1281.44	1
4H	1.4	1281.44	1
5H	1.4	1281.44	1
6H	1.4	1281.44	1
7H	1.4	630.20	1
8H	1.4	593.77	1
9H	1.4	907.01	1
10H	4.2	1281.44	1

Air biogas combustion cycle

Points	Mass fraction (kg/s)	Temperature (°C)	Pressure (bar)
1	0,27	-194,33	1,00
2	0,27	-192,53	35,00
3	0,27	-50,00	35,00
4	0,27	-21,36	35,00
5	0,27	9,95	35,00
6	0,07	2008,85	35,00
7	0,07	1126,85	35,00
8	0,28	668,18	1,00
9	0,04	99,61	1,00

Points	Mass fraction (kg/s)	Temperature (°C)	Pressure (bar)
1C	1,00	-50,00	1,00
2C	1,00	-122,40	1,00
3C	3,00	253,15	1,00
4C	3,00	250,29	1,00
5C	1,00	223,15	1,00
6C	1,00	100,67	1,00
1H	4,20	323,15	1,00
2H	4,20	433,81	1,00

Appendix II

Air-biogas data inventory

DATA TYPE	UNIT	INPUT VALUE	OUTPUT VALUE
Air	g	2671.109107	0
Electricity	kWh	1.362559691	1
Methane	g	2683.847702	0
CO2	g	3155.370115	1228.783439
OXYGEN	g	3211.904625	2677.413116
NITROGEN	g	10578.00598	14710.06884
C2H6	g	0	0
HYDROGEN	g	0	0
HYDROGEN	g	0	0
O	g	0	0
OH	g	0	0
WATER	g	0	1006.974288
HO2	g	0	0
CO	g	0	0
NCO'	g	0	0
Air ventilation	kg	24.57529251	

Oxy-biogas data inventory

DATA TYPE	UNIT	INPUT VALUE	OUTPUT VALUE
Air	g	297.0814958	0
Electricity	kWh	0.151544267	1
Methane	g	25.07385602	0
CO2	g	29.47905572	94.66864388
OXYGEN	g	357.2289233	219.685609
NITROGEN	g	0	0
C2H6	g	0	0
HYDROGEN	g	0	0.082356367
HYDROGEN	g	0	0.041178184
O	g	0	3.294254681
OH	g	0	11.69460412
WATER	g	0	76.92084679
HO2	g	0	0.164712734
CO	g	0	5.270807489
NCO'	g	0	0
Air ventilation	kg	16.721131	

Oxy-natural gas data inventory

DATA TYPE	UNIT	INPUT VALUE	OUTPUT VALUE
Air	g	291.8233658	0
Electricity	kWh	0.148862042	1
Methane	g	27.10186982	0
CO2	g	0	70.62815512
OXYGEN	g	277.2159192	163.0162611
NITROGEN	g	0	0
C2H6	g	1.299498353	0
HYDROGEN	g	0	0.061123457
HYDROGEN	g	0	0.030561729
O	g	0	2.444938299
OH	g	0	8.679530963
WATER	g	0	56.69200682
HO2	g	0	0.122246915
CO	g	0	3.973024737
NCO'	g	0	0.091685186
Air ventilation	kg	16.721131	