Patent analysis and thermodynamic evaluation of Sand Thermal Energy Storage integration into Liquid Air Energy Storage

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A thesis for the degree of
Master of Science (MSc or Dipl.-Ing. or DI)

In the
Master program Process Engineering

At the
Faculty of Mechanical and Industrial Engineering, TU Wien

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Vienna, March 16, 2023

Liesa Zhou

Abstract

Within the scope of this work, the storage of energy utilizing liquid air is investigated. Intermediate energy storage can balance the supply and demand of electricity. In the charging phase, ambient air is liquefied and stored in storage tanks, while in the discharging phase, the pressure and temperature of the air are increased to generate electricity from the compressed air flow with turbines. Heat storage tanks are therefore required between the charging and discharging phase for the intermediate thermal energy storage. The work focuses on developing an electro-thermal energy storage (ETES) system using sandTES technology as a heat storage device in the liquid-air energy storage system (LAES). SandTES is a concept of an active counter-current fluidized bed heat exchanger developed at the Institute of Energy Systems and Thermodynamics of TU Vienna. The storage and heat transport medium is sand.

Furthermore, in the course of the work, a patent analysis in the field of LAES with solid material in thermal energy storage (TES) systems is conducted. Based on this research, it is ascertained that the method of using solid material as a direct heat transport medium for the heat exchanger in the LAES system is not yet present in any patent claim. The aim of this analysis is to patent the method of sandTES technology integrated into the LAES system as a new invention.

Therefore, the described design is modeled in the simulation program EBSILON and investigated on a thermodynamic level. A system without any TES was simulated first to determine the performance of a pure LAES system without heat recovery and heat storage. For comparison, the LAES system is modeled with sandTES HEX, which has a much higher efficiency of just over 60%. For the evaluation of the system, a thermodynamic analysis is performed, considering values such as exergy losses or round-trip efficiency. The result shows that the optimization of the LAES system with sandTES has the potential to replace the conventional LAES system.

Kurzfassung

Im Rahmen dieser Arbeit wird die Speicherung von Energie mittels flüssiger Luft untersucht. Durch die Zwischenspeicherung von Energie können Angebot und Nachfrage von Strom ausgeglichen werden. In der Einspeicherphase wird Luft aus der Umgebung verflüssigt und in Speichertanks gelagert, während in der Ausspeicherphase Druck und Temperatur der Luft erhöht werden, um danach aus dem Druckluftstrom mithilfe von Turbinen Strom zu generieren. Zwischen der Ein- und Ausspeicherphase werden Wärmespeicher für die Zwischenspeicherung der thermischen Energie benötigt. Der Fokus dieser Arbeit liegt in der Weiterentwicklung eines elektro-thermischen Energiespeichers (ETES), bei dem die sandTES-Technologie als Wärmespeicher im Flüssig-Luft-Energiespeichersystem eingesetzt wird. SandTES ist ein am Institut der Thermodynamik und Energietechnik der TU Wien entwickeltes Konzept eines aktiven Gegenstrom-Wirbelschicht-Wärmetauschers, bei dem das Speicher- und Wärmetransportmittel aus Sand besteht.

Im Zuge der Arbeit wird weiters eine Patentanalyse im Bereich LAES mit festen Materialien im thermischen Wärmespeicher durchgeführt. Anhand dieser Recherche soll festgestellt werden, ob die Methode, Feststoffe als direkte Wärmetransportmittel für den Wärmetauscher im LAES-System einzusetzen, bislang noch in keinem Patentanspruch vorhanden ist. Das Ziel ist es nämlich am Ende, diese Innovation der sandTES-Technologie integriert im LAES-System als neue Erfindung zu patentieren.

Es wird daher die beschriebene Erfindung im Simulationsprogramm EBSILON modelliert und auf thermodynamischer Ebene untersucht. Ein System ohne jegliche TES wurde als erstes simuliert, um die Leistungsfähigkeit eines reinen LAES-Systems ohne Wärmerückgewinnung und Wärmespeicherung zu ermitteln. Zum Vergleich dazu, wird das LAES-System mit sandTES HEX modelliert, das einen deutlich höheren Wirkungsgrad von knapp über 60% aufweist. Für die Bewertung des Systems wird eine thermodynamische Analyse durchgeführt, bei dem Werte, wie Exergieverluste oder Umlaufwirkungsgrad, in Betracht gezogen werden. Das Ergebnis zeigt, dass die Optimierung des LAES-Systems mit sandTES Potential besitzt, das herkömmliche LAES-System zu ersetzen.

Acknowledgments

Herby, I would like to thank all those who have made a significant contribution to this thesis work through their professional and personal support.

First, I would like to express my sincerest gratitude to my supervisor Univ.Prof. Dipl.-Ing. Dr.techn. Markus Haider, for giving me the opportunity to work on the research of this interesting topic and for supporting me throughout my thesis work.

A special thank you goes to Projektass. Dipl.-Ing. Stefan Denner always supported me with his profound knowledge, critical perspective and helpful advice during every stage of my research work.

I would also like to thank Detlef Günzel for providing me the student license for the simulation program EBSILON.

Last but not least, I would like to thank my family and friends who have accompanied, supported and motivated me throughout my studies.

Contents

Nomenclature

Acronyms

CAES compressed air energy storage

CES cryogen energy storage

Ebsilon EBSILON® Professional

ETES electrothermal energy storage

HEX heat exchanger

Highview HIGHVIEW POWER

HTF heat transfer fluid

LAES liquid air energy storage

LNG liquefied natural gas

RTE round-trip efficiency

SandTES active fluidized bed thermal energy storage

TES thermal energy storage

Greek symbols

λ thermal conductivity W/(m K)

η efficiency

ε porosity

ζ exergy efficiency

Subscripts

0 at reference condition

air ambient air

c compressed air

comp compressor

f	fluid
L	liquid air
liq	liquefaction
s	sand
turb	turbine
amb	ambient
eff	efficiency
in	inlet
out	outlet
RT	round-trip
SiO_2	silicon dioxide

Roman symbols

c_{p}	specific isobaric heat capacity	kJ/(kg K)
$\dot{E}$	exergy	kJ
ΔH_{PT}	heat energy of phase transition enthalpy	kJ
Δh_{PT}	phase transition enthalpy	kJ/kg
h	enthalpy	kJ/kg
$\dot{m}$	mass flow	kg/s
m	mass	kg
$\Delta\dot{E}$	exergy loss	kJ/s
ρ	density	kg/m^3
e	specific exergy	kJ/kg
P	power	kW
P_{c}	work of the compressor	kW
p_{s}	partial pressure	bar
V	total volume of sand	m^3
$\mathrm{V_C}$	cavity of sand	m^3

Q	heat	kJ
s	entropy	kJ/(kg K)
ΔT	temperature difference	K
ϑ	temperature in celsius	°C
T	temperature in kelvin	K
x	vapor quality	
W	work	kJ
Y	liquid yield	

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1. Introduction

Energy, especially heat and electricity, is the main source that guarantees a high-quality life in modern society. Due to the rising population and industry growth, there is an increased demand for energy.
As a result, environmental problems and their effects have become serious issues in recent years. Due to the intensive use of fossil fuels, the concentration of the greenhouse gas CO_2 in the atmosphere has increased dramatically. Therefore, measures are being taken to drastically reduce emissions to achieve net-zero by 2050 and become climate-neutral europewide. In order to reduce CO_2 emissions, a lot has been invested in research, development, and the expansion of renewable energy capacities. The problem with renewable energy sources such as solar or wind is that it leads to the volatility of the energy source. With the increasing expansion of renewable energies, there must therefore be medium- and long-term energy storage facilities for intermediate storage of the electricity generated. Integrating energy storage systems into the power grid increases the utilization and economic efficiency of existing and future plants.[1]

Energy storage technologies can be classified into the following main groups:[2]

- Mechanical energy storage: e.g. compressed air, pumped hydro energy storage;
- Electrical energy storage: e.g. capacitors;
- Thermal energy storage: e.g sandTES;
- Chemical energy storage: e.g lithium batteries

As stated in O'Callaghan and Donnellan [2], electrochemical batteries mainly cover lower power ranges of below 10MW, while for grid-scale energy storage with power ratings of 100 MW or more the Pumped Hydro Energy Storage and Compressed Air Energy Storage (CAES) are considered. The disadvantages of these two technologies are the geological requirements, such as a large reservoir for the Pumped Hydro Energy Storage and underground caverns for CAES. As most suitable locations for Pumped Hydro Energy Storage in developed countries have already been utilized, it is difficult to expand this type of energy production further.

Liquid Air Energy Storage system has, therefore become an area of attention due to their advantage of being geographically unconstrained, adequately efficient, economical, and environmentally safe. In LAES systems, ambient air is used as the working fluid, which exists in infinite quantity in nature. Another main advantage is that energy is stored in a liquid form, so storage volumes are significantly lower than those required for CAES systems.[2]

For optimization purposes, the thermal energy storage system sandTES developed by TU Vienna, which uses quartz sand as the heat storage and transfer medium, is integrated into the conventional LAES plant. Therefore, models of this design are created with the simulation program EBSILON. Based on the model of Denner [3], the sandTES HEX is built in the LAES system for the TES. It is, therefore, possible to store high-temperature heat in large quantities without high pressure and at a low cost. The evaluation of the system's performance is based on size- and time-independent process key figures, such as the specific liquefaction work, the power input, and output, the round-trip efficiency, as well as on exergetic analyses.

Since the LAES system with sandTES is a new invention, a patent analysis is carried out as part of the thesis. The research aims to determine whether the current invention has already been claimed in some way in a patent. Therefore, the focus is set on patents describing LAES systems with a special emphasis on TES. More precisely, the goal at the end is to register the current invention of the LAES system comprising the sandTES technology as a new patent.

Based on this thesis work, a new energy-storing technology is presented, an innovation of the conventional LAES system. Besides the commercial liquid cryogenic technology using thermal oils, the fluidized bed technology using sand as thermal storage material is another feasible solution that has the benefits of low cost and large heat exchange area.

2. Theoretical Background

2.1. Electrothermal energy storage system

The main forms of storing energy are mechanical, electrical and thermal energy storage. TES systems can improve the flexibility of thermal energy supply systems and reduce energy consumption. Electrothermal energy storage ETES is the adaption of TES for electrical energy. ETES is a system and method to store electric energy in the form of thermal energy that balances power demand and supply. In the charging process, electricity is used for the heating or/and cooling of the TES system. This thermal energy is stored for a period of time until there is a demand for electricity. In the discharging process, the thermal energy is converted back to electricity by a power cycle or heat engine. If the ETES is used as a storage reservoir of only one end, then the counterpart of thermal energy needs to be obtained by an ambient or waste heat source. [4]

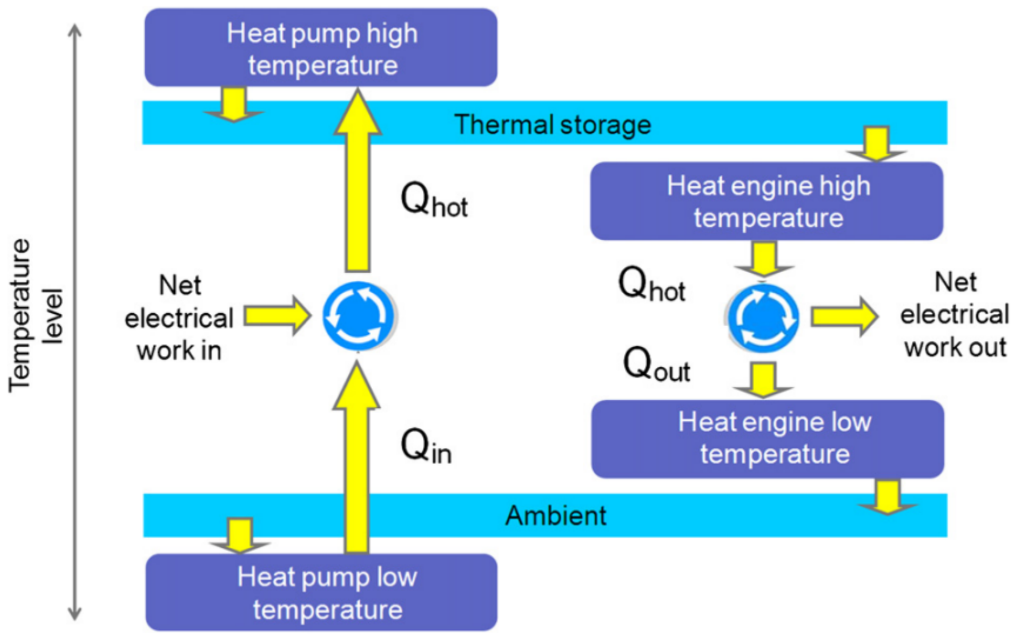


Figure 1.: *Schematic of an ETES system based on heat pump and heat engine. [4]*

The baseline of the ETES system is illustrated in fig.1. Such an energy storage system is robust, compact, and can cover a large amount of electrical energy, making it appealing for versatile applications. Thermal energy can be stored in the form of sensible heat with changes in the temperature of the storage medium or as latent heat, in which the phase of the storage medium changes.[4] More information regarding the thermal latent and sensible heat storage systems can be found in section 2.3.

For the ETES system, various thermal storage materials, such as thermal oil, molten salt or sand can be utilized. Among the thermal energy storage materials, sand can reach a high storage efficiency of 85% due to the wide range of operating temperatures.[5]

2.1.1. Round-trip efficiency

The thermodynamic performance of an energy storage system is defined as the round-trip efficiency (RTE or η_{RT}), whereas round-trip refers to the cycle of charging and discharging. The RTE of an electrical energy storage system is defined as the ratio between the electrical energy released during discharging and the electricity stored during the charging process.[6] It can also be described as the ratio of the output W_{out} during discharging to the network input W_{in} in the charging phase, given by the following equation:[2]

$$\eta_{\text{RT}} = \frac{W_{\text{out}}}{W_{\text{in}}} \tag{1}$$

2.1.2. Exergy

Exergy in thermodynamic systems is defined as work that can be extracted from the system or in other words, that part of the energy which can be completely converted into work. Compared to exergy, energy is conserved by all processes according to the first law of thermodynamics. In reality, all processes are irreversible, thus exergy losses are always expected.[7] When talking about the evaluation of TES systems energy and exergy are significant factors, whereas exergy analysis complements energy analysis and is, therefore a better method and provides a more rational evaluation and comparison.[8] In equation (2) below, the exergy flow $\dot{E}$ of the heat flow $\dot{Q}$ is shown, which applies for heat transfer at a constant temperature T. T_{amb} stands for the ambient temperature and is often defined as 273.15K.[9]

$$\dot{E} = (1 - \frac{T_{\text{amb}}}{T})\,\dot{Q} \tag{2}$$

Considering the exergy balance, the sum of all incoming exergy flows is greater than the sum of the outgoing exergy flows, which means in a real-life process, there is always exergy loss. The exergy loss corresponds to that part of the exergy converted into anergy by irreversible processes. In contrast to exergy, anergy is the part of the energy that cannot be used for performing work. The relation of energy, exergy and anergy is described below:[7]

$$Energy = Exergy + Anergy$$

The exergy of the stream $\dot{E}$ of the process can also be defined as follows, where h and h_0 are the enthalpies of the stream and the reference enthalpy, s and s_0 the entropy of the stream and the reference entropy and T_0 is the reference temperature:[2]

$$\dot{E} = \dot{m}\left[(h - h_0) - T_0(s - s_0)\right] \tag{3}$$

The exergy efficiency ζ_{eff} of work-producing processes can be defined as the ratio of the work gained W divided by the maximum work that can be obtained or in other words, the ratio of gained work W divided by the exergy difference ΔE. This relation is shown in equation (4).

$$\zeta_{\text{eff}} = \frac{W}{E_{\text{out}} - E_{\text{in}}} \tag{4}$$

Whereas, the exergy efficiency ζ_{eff} of processes that require work can be defined as the ratio of the maximum work that can be obtained divided by the work W gained. This relation is shown in equation (5).

$$\zeta_{\text{eff}} = \frac{E_{\text{out}} - E_{\text{in}}}{W} \tag{5}$$

Exergy analysis

The exergy loss $\Delta\dot{E}$ of a compressor or pump can be expressed as follows, where $\dot{m}$ is the mass flow, e_1 and e_2 the specific exergies and P_c is the compressor work:

$$\Delta\dot{E} = \dot{m}\,(e_1 - e_2) + P_{\mathrm{c}} \tag{6}$$

For the exergy loss $\Delta\dot{E}$ of a turbine the following equation is used, where $\dot{m}$ is the mass flow, e_1 and e_2 the specific exergies and P_{turb} is the turbine work:

$$\Delta\dot{E} = \dot{m}\,(e_1 - e_2) - P_{\mathrm{turb}} \tag{7}$$

The exergy loss for the heat exchanger can be written as follows, where $\dot{m}$ is the mass flow and e_{in} and e_{out} the specific exergy of the inlet and outlet flow: [9]

$$\Delta\dot{E} = \sum \dot{m}\,e_{\mathrm{in}} - \sum \dot{m}\,e_{\mathrm{out}} \tag{8}$$

The exergetic efficiency can be calculated using the equation (5) and (4), adapted to the component in the system. For heat exchangers, the exergetic efficiency ζ_{HEX} can be represented by the equation below, whereas $\dot{m}$ is the mass flow, h the enthalpy, s the entropy and T_{amb} the ambient temperature: [9]

$$\zeta_{\mathrm{HEX}} = \frac{|\dot{m}_{\mathrm{cold}}((h_{\mathrm{out,cold}} - h_{\mathrm{in,cold}}) - T_{\mathrm{amb}}(s_{\mathrm{out,cold}} - s_{\mathrm{in,cold}}))|}{|\dot{m}_{\mathrm{warm}}((h_{\mathrm{out,warm}} - h_{\mathrm{in,warm}}) - T_{\mathrm{amb}}(s_{\mathrm{out,warm}} - s_{\mathrm{in,warm}}))|} \tag{9}$$

For the compressors and the cryogenic pump the exergetic efficiency ζ_{comp} and ζ_{pump} can be calculated with the following equation, with $\dot{m}$ representing as the mass flow, e the specific entropy and P_{in} the power input: [9]

$$\zeta_{\mathrm{comp,pump}} = \frac{\dot{m}\,(e_{\mathrm{out}} - e_{\mathrm{in}})}{P_{\mathrm{in}}} \tag{10}$$

To determine the efficiency of the turbine ζ_{turb} the following equation can be used, with $\dot{m}$ representing as the mass flow, e the specific entropy and P_{out} the power input: [9]

$$\zeta_{\mathrm{turb}} = \frac{P_{\mathrm{out}}}{\dot{m}\,(e_{\mathrm{out}} - e_{\mathrm{in}})} \tag{11}$$

2.2. Liquid Air Energy Storage

Liquid Air Energy Storage LAES can be classified as an electrothermal energy storage system, storing energy as a temperature difference between two thermal reservoirs. The principle of ETES storage can be described in such a way that work is extracted from the system by transferring thermal energy from the higher-temperature reservoir to the lower one, as described in section 2.1. And for the charging mode, this process is reversed by transferring the thermal energy from low to high temperature.[10]

The principle of this energy storage is mainly based on three steps shown in fig.2: liquefaction of gaseous air, storage of liquid air in tanks and expansion of liquid air through turbines to generate power. The following section, the main process steps of LAES are described in more detail by O'Callaghan and Donnellan [2].

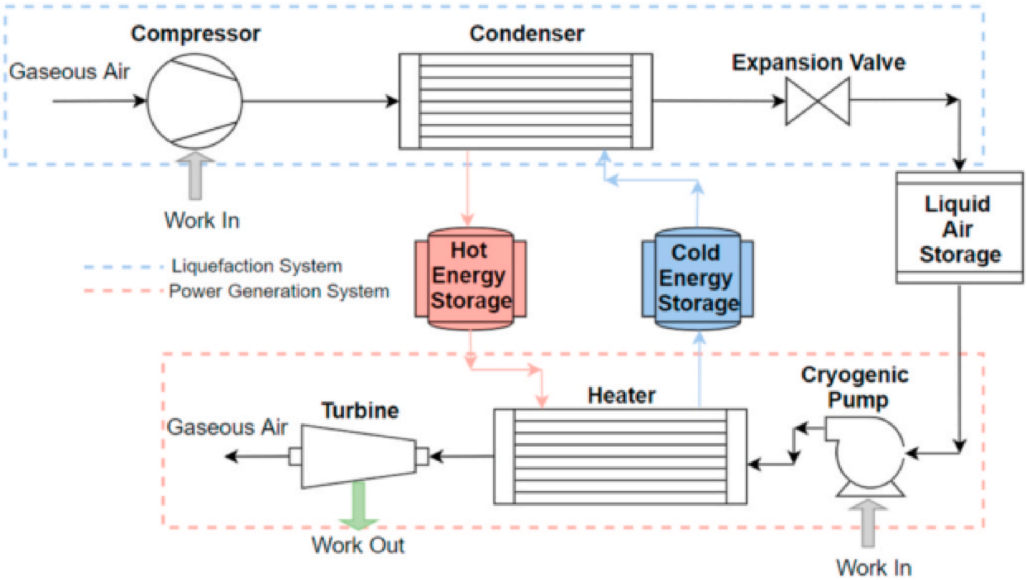


Figure 2.: *Baseline of the LAES system with its main components. [2]*

Each process step consists of the following main components:

- charging cycle: compressor, heat exchanger, cold box, throttle, expander
- storage: hot storage, cold storage, liquid air storage tank
- discharging cycle: expander, preheater, evaporator, cold box, cryopump

The idea of liquefaction of air is based on the Joule-Thompson effect. Due to the expansion after the throttling, a reduction of the velocity of the gas molecules can be achieved, leading to the cooling of the gas. The Joule-Thompson effect works in such a way that the molecules adhere to each other due to the reduction in velocity and thus, the cooled gas becomes liquid. It is important to note that gaseous air can only be liquefied if the pressure and temperature are below the critical points of -140.7 °C and 37.2 bar. The advantage of liquid air is that air liquefaction plants can be located anywhere without geographical restrictions. Moreover, this technology uses ambient air as the main heat transfer medium, which is available in unlimited quantities and free of charge.[11]

To generate electricity from liquid air, a pressure and temperature increase of the liquid air takes place. By doing this, the liquid air vaporizes and is converted into electricity by the turbines. Thermal energy is stored both in a hot and a cold TES. During the charging phase, the air is compressed to the supercritical state and the heat recovered from the compression of ambient air is later used in the intermediate heating in the turbine stage. In the discharging phase, the cold recovered during the evaporation of the air is stored and can be used for cooling the main stream.

Fig. 3 shows the three sections of a LAES system according to its mode of operation. In the charging mode, the air is liquefied using electric power during periods of low power demand. Then, liquid air and thermal energy are stored in the insulated tanks. In the discharging mode, liquid air is used to generate electric power during periods of high-power demand[1].

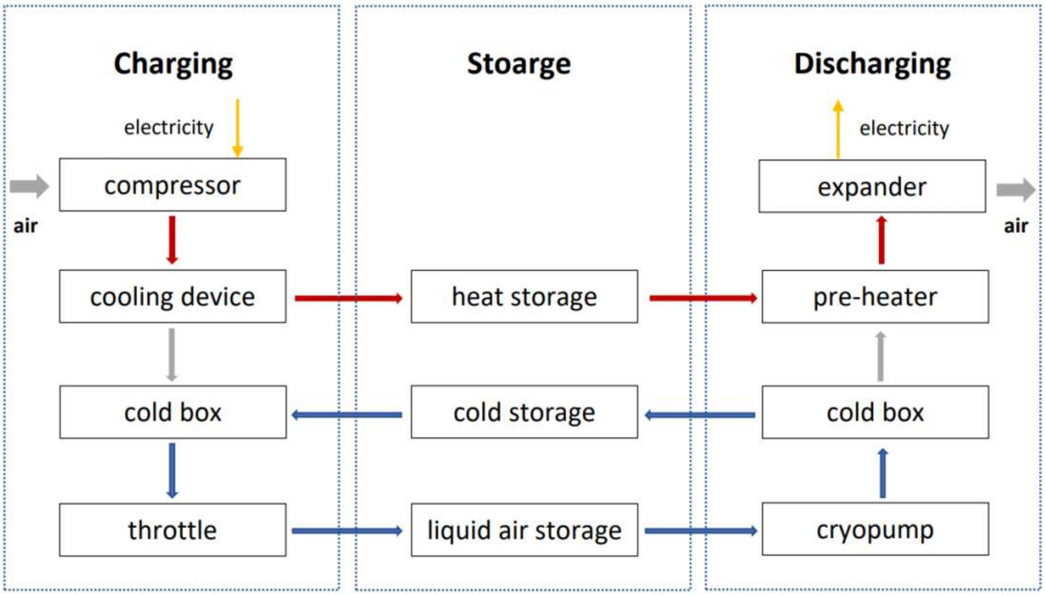


Figure 3.: *Schematic diagram of the LAES system with the main components and flows; adapted from [1]*

In the liquefaction unit, ambient air is pressurized in a multistage process, while the thermal energy produced in the compression stage is transferred to a heat transfer medium. This high-temperature heat transfer fluid in the thermal storage is utilized later in the discharging section. The compressed air then passes through the cold box representing various heat exchangers. During this process, the air is split into two streams. The main stream is cooled in counter-current flow by the colder non-liquefied fraction of the air, which is reintroduced in the heat exchanger after the phase splitter. The main stream is further cooled by the cold stored in the cold storage tank, which is recovered from the evaporator in the discharging phase. After the cold box, the cold compressed air is directed to an expander and throttle, thereby cooled and partially liquefied. The gaseous air fraction is directed back to the heat exchanger, while the liquid air is stored in a tank.

In the discharging section, the liquid air is raised to high pressure by a cryopump before it is evaporated and heated up. The released cold exergy obtained in the evaporator is then stored in the cold storage, which is used in the charging phase for cooling the main stream in the liquefaction unit. In the last section, the air is expanded in a multistage expander unit with intermediate heating devices, whereas the recovered thermal energy from the charging section is again used for the intermediate heating.[1]

2.2.1. Liquefaction cycles

By liquefying a gas, the volume can significantly be reduced. Hence the liquid can be stored in smaller tanks, at atmospheric pressure and lower cost. The described liquefaction systems below follow similar steps, e.g., single or multistage compression, cooling, condensation and throttling, as shown in fig. 4.

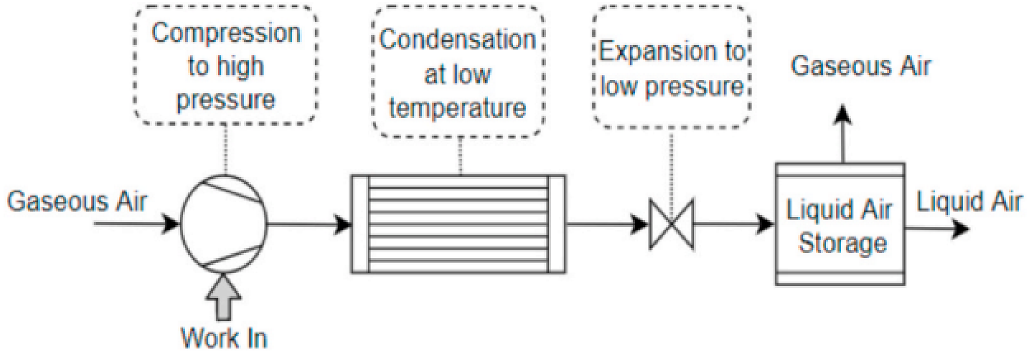


Figure 4.: *Schematic of the basic liquefaction cycle. [2]*

Ambient air enters the compression stage resulting in a significant rise of temperature, whereby this thermal energy is stored for later use in the subsequent power generation cycle. In the next step, the heat exchanger cools the high-pressured gaseous air and condenses it at a cryogenic temperature. The now liquefied air flows through a throttle valve, where it gets expanded. The temperature is further reduced, causing a fraction of liquid air to evaporate, resulting in a gaseous-liquid air mixture. The liquid fraction is then directed to a low-pressure vessel and stored until it is required. The most common liquefaction methods mainly studied in literature are Linde-Hampson, Claude and Kapitza cycles.[2]

In the Linde-Hampson cycle, air enters the vapor compression refrigeration process and is compressed to high pressure at constant entropy. The high-temperature and high-pressure gaseous air are then cooled and condensed in a heat exchanger at constant pressure. The now liquefied air passes through the isenthalpic Joule-Thomson expansion valve, causing it to be further cooled and the pressure to be reduced. Due to this pressure reduction, a fraction of the liquid air evaporates, resulting in a mixture of gas and liquid. The gaseous fraction is directed back to the heat exchanger to liquefy the incoming high-pressure air. The process of liquefaction by Linde-Hampson is illustrated in fig. 5. [2]

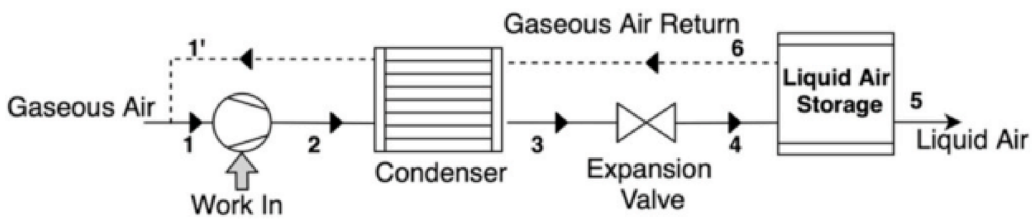


Figure 5.: *Liquefaction cycle based on Linde-Hampson process. [2]*

The thermodynamic cycle for the Linde cycle is shown in fig.6. The derivates of Linde-Hampson cycles, such as Claude or Kapitza, look similar in the diagram. In the liquefaction process, the temperature of the liquid air must be low enough before it enters the Joule-Thompson expansion valve. If the temperature is too high, the liquid-gas mixture cannot be obtained. The result of this situation is illustrated in fig. 6 in stages 3' and 4' of the enthalpy curves.[2]

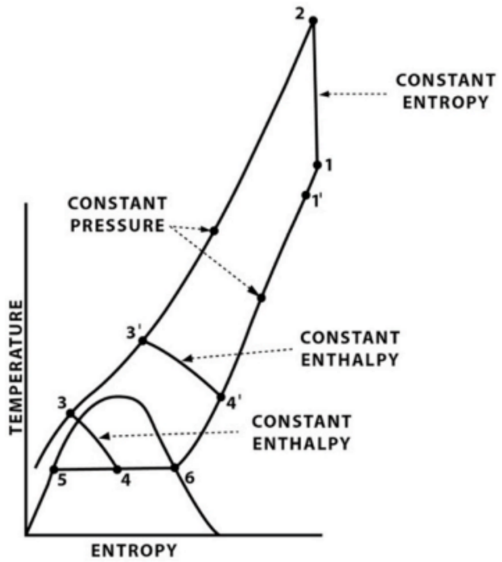


Figure 6.: *T-S diagram of the Linde-Hampson cycle. [2]*

One parameter to describe the performance of LAES systems is the liquid yield Y, which is defined as the ratio of liquid airflow $\dot{m}_{\mathrm{L}}$ being produced, divided by the total compressed air flow $\dot{m}_{\mathrm{C}}$. The relation is given by the equation (12) below, where $\dot{m}_{\mathrm{L}}$ is the mass of liquid air and $\dot{m}_{\mathrm{C}}$ is the mass of the total compressed air.

$$Y = \frac{\dot{m}_{\mathrm{L}}}{\dot{m}_{\mathrm{C}}} \tag{12}$$

According to O'Callaghan and Donnellan [2], the Linde-Hampson cycle is infeasible for commercial scale LAES due to the great irreversible losses caused by the expansion device. By choosing the Claude cycle, fig. 7, the undesirable effect of energy loss occurring in the Linde-Hampson cycle can be mitigated. Therefore, a fraction of the gas stream is removed and is directed back in a bypass line through an expansion turbine to the heat exchanger. As the expansion reduces the temperature significantly, this stream is further used to cool the incoming air. The main stream is cooled and condensed by two more heat exchangers and further directed to the Joule-Thomson expansion valve. The reduction of pressure caused by the valve makes a part of the liquid air evaporate, again resulting in a liquid-gas mixture. The gaseous fraction is directed back to the heat exchanger for cooling the incoming high-pressure air.[2]

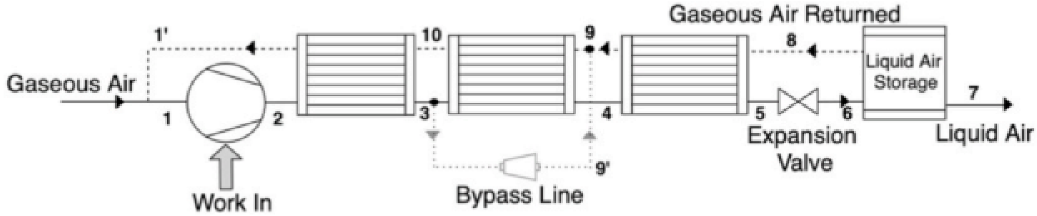


Figure 7.: *Liquefaction cycle based on the Claude process. [2]*

The Kapitza cycle, shown in fig. 8, is a derivative of the Claude cycle. The only difference is that the third heat exchanger of the Claude system is removed. As the temperature reduction achieved by the third heat exchanger is minimal, the system is reduced to two heat exchangers. [2]

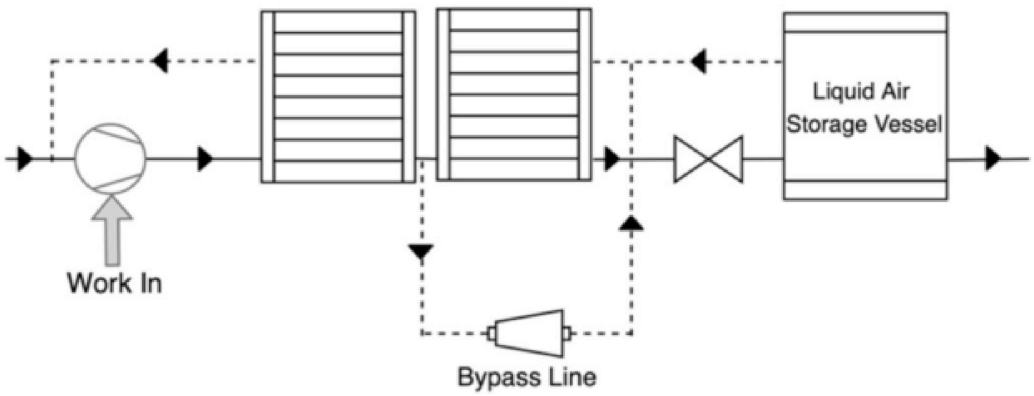


Figure 8.: *Liquefaction cycle based on the Kapitza process. [2]*

2.2.2. Power generation

For the part of power generation, it is referred to O'Callaghan and Donnellan [2]. For converting energy stored in the liquid air to electricity, a power cycle is required. The process steps of the power generation using liquid air are shown in fig. 9. At first, liquid air from the storage tank is pumped to high pressure using a cryogenic pump. Then the air is superheated using the heat recovered from the liquefaction process. The evaporation and superheating results in a significant volume increase of 700 times. This air stream is used to generate power by passing through the multistage turbines. Due to the temperature decrease of expansion stages, there is a need to heat the air stream between the turbines to maintain a high power generation efficiency. The process of heating and expansion is repeated several times before the air is finally released into the atmosphere at ambient temperature and pressure.

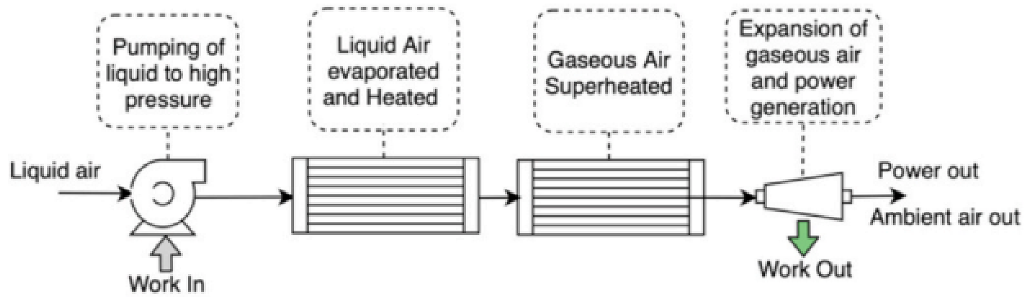


Figure 9.: *Schematic of power generation with direct expansion process. [2]*

2.2.3. Case study

Due to the high interest in the use of LAES, pilot and demonstration plants have been constructed in recent years. Highview LAES systems are thermo-mechanical systems that thermally store energy and charge it mechanically. According to Morgan, Nelmes, Gibson, *et al.* [10], a relatively low round-trip efficiency of only 8% was achieved on the pilot plant of the first LAES plant by Highview Power. The low performance is due to the small size of the plant. At the commercial scale, the plant would achieve round-trip efficiencies of over 50%. [10] The first ever LAES pilot plant by Highview Power was a 350kW/2,5 MWh facility in the UK, which was put into operation in 2011. After successfully demonstrating the cycle, construction began on much larger plants to provide reserve power for the grid. Several projects in the 50 MWel/250-400 MWh class and more are currently under development at Trafford Energy Park in Manchester.[12]

Process description

The LAES process from Highview Power is being used as the basis for this work. In the liquefaction process, the compressed air is expanded in a modified Claude cycle refrigerator, using the recycled energy from the evaporation stage to enhance the performance of the cycle. The resulting liquid air is then stored in low-pressure tanks. When energy is required, the liquid air is pumped to high-pressure and is vaporized, whereas the cold energy is stored for later use in the liquefaction process. The regasified air is then further heated with the thermal energy from the compression and expanded in the multistage expander with reheating devices between the turbines, which drive the generator. The simplified flow diagram of Highview's pilot plant is shown in fig. 10. In the following section, the energy-storing method process steps are described in detail, referring to Hennemeyer and Szastok [12].

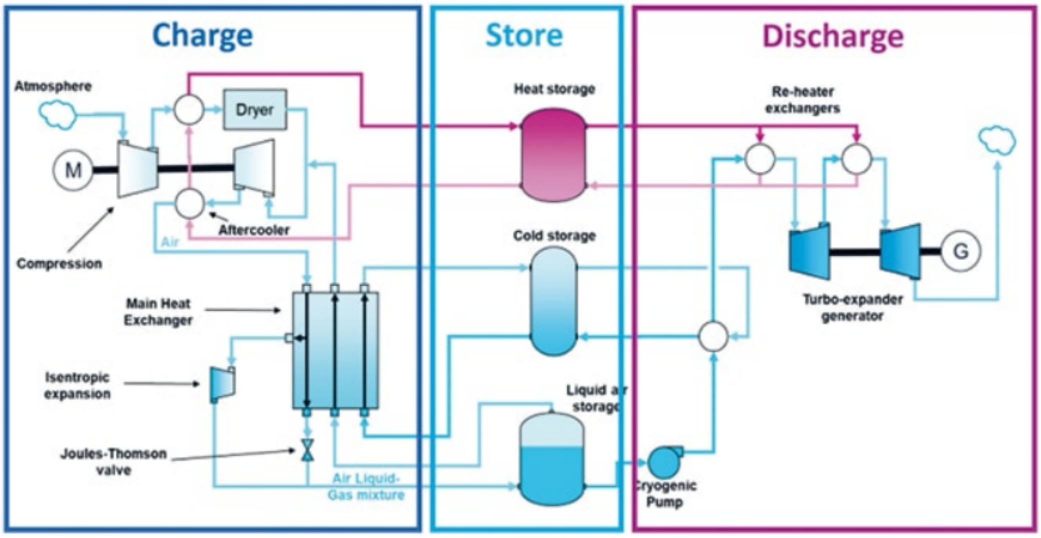


Figure 10.: *Schematic diagram of Highview LAES process in the charging, storing and discharging mode. [12]*

Charging phase

In the liquefaction process, atmospheric air is compressed to intermediary pressure of 17 bar and cooled by a thermofluid. In the absorption purification unit, the carbon dioxide and water are removed before entering the high-pressure compression stage of 60 bar. The gaseous air is then cooled again with a water/glycol mixture and directed to the main heat exchanger, further lowering the temperature. From this point on, the air is split into two streams: A part of the stream flows to the cryo-expander, while the main stream passes through the Joule-Thomson valve, where it is throttled to 17 bar again. The mixture of gaseous and liquid air from the two streams is collected in the phase separator. The gaseous phase acts as one of the cold streams in the main heat exchanger to cool the incoming high-pressure air and is directed back to the second compression stage after the main heat exchanger. The cooling of the main heat exchanger is therefore provided by the gaseous fraction from the separator and the dry air stream from the cold storage. On the other hand, the liquid air is stored in a storage tank. [12]

Discharging phase

In the discharging phase, liquid air from the storage tank is pumped to the evaporator by a high-pressure cryogenic pump. The cold recovered from the evaporator is stored in the cold storage tank to further provide cooling for the main heat exchanger, as described in the charging process. The now evaporated air flows through a preheater to the multistage turboexpanders, which are coupled with a generator. Before entering the next turbine, the air is reheated again. The reheating is carried out by the recovered thermal energy from the compression stages of the charging process, which is stored in the heat storage tank. At the end of the process, the air is released into the atmosphere.[12]

2.3. Thermal Energy Storage

Thermal energy storage TES is used to store heat and cold to be used later at different temperatures or places. The energy storage process consists of charging, energy storage and discharging, illustrated in fig. 11. TES can be divided into direct and indirect systems. In direct systems, the heat transfer medium is also used as the storage material, while in indirect systems, the heat is transferred from the heat transfer medium to a separate storage medium.[1]

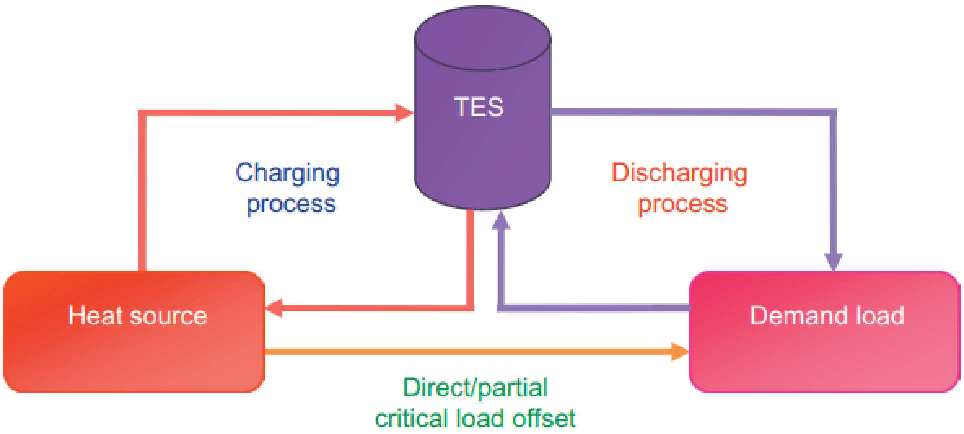


Figure 11.: *Simple schematic of TES cycle. [13]*

For the design of a TES system, the following main requirements should be met:[14]

- high-energy density of storage material
- good heat transfer between the HTF and the storage material
- mechanical and chemical stability of storage material
- low thermal losses during the storage period

By implementing an energy storage system, the following benefits can be obtained:

- reduction of capital and operational costs
- greater energy efficiency
- less pollution and CO_2 emissions
- increased system performance and reliability

Furthermore, TES can be categorized based on their properties in three groups: latent, sensible and thermochemical storage systems. The thermochemical storage principle relies on heat storage as part of a chemical reaction. This kind of storage is out of the scope of this thesis.[14] In this work, the focus is directed toward the latent and sensible storage systems.

2.3.1. Latent heat storage

Latent heat storage is based on the phase transition of the storage material for storing or discharging thermal energy. During the phase change process, which normally occurs near isothermal conditions, a large amount of thermal energy can be stored in the storage material.[1] The phase-change enthalpy is, therefore, the amount of energy that a substance requires to change its state of aggregation or its internal structure. During this transition process, the temperature of the substance does not change since all the energy supplied must be used for the phase change. In fig. 12, the difference between sensible and latent heat storage is illustrated.

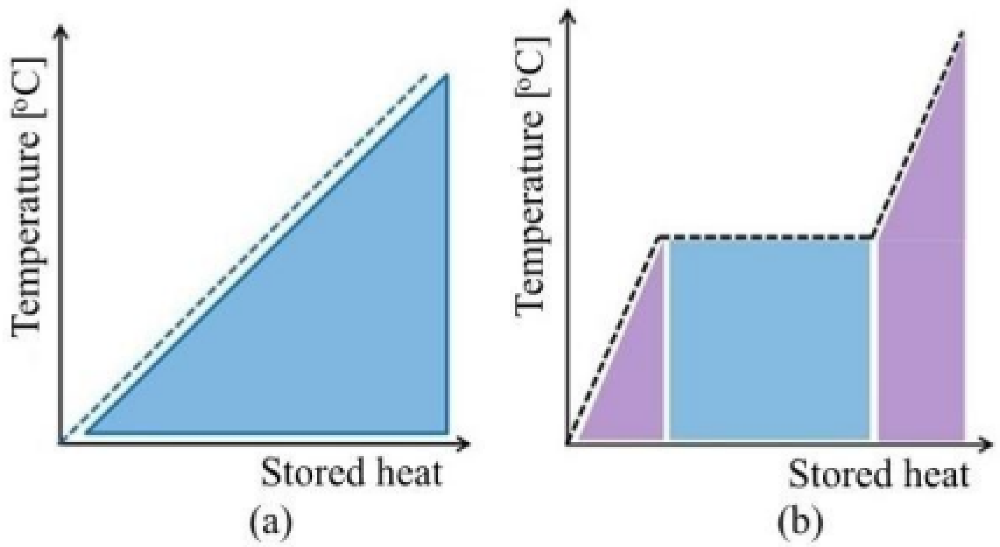


Figure 12.: *T-Q Diagram of the two energy storing methods: a) sensible heat energy storage, b) latent heat energy storage. [15]*

It is easy to see that the phase change enthalpy is very high, which allows a significantly higher amount of stored heat at a lower storage temperature. The amount of energy required for a phase change is given by equation (13), whereas ΔH_{PT} is the amount of heat stored in the material, $\dot{m}$ the mass flow of storage material and Δh_{PT} is the phase transition enthalpy:

$$\Delta \dot{H}_{\mathrm{PT}} = \dot{m}\, \Delta h_{\mathrm{PT}} \tag{13}$$

However, since not only energy in the form of latent heat, is stored in a latent heat storage system, sensitive components must also be included in calculating the total amount of heat stored. The total amount of heat Q stored during a storage process can be determined using equation (14), where m is the mass, c_p the specific heat capacity and h_{PT} the enthalpy of phase change. The sensible heat before the phase change is described in the first term and the heat after the phase change is described in the last term.[16]

$$Q = \int_0^{PT} m\, c_p\, dT + m\, \Delta h_{PT} + \int_{PT}^{1} m\, c_p\, dT \qquad (14)$$

Liquid Air Energy Storage

The original LAES system developed by Highview Power uses latent thermal energy for storing the liquid air. As described in chapter 2.2, ambient air is cooled to cryogenic temperatures using electricity. Due to the phase transition of the gas to a liquid, the volume of liquid air is decreased significantly. The liquid air is pumped to higher pressures and directed to a vaporizer at peak times. Through the expansion of the gaseous air, electricity can be generated in the turbine stages.[17]

2.3.2. Sensible heat storage

The method of a sensible storage system is based on storing thermal energy by heating or cooling a storage material, which can be liquid or solid. During the process of charging and discharging, the heat capacity and the temperature change of the storage medium are used for energy storage.[15] In table 1 the physical properties of the storage media are listed. The physical dependence of the heat being stored is given by the following equation (15), whereas Q refers to the stored heat, m is the mass of the heat storage medium, c_p the specific heat and ΔT the temperature difference:

$$Q = \int_0^{1} m\, c_p\, dT \qquad (15)$$

An interesting point to note for sensible storage systems is that the relatively low thermal capacity of the sensible storage material is usually balanced by the high-temperature difference. Due to this reason, sensible storage materials are largely preferred for high-temperature applications at large temperature fluctuations.[13] Water is shown to be the best sensible heat storage medium due to the high specific heat and low cost. However, oil, salt or sand are the commonly used storage media at higher temperatures.[15]

Table 1.: *Physical properties of storage media. [18]*

Storage material	Unit	SiO_2 300-600 °C	Air 0-20 °C	Water 10 °C
thermal conductivity	W/(m K)	1.5–2.4	0.02	0.59
specific heat capacity	MJ K/m^3	1.3–1.6	0.0012	4.15
volumetric density	10^3 kg/m^3	1.25	0.0012	0.999

Packed-bed thermal energy storage

A packed-bed storage system uses the heat capacity of the packed, particle-sized material to store energy. A heat transfer fluid, usually air, is circulated through the bed in order to add or remove energy. During the charging cycle, hot air flows through the packed bed to heat the solid storage medium, while during discharging, the incoming cooled air is heated by the packed bed.[19] There is already a wide range of publications related to models for sensible heat storage in fluidized beds, including the sandTES technology, which will be further described in the next section.

2.4. SandTES technology

The Active Fluidized Bed Thermal Energy Storage (sandTES) is a high-temperature energy storage system using active fluidized bed technology and sand as the heat storage medium. SandTES is operable at temperatures over 600°C and can be used in a wide range of applications. The sandTES technology enables heat transfer between a heat transfer medium flowing through tubes and the storage medium in a fluidized bed. The driving force for transporting the fluidized storage medium through the heat exchanger (HEX) is the height difference between the inlet and outlet of the fluidized bed. The resulting pressure gradient sets the storage medium in motion.[20] In the next sections, the basic principle of the technology of sandTES is described.

The sandTES HEX technology combines the counter-current heat exchanger and the fluidized bed technology, as described in [20] and shown in fig. 13.

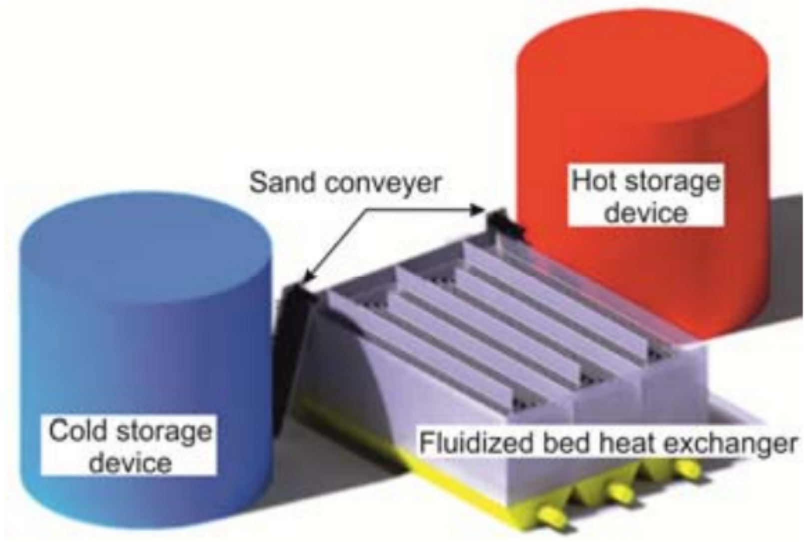


Figure 13.: *Simplified sketch of the sandTES storage system including the cold and hot storage device with the fluidized bed heat exchanger. [20]*

In the charging process, sand from the cold storage is transported to the fluidized bed heat exchanger by a conveying system. Fluidization of the sand is carried out by air blown into the HEX at the bottom. The now fluidized sand is then heated up by the HTF, which flows inside a tube bundle within the HEX. The counter-current heat exchanger works in such a way that sand moves from the cold bunker through the HEX to the hot bunker while the HTF inside the tubes flows in the opposite direction. During discharging, the process is the same, only with different flow directions of the sand and the HTF.

2.4.1. Heat storage medium

Sand is made of the mineral quartz, which is used as the storage medium for the sandTES HEX technology. In [21] it is shown that quartz sand is suitable as the thermal storage medium at cryogenic temperatures in a liquid air energy storage system, having a storage efficiency of almost 29 %. It is known that quartz sand is a promising storage medium for large-scale applications due to its low prices and wide temperature ranges. If particles are too small, it is hard to fluidize them. Considering the material's density, the particle diameters used for the sandTES technology are in the range of 50 to 100 µm. As shown in fig. 14 the particle size, based on Geldart, is classified into groups A and B. Nevertheless, the particle diameter used for the sandTES-HEX should be around 100 µm, as sieving becomes more costly for smaller sizes. [20]

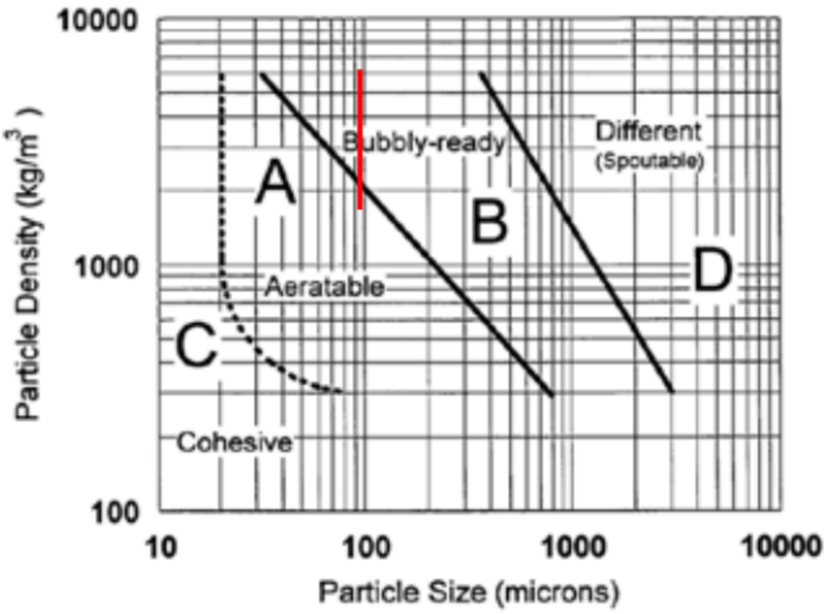


Figure 14.: *According to the Geldart classification, the particle size is in the group A and B. [20]*

2.4.2. Heat exchanger

According to P. Steiner [22], a counter-current HEX seems to be the best option for using fluidization technique for particle transport. To fluidize the particle bed, there is a need to blow air through the bottom of the bed, hence resulting in a particle-air suspension. On the one side, a particle mass flow is inserted into the HEX, while on the other side, the same mass flow is removed at a different height. This results in a pressure difference between the in- and outlet. The sandTES heat exchanger is illustrated in fig. 15, where the black arrows show the sand flow and the blue arrows represent the fluidization airflow. The valve at the top is configured to create an air cushion for controlling the sand pressure below. A tube bundle is installed inside the HEX, where the HTF flows through it. In order to determine the optimal tube bundle configuration for a maximum heat transfer coefficient, experiments are conducted. According to Thanheiser, Haider, and Schwarzmayr [23], helically finned tubes with transversal sand flow proved to be the best configuration. A more detailed description of the HEX can be found in the reference from P. Steiner [22] and Thanheiser, Haider, and Schwarzmayr [23].

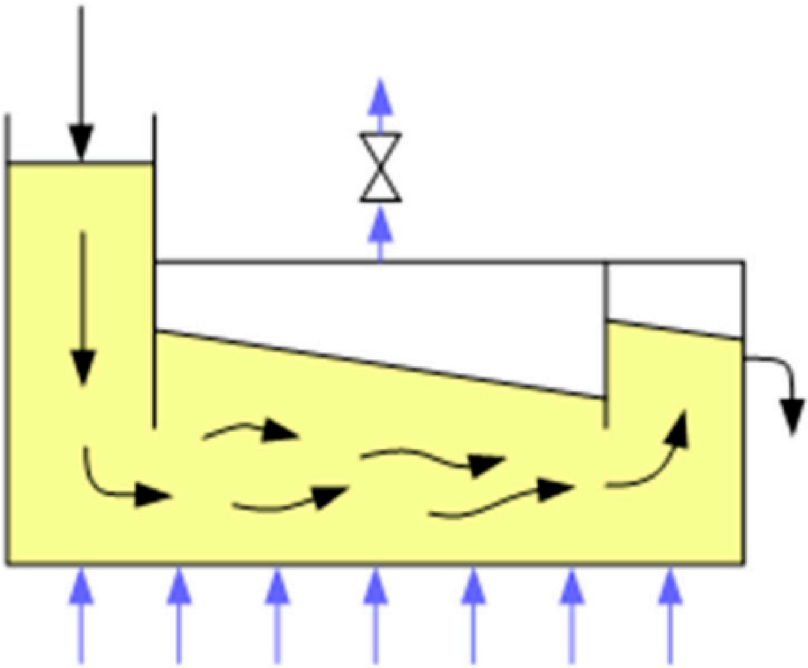


Figure 15.: *Sketch of the sandTES fluidized bed HEX with the direction of the HTF flow and the air flow. [23]*

2.4.3. SandTES process description

To better understand the process, a simplified flow sheet is illustrated in fig. 16. For fluidization, the air is blown into the HEX. Therefore, the system also comprises additional equipment, such as blowers, recuperators, filters and induced draft fans.[22] According to [24], fluidization is realized by inserting a gas stream upwards through a bed of particles. This loosens and moves the particles, making the bed behave like a fluid.

As described in [22], for the charging process the sand from the cold silo is transported by a conveyer into the U-shaped HEX. The HTF flowing through the tube bundle then heats the fluidized particles. The now hot particles are again transported via a conveyer to another storage tank. The discharging process reverses the flow directions of the heat transfer medium and of the HTF. Recuperators are used to recover the heat from the exhausted fluidization gas. The exhausted air finally leaves the system through the filter and the induced draft fan. Medium-fine to fine particles are applied for the present sandTES technology, which could lead to health problems. To solve the problem, fine particles are removed from the exhaust air with filters.[24]

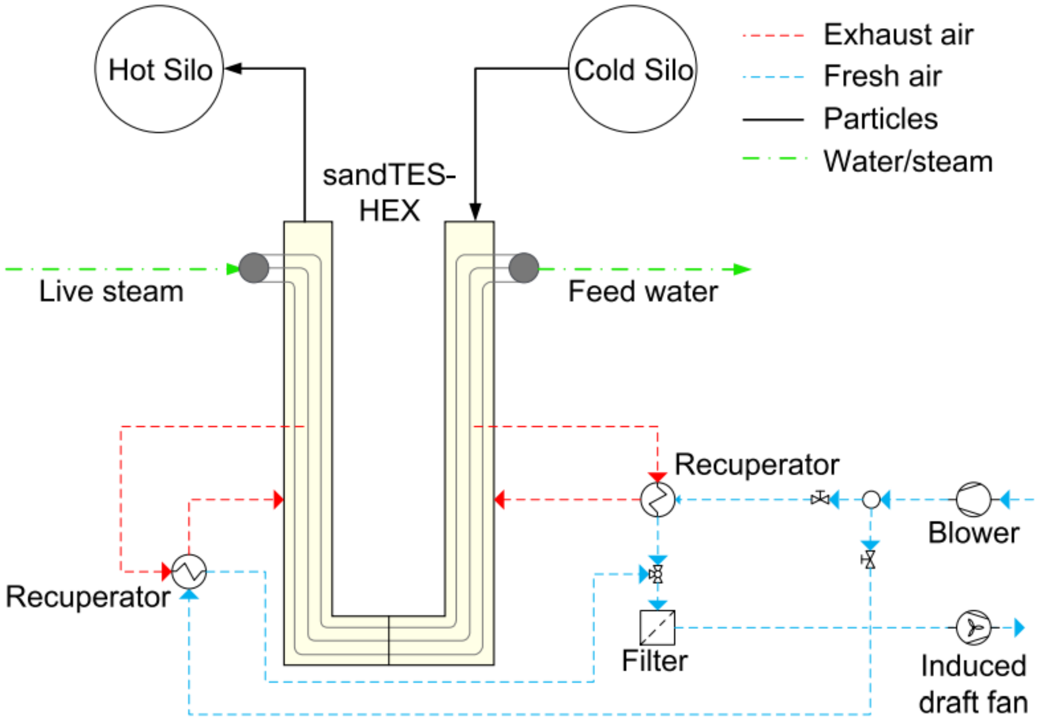


Figure 16.: *Sketch of the sandTES fluidized bed HEX with its main components. [22]*

2.4.4. Advantages of the sandTES technology

Firstly, the storage medium sand is a cheap, non-hazardous and readily available material. Sand in the fluidized state ensures high heat transfer coefficients. The low thermal conductivity of sand in the non-fluidized state during the storage phase reduces the heat loss to the environment. Moreover, the system can be operated at high temperatures without changes in the physical properties of the storage material. Quartz sand also has a high heat capacity compared to other solid materials, which ensures high energy storage densities. The sandTES concept has great potential for combining other energy generation technologies already available on the market.[25] The fact that the energy is stored without high pressure enables simplifications both in the area of safety and plant engineering. Another advantage is that sand can be transported in many different ways. According to the situation of the plant, any appropriate conveying technology can be used for sand transportation.[26]

3. Methods

3.1. Patent research

One of the objectives of the thesis is to research the Liquid Air Energy Storage System in combination with thermal storage. The purpose of this research is to determine whether solid material as the direct heat transfer medium is already patented. The aim, in the end, is to present an innovation of the LAES application with the thermal storage device, sandTES. The methodology includes literature research in the field of LAES technology. Therefore, all patents related to LAES systems are being examined. To conduct comprehensive research, the patent database 'Espacenet' is being used, a worldwide database developed by the European Patent Office.

At first, all patents assigned to the company Highview are being reviewed and studied, as many important patents related to LAES are held by Highview. Screening through all the current patented inventions regarding LAES is being done and relevant ones are sorted out and studied in more detail. After the research of the patents assigned to Highview, other patents from the USA, Europe and worldwide patents are being studied for the research. Therefore, the patent database 'Espacenet' is used for the research and some search criteria are applied. To ensure that the search includes all patents that may be relevant to the current invention, the search result is narrowed down to the following keywords:

- cryogenic energy storage
- liquid air storage
- liquid air energy storage

The search furthermore focuses on patents from EP, US and WO, which in the end, resulted in a total of 211 relevant patents. EP stands for European patent, US for US patents and WO refers to patents from the World Intellectual Property Organization.

A first screening through all the current patented inventions related to LAES is being done, wherein the patents only relating to single engines or Liquid Natural Gas and Cryogen Carbon Capture systems are not deemed relevant for the thesis and are therefore being filtered out. Then, more detailed research is being conducted by focusing on the use of a TES system in a cryogenic energy storage system. The search is further narrowed down to solid components in the TES, which are integrated into a LAES system. Relevant inventions for the thesis are summarized at the end. To better understand the relevant inventions, for each patent, a short description with figures describing the technologies is drawn up, and the claims are studied. Some patents comprise more than 80 claims, most of which are redundant or do not relate to the integration of TES into a LAES system. Hence, only the main most important claims are being sorted out in this research. In table 4, the result of the analysis containing all the relevant patents is listed.

3.2. Simulation and calculation with EBSILON

The second aim of the thesis is to model a system that combines the energy storage system LAES with the thermal storage technology sandTES. In this work, two models are simulated: a LAES system without a thermal storage device and a LAES system combined with the thermal energy storage technology of sandTES.

There are a variety of software programs that can be used for the simulation of the described LAES implementations. To successfully simulate the complex system, many issues have to be considered. The software must provide extensive material data and a component library for describing gases and vapor-liquid mixtures as accurately as possible. To determine the efficiencies of the system, complex calculations are made in EBSILON. A model from Denner [3] for designing the Highview LAES system and the sandTES technology from Striok [27] have already been successfully simulated with this program. Therefore, the iterative software EBSILON Professional was also chosen for the simulation of the present LAES system with the sandTES HEX technology. The software offers a good and intuitive graphical user interface and is suitable for the simulation and calculation of energy-related problems.

In order to compare the process, a thermodynamic evaluation of the LAES system was carried out. All results that are important for the evaluation of the system, such as liquid yield, round-trip efficiency, exergy losses, etc., are listed in table 10, 11 and 14. These values were all calculated using the program Ebsilon. Formulas from chapter 2 are used for the respective calculations. In Ebsilon, the corresponding formulas are simply entered in the calculation area and the values are calculated automatically.

4. Simulation

4.1. Basics of EBSILON

EBSILON Professional, a simulation program of the company STEAG Energy Services GmbH, was developed to plan and optimize energy and power plants. EBSILON is a program calculating stationarily and transient processes cannot be simulated. Therefore, the simulations on EBSILON for the thesis were done time-independent. For this reason, the charging and discharging of the LAES system take place at the same time. In a steady state, the start-up time, pauses, stops and their resulting energy losses are being neglected for the present simulations.

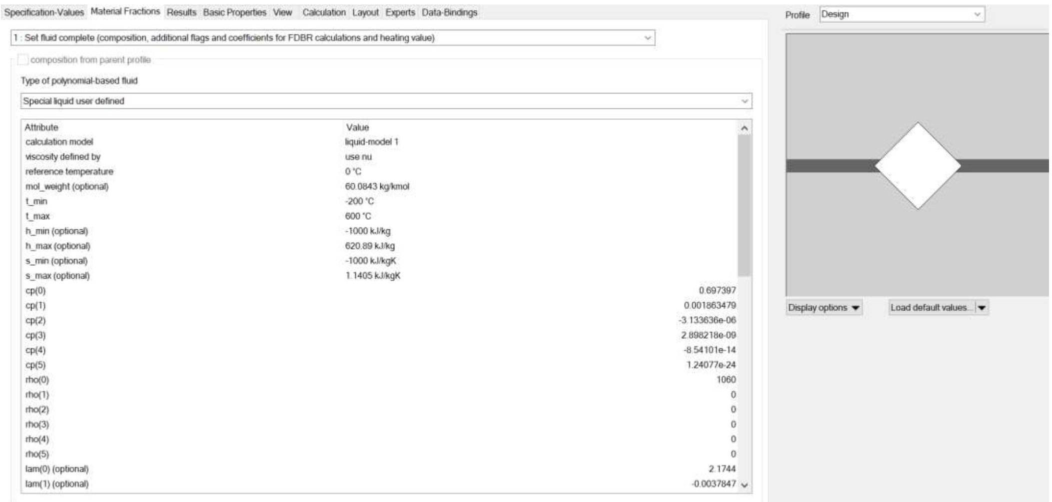


Figure 17.: *Definition of quartz sand in EBSILON.*

EBSILON has a comprehensive component library, as well as a large number of working fluids and fuels that can be chosen for the current system. In table 2, an excerpt from the component library is shown, which includes all the components used for the simulation of the LAES system in this thesis. The predefined working fluids and fuels can easily be selected from the data library and there is also the possibility to redefine user-specific substances or components. In the case of silica sand SiO_2, the new material can be created in component 33, in which the material properties can be redefined, as shown in Fig. 17.

4.1.1. Controller

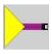
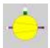
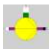
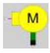
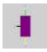
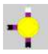
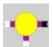
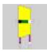
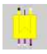
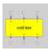
To adjust the process with all its possible states, a control device is required to regulate the mass flow, pressure or temperature of the system. This way, parameters, such as the mass flow of the air, can be manipulated without causing unwanted changes in other values. Since the various states influence each other, the manual adjustment of each particular state would be unfeasible, or too time-consuming. As performed in the LAES system without a thermal energy storage device, the parameter being controlled is the mass flow, while in the LAES system with the sandTES technology, the mass flow, as well as the temperature, are regulated with the help of the control device.

4.1.2. Boundary conditions

To compare the LAES systems, the same boundary conditions were set, with the ambient temperature T_{amb} at 293.15 K and the ambient pressure p_{amb} at 0.101 325 MPa. The working fluid, dry air, comprises nitrogen, oxygen and argon. The mass composition of ambient air is defined as follows: $x_{\mathrm{N2}} = 0.755\,626$, $x_{\mathrm{O2}} = 0.231487$ and $x_{\mathrm{Ar}} = 0.012\,888$. In reality, ambient air also contains CO_2 and water, which are neglected in the present simulations.[21]

All storage devices are operated in a stationary, isothermal mode. All the heat exchangers in the system have a pressure drop of 0.1 bar. The charging and discharging of the sensible storage are carried out by heat transfer and transport of storage mass from tanks with lower to those with higher temperatures or vice versa. In the case of latent heat storage, the phase ratios change in the storage tanks.

Table 2.: *List of all used components for the simulations on EBSILON.*

number	component	description
1		boundary value
24		compressor
8		pump
11		generator
29		motor
46		measured value input
12		controller
14		control valve
157		phase splitter
18		splitter
37		mixer
6		turbine
55		heat exchanger
33		input value
-		cold box

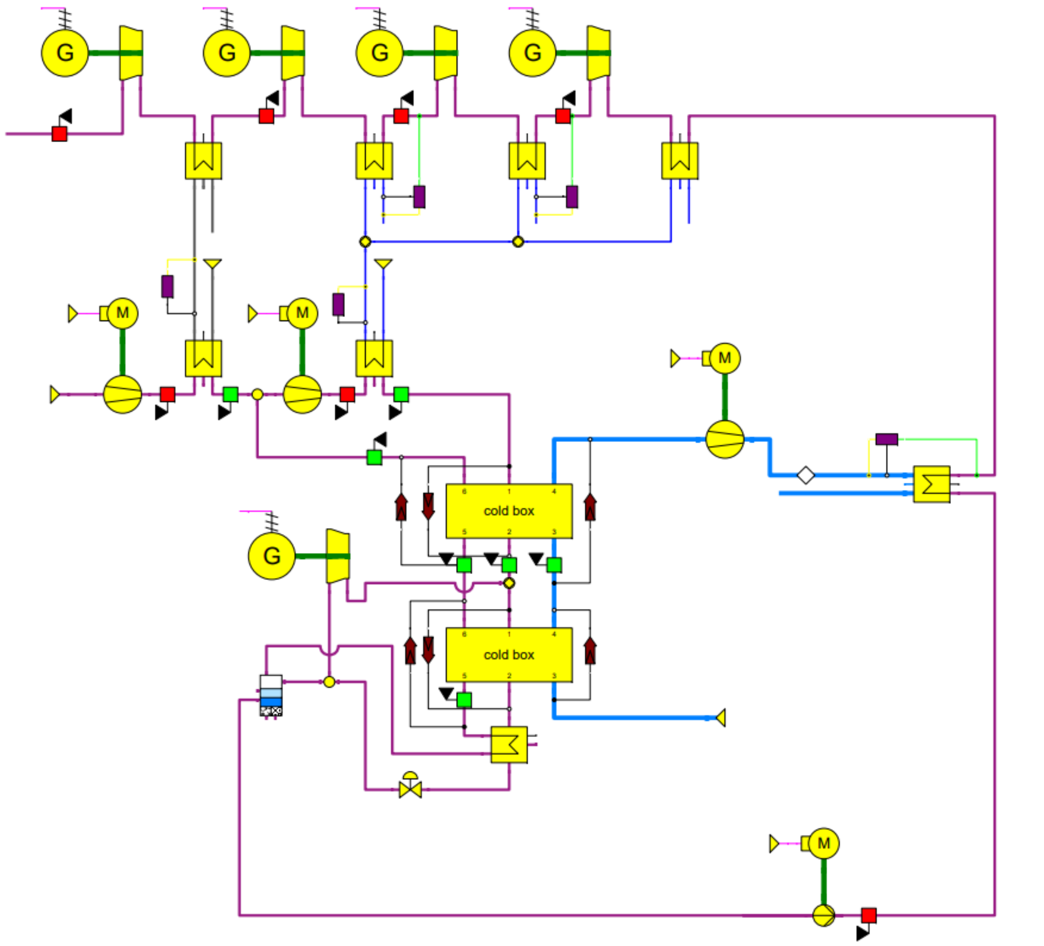


Figure 18.: *Model of the Highview LAES system from Denner [3].*

4.1.3. LAES system without thermal energy storage system

In the first simulation, a LAES system is implemented without any thermal energy storage device. For this model, the already prefabricated LAES model from Denner [3] based on Highview [12], illustrated in Fig. 18, was used as a basis for the present implementation. In the current simulation, all the heat and cold storage devices are removed, which are built in Highview's model, presented in the work of Denner [3]. The aim is to thereby demonstrate the importance of capturing, storing and recycling thermal energy on the LAES cycle efficiency. Without any energy storage systems, there is neither heat energy recovered from the liquefaction cycle nor cold exergy recovered from the expansion stage. As described in [12], the relation of energy recovery can improve the system performance significantly. On the one hand, heat energy from the cooling process is stored and used for the heating between the turbine stages. On the other hand, cold energy released from liquid air during evaporation is stored and used to support the cooling of the liquefaction cycle. Only this way an overall efficiency of 50-65 % can be achieved for the LAES system.

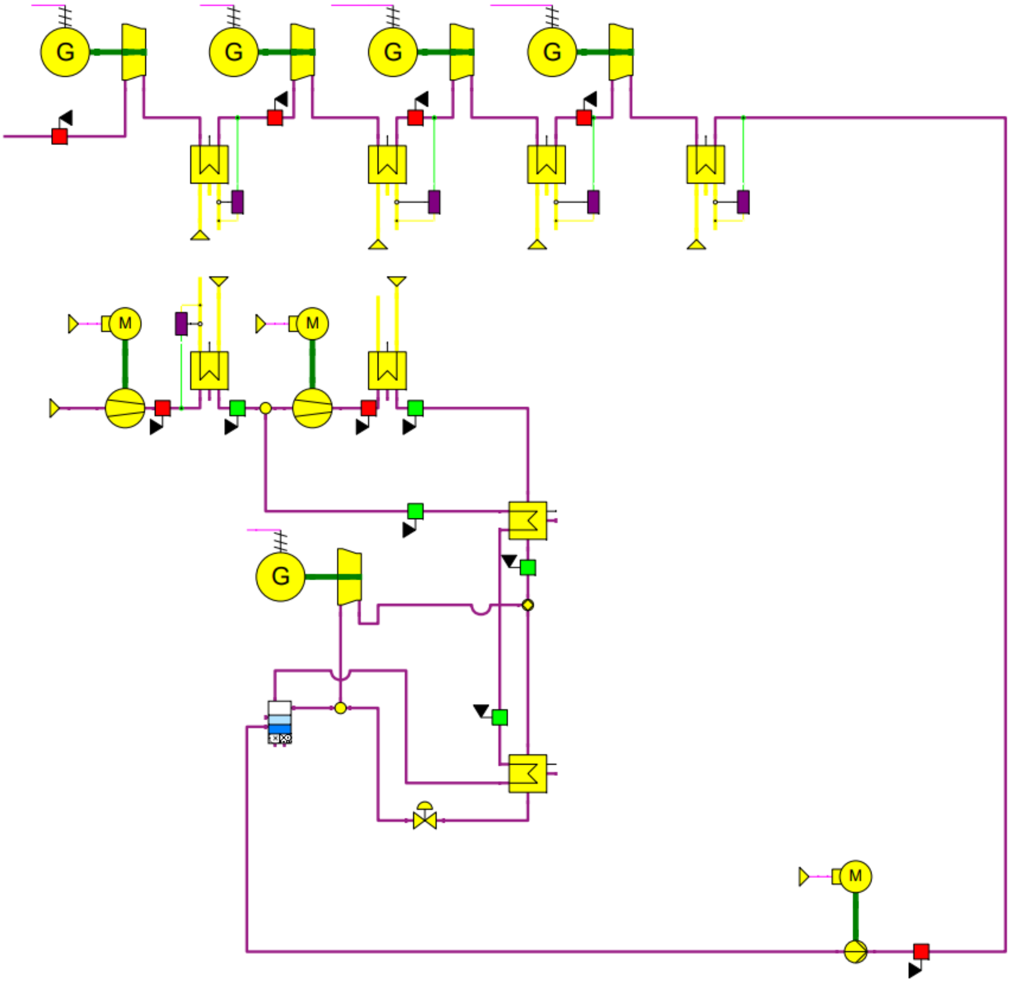


Figure 19.: *LAES model without thermal energy storage device.*

Firstly, the cold boxes, representing the main heat exchangers in Highview's LAES system, are being removed. Therefore, temperature measuring points need to be redefined in the streams. To not cause errors in the heat exchanger due to pinch point issues, temperatures need to be adjusted accordingly. No changes were made in the pressure values compared to the LAES system from Highview. One more heat exchanger is also being removed in the discharging phase, as in the present system, there is no need to recover cold energy from the evaporator. In the next step, all the implementations depicting the heat storage devices for heat recovery during discharging are being removed and the cold store for recovering cold energy from evaporation. Only ambient air is being used for cooling and heating up the air stream. As a result, there is a significant difference in the overall round-trip efficiency compared to the LAES systems, in which the thermal storage devices are included. In Fig. 19, the model without any thermal storage is illustrated.

4.1.4. LAES system in combination with sandTES technology

Also, the simulation for the LAES system with the integrated sandTES technology is based on the already published, largely idealized LAES process by Hennemeyer and Szastok [12]. The thermal storage system sandTES has already successfully been simulated with EBSILON in recent works, such as in [28]. For the thesis, a simplified sandTES model is therefore presented with quartz sand as the heat transfer medium. The model with sandTES technology represents another possible option for the implementation of a LAES system. As mentioned in the previous chapters, sand can be used in very high and low temperatures, which perfectly fits the LAES system. The material properties of silica sand are listed in table 3. The component with the newly defined material can be easily installed in the Highview LAES system in EBSILON. Other parameters, such as pressure settings and composition of air, stay the same as in the model [12]. Some modifications have been made to adjust to the new application with the sandTES technology. Due to pinch-point issues, the controllers for the temperature are adjusted accordingly. This new invention of a LAES system using the thermal energy storage sandTES is shown in Fig. 20.

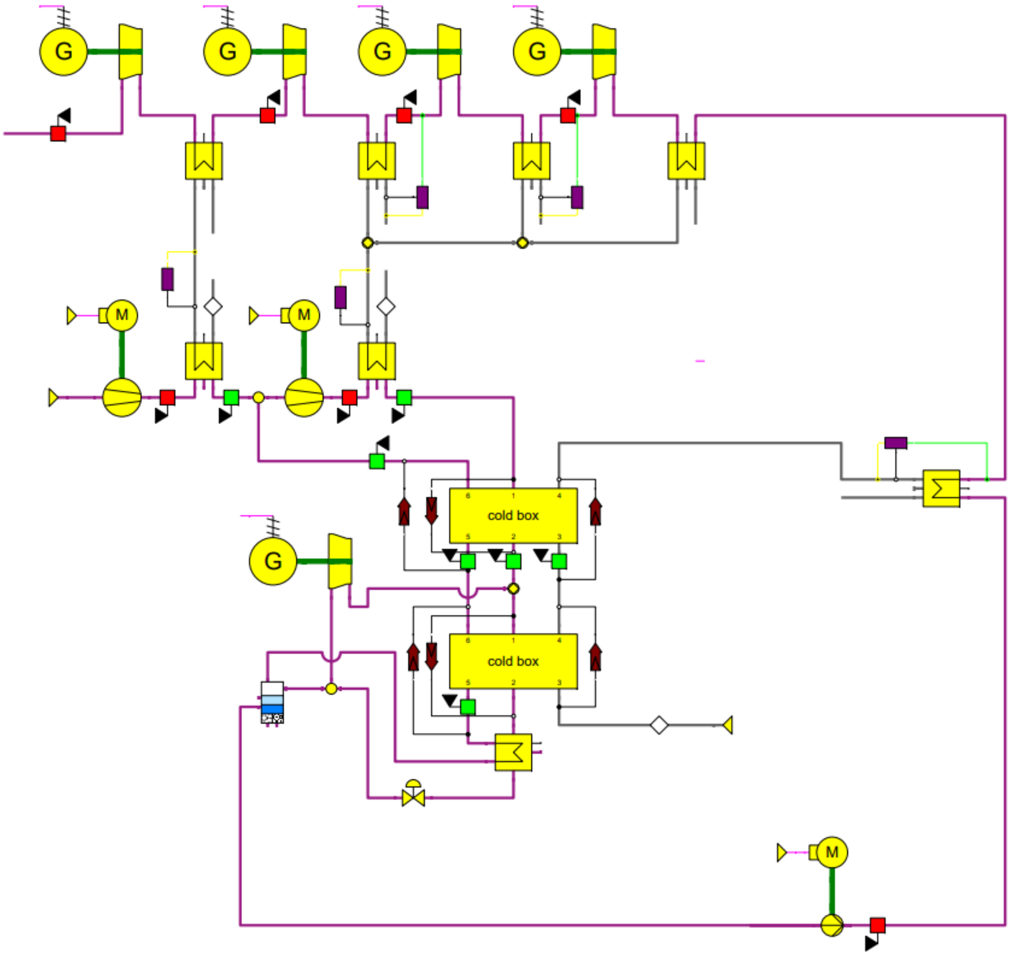


Figure 20.: *LAES model in combination with SandTES technology.*

Silica sand (SiO_2)

In the present invention of LAES in combination with the sandTES technology, silica sand has been contemplated as the heat transfer medium. Silica sand is a material that exists in excess in nature, has an appropriate thermal capacity and is also available in many grain sizes. As stated in [24], sand is suitable for implementations of the fluidization technology of sandTES. Moreover, sand as the heat transfer medium is not only applicable at high temperatures, but according to Hüttermann Aus Oberhausen [21], it is also well-suited in a LAES implementation at cryogenic temperatures.

As mentioned in 4.1, the material properties of the new fluid can be defined within component 33. For describing the new substance, the polynomial coefficients for the specific heat capacity, the density of the fluid, the thermal conductivity and the vapor pressure must be determined first. Furthermore, values such as molar mass, maximum and minimum temperatures, enthalpy and entropy, must also be described. The coefficients for defining the relevant values for silica sand are based on the work of König [28]. The coefficients for the thermal conductivity λ and the heat capacity c_p are taken from the program 'Barracuda' and are listed in table 3.

The polynomial used for thermal conductivity λ is described in equation (16):

$$\lambda(T) = \lambda(0) + \lambda(1)\,T + \lambda(2)\,T^2 \tag{16}$$

For the heat capacity, the following polynomial in equation (17) is used:

$$c_p(T) = a(0) + a(1)\,T + a(2)\,T^2 + a(3)\,T^3 + a(4)\,T^4 \tag{17}$$

As stated in [28], the vapor pressure p_s for silica sand is set to an infinitely large value of 999 999 bar. From the polynomial of the heat transfer fluid a_i, the enthalpy, as well as the entropy can be derived. As quartz sand is a material not listed in the data library of EBSILON, it needs to be defined beforehand. The relevant coefficients are summarized in table 3. Since the fluidized sand is a porous system, the density has to be calculated, in which the porosity is taken into account. Porosity ε is defined as the proportion of the cavity V_C in the total volume V of the system, as shown in equation (18).

$$\varepsilon = \frac{V_C}{V} \tag{18}$$

According to König [28], the minimum fluidization point is at the porosity ε of 0.6 and the density of the solid material ρ_s, the sand itself, is 2650 kg/m^3. Thus, the density of the fluidized sand $\rho_{s,f}$ can be obtained in the following equation:

$$\rho_{s,f} = \rho_s\,(1-\varepsilon) + \rho_f\,\varepsilon \tag{19}$$

Since the fluid is in a gaseous form, the fluid density ρ_f can be neglected compared to the solid density and a result of 1060 kg/m^3 is obtained using the equation eq:sand density:

$$\rho_{s,f} = \rho_s\,(1-\varepsilon) \tag{20}$$

The initial maximum and minimum temperature of quartz sand, required for the simulation on EBSILON were set to 600 °C and 0 °C, respectively. The maximum and minimum permissible values for enthalpy and entropy are also obtained by inserting them into the respective polynomial. As sand is used at cryogenic temperatures during the evaporation process, the minimum temperature is set to −200 °C and also the enthalpy as well as entropy are adjusted accordingly. For calculations of the outcome values listed in table 3, relevant to the simulation in EBSILON, see chapter 6.2. In table 3, the substance properties of silica sand are listed.

Table 3.: *Component properties for* SiO_2.

attribute	value	unit
reference temperature	0	°C
mole weight	60.0843	kg/kmol
t_{min}	−200	°C
t_{max}	600	°C
h_{min}	−1000	kJ/kg
h_{max}	620.89	kJ/kg
s_{min}	−1000	kJ/(kg K)
s_{max}	1.1405	kJ/(kg K)
a_0	0.697 397	kJ/(kg K)
a_1	0.001 863 47	kJ/(kg K)
a_2	$-3.133\,636\times10^{-6}$	kJ/(kg K)
a_3	$2.898\,218\times10^{-9}$	kJ/(kg K)
a_4	$-8.541\,01\times10^{-14}$	kJ/(kg K)
$\rho(0)$	1060	kg/m^3
$\lambda(0)$	2.1744	W/(m K)
$\lambda(1)$	−0.003 784 7	W/(m K)
$\lambda(2)$	4.6353×10^{-6}	W/(m K)
p_s	999 999	bar
b_0	−242.731 596 2	kJ/(kg K)
b_1	0.697 397	kJ/(kg K)
b_2	0.000 931 74	kJ/(kg K)
b_3	$-1.044\,55\times10^{-6}$	kJ/(kg K)
b_4	$7.245\,54\times10^{-10}$	kJ/(kg K)
b_5	-1.7082×10^{-15}	kJ/(kg K)
c_0	0.697 397	kJ/(kg K)
c_1	−4.324 089 104	kJ/(kg K)
c_2	0.001 863 479	kJ/(kg K)
c_3	$-1.566\,82\times10^{-6}$	kJ/(kg K)
c_4	$9.660\,73\times10^{-10}$	kJ/(kg K)
c_5	$-2.135\,25\times10^{-14}$	kJ/(kg K)

5. Patent analysis

In this chapter, relevant patents of the current existing LAES inventions with TES systems comprising solid materials are described. There are a lot of patents that belong to the same patent family. A patent family is a group of patent applications covering the same or similar technical content and comprises the patents filed in different countries for the protection of one and the same invention. Hence, for the Highview patents, only the most recent ones that are currently valid in Europe are listed. It was compared with the predecessors of the patent family and no changes regarding heat storage or heat transport means, which would be important for the present search, were found. Table 4, in which all the seven relevant patents are listed, was created as an overview of the result of the patent analysis.

The type of patent document is distinguished by the kind code that includes letters. The standard for document kind codes is set by the World Intellectual Property Organization. For example, EP-A documents are European patent applications being published and EP-B documents are European patent specifications that are granted.[29]

Table 4.: *Overview of relevant patents found in the research.*

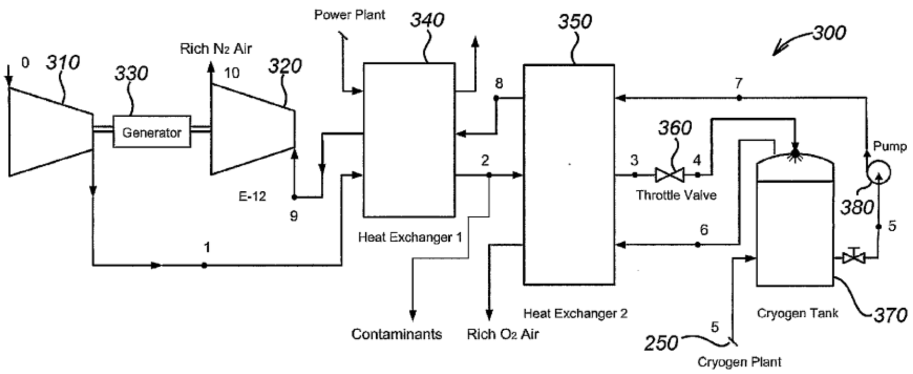
No.	Title	Assignee/patent no.	Date
1	A method of storing energy and a cryogenic energy storage system [30]	Highview Enterprises Ltd. EP1989400B1	Apr. 05, 2017
2	Integration of an energy storage device with a separate thermal process [31]	Highview Enterprises Ltd. EP2603762B1	Oct. 23, 2019
3	Liquid Air Energy Storage Systems, Devices, and Methods [32]	Mada Energie LLC US2017016577A1	Jan. 19, 2017
4	Method and apparatus for power storage [33]	Highview Enterprises Ltd. EP2753861B2	Jan. 11, 2023
5	Method and apparatus for storing thermal energy in thermal masses for electricity generation [34]	Highview Enterprises Ltd. EP2603761B1	Oct. 11, 2017
6	Cryogenic thermal storage [35]	Pourrahimi Shahin, Bromberg Leslie US10107543B2	Oct. 23, 2018
7	Method for operating a heat exchanger, arrangement with a heat exchanger, and system with a corresponding arrangement [36]	LINDE GMBH WO2021037391A1	Mar, 04, 2021

5.1. A method of storing energy and a cryogenic energy storage system (Highview, 2017)

The present invention describes a CES (Cryogenic energy storage) system for storing energy and using it to generate electrical energy or drive a propeller. The system uses stored cryogen, produced during off-peak hours, to generate electricity during peak hours. The current invention is one of the first forms of LAES application being patented.

The process consists of the following main components:

- compressor 310
- turbine 320
- generator 330
- first heat exchanger 340
- second heat exchanger 350
- throttling valve 360
- cryogen tank 370
- pump 380



310: Compressor	320: Turbine	330: Generator	340: Heat exchanger 1
350: Heat exchangers 2	360: Throttle valve	370: Cryogen tank	380: Pump

Figure 21.: *A schematic diagram of CES according to the present invention. [30]*

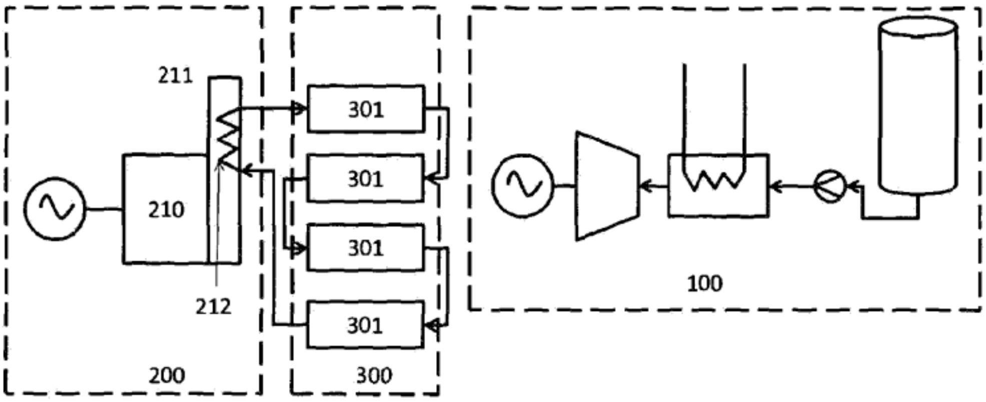
The process flow of the present CES system is shown in Fig. 21. Different kinds of cryogens are used as the drive fluid, such as liquid air, nitrogen, or other gases. Liquid air as the cryogen can be provided by an air liquefaction plant and directed to the cryogen tank (370) during off-peak hours, whereas other side products such as O_2, N_2, Ar and CO_2 in both gas and liquid states can be produced. In order to improve the overall efficiency of the CES system, cold energy recovered from the expansion is being used for cryogen production, and waste heat, as well as heat recovered from the compression stage, can be used for heating the cryogen during discharging.[30] This invention is similar to the simulated model of LAES with no cold or hot thermal storage in section 6.2.1 of the thesis.

Claims:

- The CES system provides a method of storing energy comprising:
  - producing a cryogen from the gaseous input, such as liquid air by an air liquefaction plant
  - storage of the cryogen
  - expanding the cryogen and using it to drive a turbine
- This method further comprises a turbine coupled to the generator to produce electricity using liquid air.
- The step of expanding the cryogen comprises heating the cryogen using ambient heat, geothermal heat or waste heat resources.
- The step of expanding the cryogen comprises:
  - heating the cryogen to approximately the environmental temperature using ambient air
  - then heating the cryogen further using waste heat
- The second heat exchanger is arranged to heat the cryogen to approximately the environmental temperature using ambient air and the first heat exchanger is arranged to heat the cryogen further using waste heat.

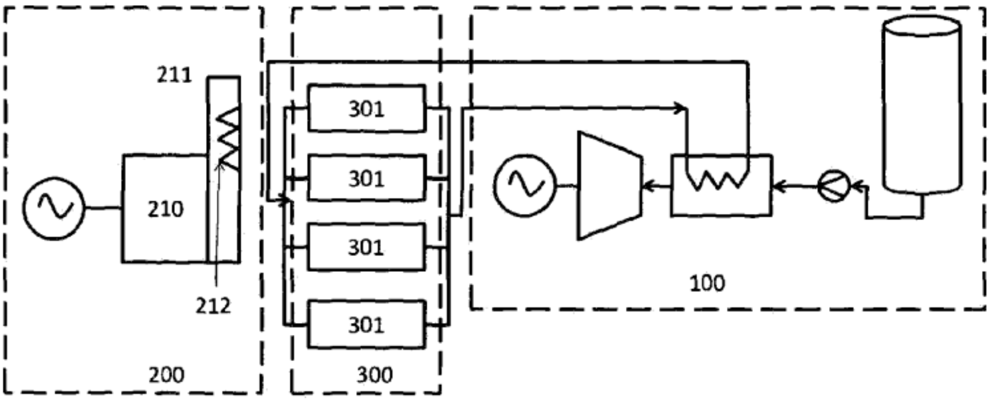
5.2. Integration of an energy storage device with a separate thermal process (Highview, 2019)

In this invention, the integration of separate thermal storage in a cryogenic storage system is described. The thermal store is installed either within the CES or between the CES device and a co-located process, such as a thermal power station or an industrial process. By installing the thermal store between the two systems, the overall performance of the two systems can be improved. The thermal cells may comprise a packed bed of solid particles through which the HTF can pass to carry thermal energy to and from the thermal energy storage devices.



200: Co-located thermal process 210: Gas engine 100: Cryogenset
300: thermal store 211: Exhaust stack 301: Thermal cell

Figure 22.: *Schematic of the integrated thermal storage during charging. [31]*



200: Co-located thermal process 210: Gas engine 100: Cryogenset
300: thermal store 211: Exhaust stack 301: Thermal cell

Figure 23.: *Schematic of the integrated thermal storage during discharging. [31]*

Fig. 22 shows a configuration of an integrated system comprising a co-located process (200) with the gas engine (210), a cryogenset (100) and a thermal store (300). In the charging process, the exhaust stack (211) of the gas engine from the heat exchanger goes to the thermal store. The thermal storage cells are usually made out of packed gravel beds, arranged in series during the charging.

In the discharging phase, shown in fig.23, the heat transfer rate needs to be higher than during the charging phase. Therefore, the thermal cells (301) are arranged in parallel, presenting a larger flow area to the heat transfer fluid, resulting in an acceptable flow velocity and a lower pressure drop.[31]

Claims:

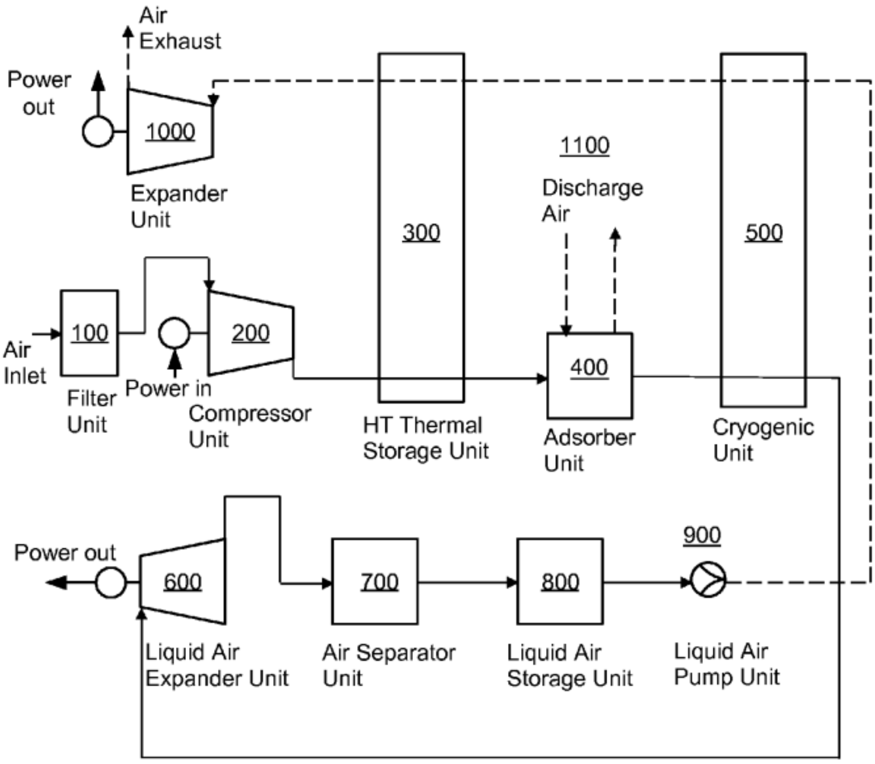
- Methods for integrating thermal processes with different rates of heat transfer are described. The method includes:
  - providing a first thermal store;
  - managing receipt of the first thermal energy;
  - managing a supply of the first thermal energy;
  - providing a second thermal store;
  - charging and discharging of the second thermal store;
  - valves for directing a heat transfer fluid to pass through the thermal masses
- The charging process is carried out by transferring the thermal energy to the thermal store, while in the discharging process, the stored thermal energy is transferred to components of the thermal process.
- Thermal energy can be stored in a cryogenic or compressed air storage device.

5.3. Liquid Air Energy Storage Systems, Devices, and Methods (Mada, 2017)

The invention relates to a standalone LAES system with a recovery unit of hot thermal energy extracted from the compression stage and cold thermal energy from the discharged air. At periods of low-priced excess electricity, the storage of the LAES system can be charged with hot thermal energy using power from the grid. And at times when electricity is needed, the LAES system can discharge the stored liquefied air by conversion of the thermal energy into power. The proposed LAES system comprises the following main components:

- Compressor unit 200: in the charging mode, the ambient is pressurized above a critical pressure;
- Hot thermal energy storage unit 300: for capturing, storing and recovering the compressed heat for reheating the discharged air in the turbine stage;
- Adsorber unit 400: removing CO_2 and atmospheric moisture from the charging air;
- Cryogenic unit 500: cold thermal energy storage for deep cooling and liquefaction of pressurized charging air;

- Liquid air storage 800 for storing the liquefied air;
- Pumping unit 900 for pumping the discharge liquid air to high pressure;
- Expander stage 1000: for expanding the pressurized discharging air stream;



100: Filter unit	200: Compressor unit	300: Thermal storage unit
400: Absorber unit	500: Cryogenic unit	600: Liquid air expander unit
700: Air separator unit	800: Liquid air storage unit	900: liquid air pump unit
1000: Expander unit	1100: Discharge air	

Figure 24.: *A LAES system, according to the described embodiments. [32]*

Fig. 24 illustrates the LAES system described above. In the charging mode, the inlet filter unit (100) removes undesirable contaminants from the captured air from the atmosphere. The air stream is pressurized to a supercritical pressure in the compressor unit (200) using the power from the grid before it is stored in the hot thermal energy storage unit (300). The adsorber unit (400) removes contaminants, such as CO_2 and atmospheric moisture, from the now cooled and pressurized air stream. In the cryogenic unit (500), the charging air stream is further cooled and turns liquid by a cold storing media and a cold vapor stream. The pressure of the air stream is then reduced in the expander unit (600) with additional cooling, resulting in the two-phase state of the air stream. In the separator unit (700), the mixture of liquid and vapor air is separated, with the liquid air stream being the main product and the vapor fraction the by-product of the charging process. The liquid air is stored in the storage unit (800) in the periods between the charging and discharging of the LAES system.

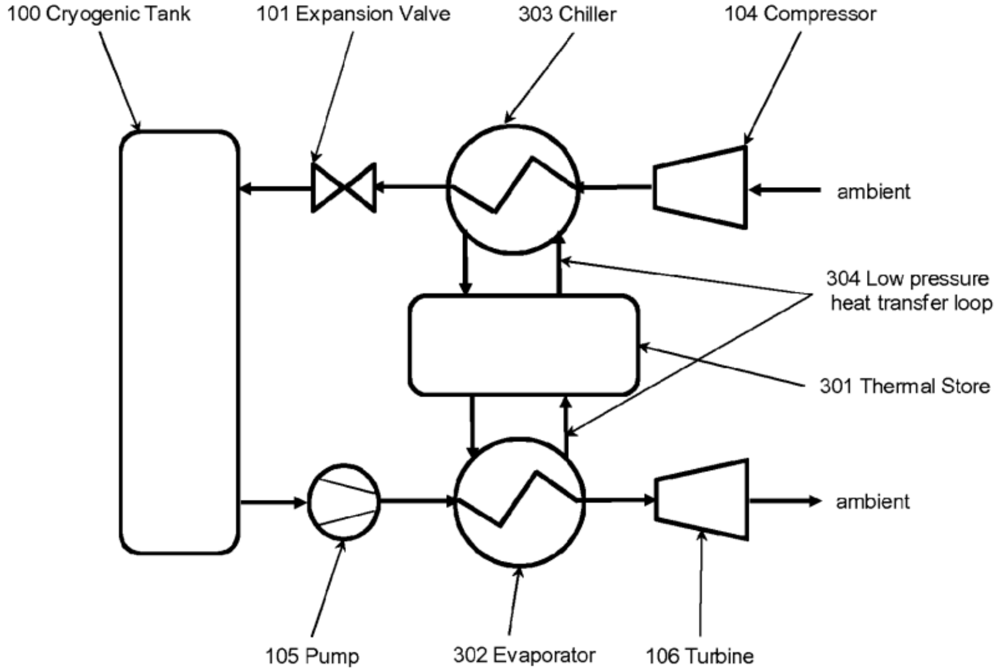
When the LAES system is operated in the discharging mode, stored liquid air is pumped to high pressure in the pump unit (900) and conveyed to the cryogenic unit (500), where it gets heated and re-gasified by releasing cold thermal energy to the cold storage media. The hot thermal energy storage unit (300) further reheats the discharged air stream by recovering stored compression heat. The air stream is finally directed to the expander unit (1000) to deliver the generated power to the grid or consumer.[32]

Claims:

- A LAES system comprising a compressor unit, a hot thermal energy storage, an adsorber unit, a cryogenic unit, a liquid air expander unit, a liquid air separator unit, a liquid air storage unit, a liquid air pump unit, the cryogenic unit, an expander unit, the piping unit, the compressor unit.
- The hot thermal energy storage unit is adapted to capture, store and recover compression heat for superheating and reheating the discharged air.
- The hot thermal energy storage is integrated with the discharge air preheater and the charging air aftercooler. The heat-storing media, including solid, liquid, and phase-change materials, provide a direct or indirect exchange of thermal energy stored by this media with the charging and discharging air streams.
- The cryogenic unit is adapted to liquefy the pressurized charging air by capturing cold thermal energy from a cold storing media in an integrated cold thermal energy storage and from a cold vaporized air stream in an integrated vapor cold exchanger;

5.4. Method and apparatus for power storage (Highview, 2023)

In this invention, methods of capturing and reusing cold thermal energy are being described to increase the efficiency of the production of cryogen. The system is set up so that the cold energy can be stored at low pressure in thermal stores and recovered from several components of the system. The thermal storage may comprise solid particles as the thermal energy storage medium.



100: Cryogenic tank	101: Expansion valve	104: Compressor
105: Pump	106: Turbine	301: Thermal store
302: Evaporator	303: Chiller	304: Low pressure heat transfer loop

Figure 25.: *A schematic of a CES system according the present invention. [33]*

As shown in Fig. 25, during the discharging, the cryogenic fluid is first transferred from the storage tank (100) to the pump (105), compressing it to high pressure. Cold thermal energy is transferred to the heat transfer fluid, which circulates between the evaporator and the thermal store. During the charging phase, ambient air is first compressed to high pressure, whereas impurities such as CO_2, water and hydrocarbon contaminants are removed from the high-pressure gas. The heat exchanger transfers cold thermal energy from the store to the high-pressure gas (303). The cold gas is then expanded through a valve to liquefy the air and is further stored in the cryogenic storage tank (100). Typically, the composition of the cold air after the expansion valve is a mixture of liquid and gaseous air. The gaseous air is returned to the chiller to provide additional cooling of the high-pressure air before expansion.

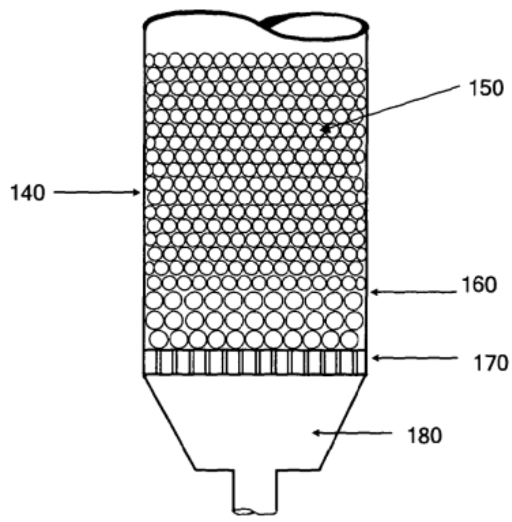
Claims:

- The cryogenic energy storage system comprises:
  - a cryogenic storage tank for storing a cryogen,
  - a pump for compressing the cryogen from the storage tank,
  - a co-located liquefier,
  - a power recovery system including one or more expansion turbines for expanding the heated cryogen to generate power.
- The cryogenic liquefaction plant further includes an expansion turbine, gas compressors and heat exchangers, such as pre-coolers, intercoolers and superheaters.
- The heat transfer fluids consist of a liquid or a gas, such as dry air or dry nitrogen.
- The cryogen used in the energy storage system comprises liquid air.

5.5. Method and apparatus for storing thermal energy (Highview, 2017)

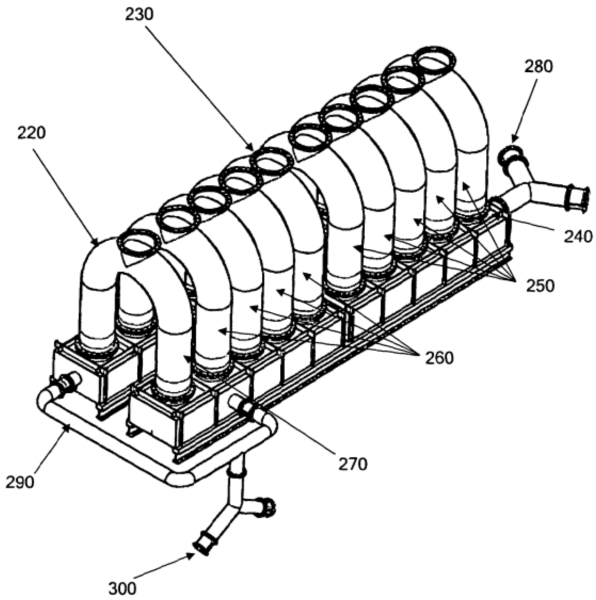
In this invention, thermal energy storage devices are used to store thermal energy at high and low temperatures. The system can store thermal energy temporarily at cryogenic temperatures for later use, such as for the air liquefaction process or provide cooling for co-located processes. The thermal cells may comprise a packed bed with solid particles, which the HTF passes through to deliver thermal energy to and from the thermal energy storage device.

In Fig. 26, an example of a thermal mass is shown. Each thermal mass comprises a container (140), consisting of a packed bed of spherical particles (150), typically with a diameter of 1 to 25mm. At the bottom of the container, there is an optional layer (160) of larger particles, which helps the flow distribution, and a grid (170) to distribute the flow through the particles further. The embodiment of thermal energy storage could look as shown in Fig.27. The thermal store consists of tubes or thermal cells (220) in a “U” shape filled with thermal storage media.[34]



140: Container 150: Packed bed of particles 160: Layer of larger particles
170: Grid 211: Plenum

Figure 26.: *A thermal mass for use in an embodiment of the present invention consisting of a packed bed with spherical particles[34].*



220: Tubes (thermal cells) 250: First set of 5 tubes 260: Second set of tubes
280: Inlet pipe 290: Bypass pipe 300: Outlet pipe

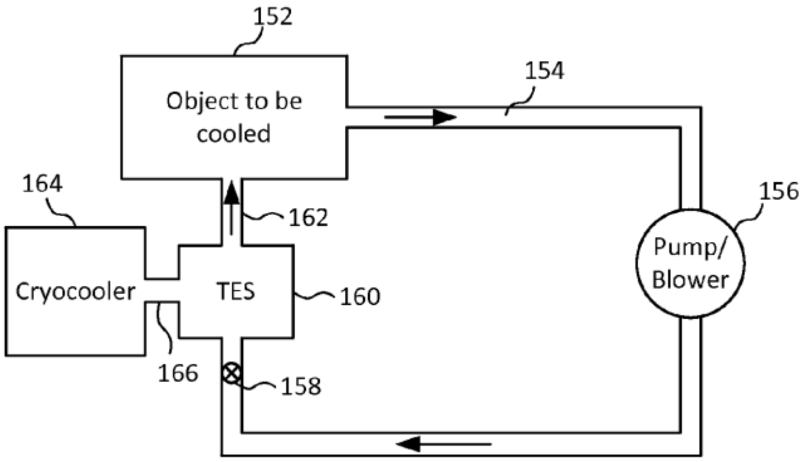
Figure 27.: *Embodiment of a thermal energy store with the thermal cells formed in a "U" shape. [34]*

Claims:

- The storage system comprises:
  - a heat transfer fluid passing through a combination of the thermal masses, wherein the conduits and valves are arranged in such a way that the thermal masses can be isolated from one another;
  - charging the thermal energy storage device with thermal energy by directing a heat transfer fluid through thermal masses;
  - storing the thermal energy in the thermal energy storage device for some time;
  - discharging the thermal energy storage device by directing a heat transfer fluid through the thermal masses;
- The heat transfer fluid comprises a gas or a liquid, and the thermal masses may comprise solids.
- Each thermal cell comprises a packed bed of solid particles through which the heat transfer fluid can pass directly to carry thermal energy to and from the storage device.
- The CES system comprises a device to store cold thermal energy released during power generation and provide cold thermal energy to liquefy cryogen or cooling for co-located processes during the discharging mode.
- The CES system further comprises a device to store hot thermal energy from a source of waste heat and discharge the hot thermal energy during electricity generation.

5.6. Cryogenic thermal storage (Shahin, 2018)

In this application, a refrigeration system is described, which includes a thermal storage device with solid materials stored at cryogenic temperatures. The cooling unit is formed by coupling blocks of TES modules together with an active cooling component to maintain a cryogenic temperature. The TES is made out of thermal conducting elements and solid storage elements.



152: Cooling vessel | 154: Refrigerant channel | 156: Pump/Blower
158: Control valve | 160: TES module | 164: Cryocooler

Figure 28.: *Embodiment of a cryogenic cooling system of the described invention. [35]*

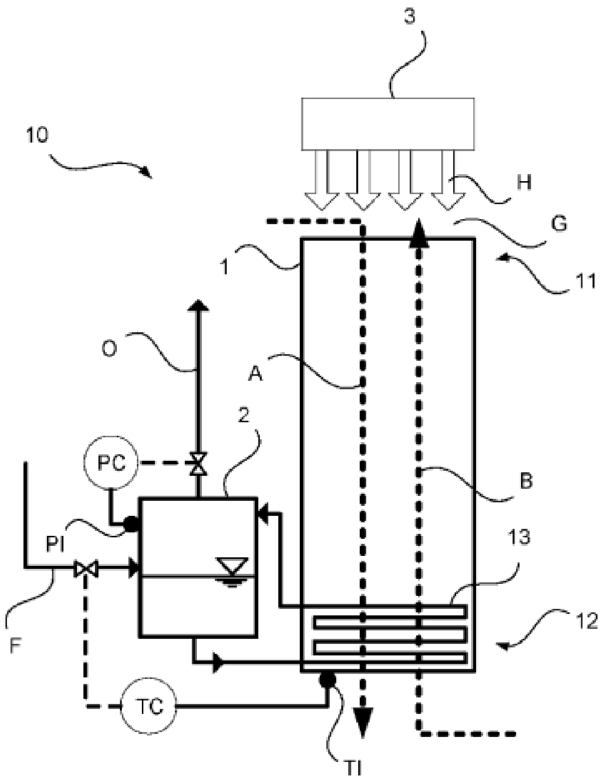
In Fig. 28, the cryogenic cooling system, according to the present invention, is shown. This embodiment comprises the cooling vessel (152) with the cold thermal mass, which is the object to be cooled, a refrigerant channel (154), a pump or blower (156), the flow control valve (158) and the TES module (160) connected with the cryocooler (164). In this system, a composite of solid materials suitable for thermal storage at cryogenic temperatures is being used, giving the advantage of combining materials with the properties of good thermal conductivity and heat capacity. The storage material may also include some filler materials such as metal, ceramic or chemical compound powders. [35]

Claims:

- The TES unit comprises a conductive substrate configured to conduct heat and a solid thermal storage element coupled with the conductive substrate;
- The cooling system comprises a plurality of TES modules, with each module containing a plurality of TES units, and each TES unit having a conductive substrate and a solid thermal storage element;
- The method of cooling uses a refrigerant fluid to transfer heat from a cryogenic vessel;

5.7. Method for operating a heat exchanger, arrangement with a heat exchanger, and system with a corresponding arrangement (Linde, 2021)

The present invention relates to a method for operating a heat exchanger. In the following, the invention is described mainly regarding an air separation plant. Still, it is also suitable for use in other application fields, such as plants for the liquefaction of gaseous air products. Thermal energy may be transferred to the heat exchanger using the heat source by solid-state heat conduction. This can be done, for example, via metallic or non-metallic elements such as heat-conducting elements.



A: First fluid flow B: Second fluid flow 1: Heat exchanger
2: First region 13: Evaporation passages 3: Second region

Figure 29.: *Embodiment of the heat exchanger according to the present invention. [36]*

Fig. 29 illustrates an arrangement of a heat exchanger according to a preferred embodiment of the present invention. Two fluid streams A and B, pass through the heat exchanger (1). The first fluid stream A is cooled in the heat exchanger, while the second fluid stream B is heated up. The liquid is withdrawn from the container (2) and fed into the evaporation passages (13). Heat is extracted from the refrigerant by the heat exchanger and evaporation occurs. The gas formed during evaporation flows back into the tank.

Claims:

- The transfer of the provided heat is performed by solid-state heat conduction via a heat-conducting element.
- The cooling fluid is a liquid taken from the container and evaporated in the evaporation passages, wherein gas formed during the evaporation of the liquid is returned to the container;

6. Results and Discussion

6.1. Results and discussion of the patent analysis

From the patent research, it was found that there is no patent claim existing explicitly defining solid particles acting as the direct heat transport medium that transports thermal energy from one to another medium in a LAES system. However, there are currently patents describing solid materials within the TES in a LAES system that provide a direct or indirect exchange of thermal energy with the air stream. In most patents regarding LAES, the thermal storage devices are not defined in a claim, or the heat transfer medium comprises only gases. Cryogenic energy storage or liquid air energy storage systems, including solid materials in the TES, are considered relevant inventions for this thesis. From the 211 patents being examined, there are only seven inventions found which are of interest for the thesis work.

In invention 5.3, the whole LAES process with recovering energy in the TES device is patented. The heat storage media of the TES comprises solid materials, which provide a direct or indirect exchange of thermal energy between the thermal energy stored by the storage media and the discharge air streams. The solid material is described to work as a heat storage medium and it is not explicitly claimed that the solids are used for the transport of thermal energy from one medium to another.

In patent 5.5, a thermal storage device containing a packed bed with solid particles as thermal masses is described. However, the heat transfer medium that passes through the thermal masses consists of a liquid or gas and only the thermal masses comprise solid particles. The patent claims a thermal cell comprising a packed bed of solid particles through which the HTF (liquid or gas) can pass directly to carry thermal energy to and from the thermal energy storage device.

In invention 5.2, the integration of a separate thermal store in a CES system is described. The thermal cells may comprise a packed bed of solid particles through which the HTF can pass. The packed bed with solids is only mentioned in the description and not claimed in the patent.

In invention 5.4, methods of capturing and reusing cold thermal energy are described. Cold thermal energy is transferred to the HTF that circulates between the evaporator and the thermal store. The thermal storage may comprise solid particles as the thermal energy storage medium, which is also only mentioned in the description and not claimed in the patent.

In application 5.6, a refrigeration system is described, which includes thermal storage with solid material stored at cryogenic temperatures. The solid is used as the thermal storage device, while a refrigerant fluid is used for heat transfer.

Invention 5.7 relates to a method for operating a heat exchanger. Heat may be transferred to the heat exchanger utilizing the heat source by solid-state heat conduction. However, only the method for operation of the heat exchanger is being described, not the whole LAES system with TES.

In patent 5.1, a CES system for storing energy and using the stored energy to generate electrical energy is described. The invention is one of the first forms of LAES application being patented, however, in this patent, there is no thermal storage with solid material claimed.

Summary:

Using sand or other solid particles as the medium transporting thermal energy from one medium to another in both cold and hot storage is not covered by the analyzed patents. However, based on this research, there are patents claiming solids as the heat storage medium that provides a direct or indirect exchange of thermal energy with the air stream. Therefore, from this research, it cannot be 100 % ruled out that solids as a heat transport medium in a LAES are not present in any patent. However, according to the description of the patent of [32] in section 5.3, it seems likely that the solids are only used as a heat storage medium and are not directly in charge of transporting thermal energy. In order to analyze 'freedom to operate', it has to be checked, if a general patent without double sensible storage, e.g. 5.1 (Highview, 2009) or 5.3 (Mada, 2017), would be an obstacle or not. In other words, it has to be verified, whether introducing additional process components, which dramatically improve the performance, would overrule basic general patents.

6.2. Results of the simulation

This chapter contains a detailed presentation and discussion of the described simulations of the current study. For better analysis and comparability, the same boundary conditions for ambient air were used for the simulations in EBSILON, which are summarized in table 5. Within the thesis, two simulations based on the initial LAES model of [3] were created. In the first model, a LAES system without a heat storage device is modeled. In the second one, a LAES system with the heat storage technology sandTES is presented. As the performance of the system is a significant factor for ETES systems, the overall round-trip efficiency, liquid yield and exergy efficiency are being studied and discussed in detail.

Table 5.: *Material properties for ambient air.*

	value	unit
ϑ_0	20	°C
p_0	1.013	bar
$\dot{m}_0$	19.36	kg/s

6.2.1. LAES without thermal storage devices

Charging cycle

The initial mass flow and the mass flow of liquid air being produced respectively are 19.36 kg/s. After the first compression stage, the main air stream is mixed with the gaseous fraction coming from the phase separator with a mass flow of 186.31 kg/s, which together result in a total mass flow of 205.67 kg/s. This stream is further directed to the next compressor and then to the cooler. After the first HEX, part of the main stream of 164.536 kg/s is directed to the turbine via a bypass line, resulting in a temperature drop to −153.989 °C of this stream. From this turbine, a power output (P_{turb5}) of 5432.463 kW can be additionally obtained. The main stream is cooled by the second HEX and the Joule-Thompson valve, resulting in a part of the air stream being liquefied and cooled to −158.307 °C. The stream after the Joule-Thompson throttling process is mixed again with the stream coming from the bypass line, giving a vapor quality x of 0.906. The gaseous fraction is directed back for cooling the stream.

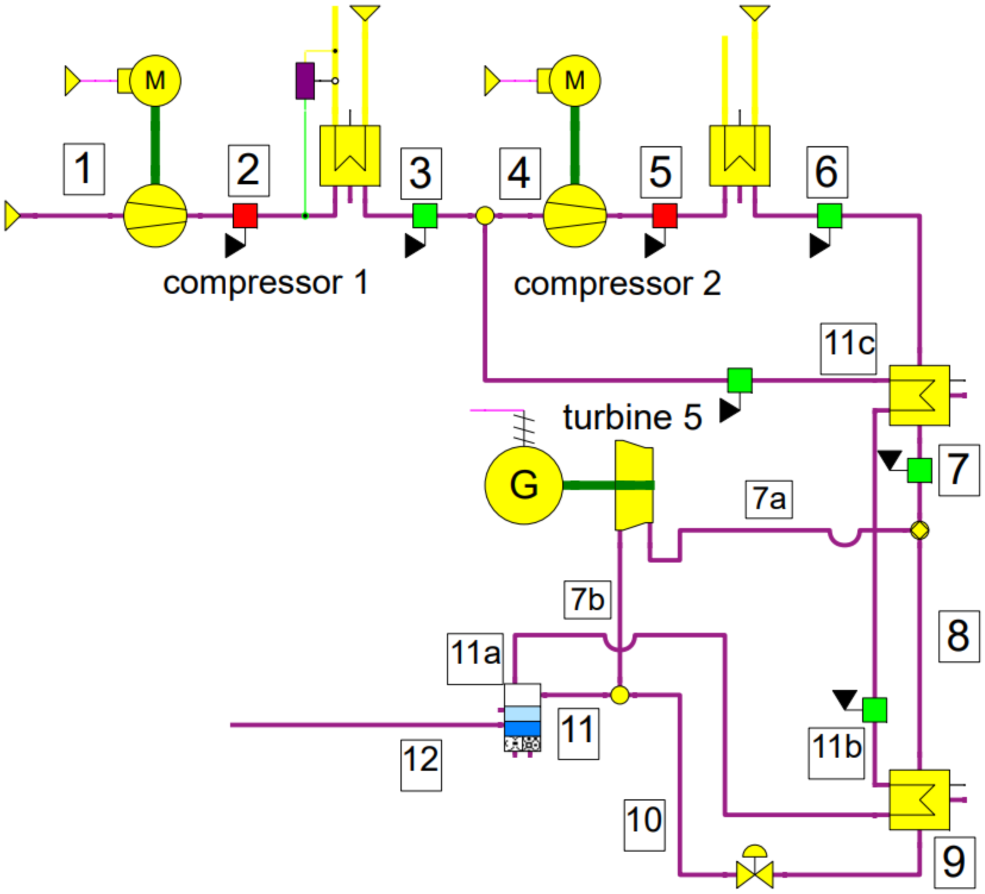


Figure 30.: *Charging process of LAES system without TES.*

Discharging cycle

In the discharging cycle, the liquefied air from the phase separator is further directed to the cryopump to pressurize it to 150 bar, in which a power input (P_{pump}) of 466.26 kW is needed for the motor. The high-pressure air is then turned into a gaseous state in the evaporator before it enters the multistage turbine cycle. Between the turbines, there are heat exchangers for intermediate heating. The pressure is dropped over a series of turbine stages. From the initial 150 bar after the cryopump, there is a pressure decrease to 70 bar in the first turbine stage, in which a power output ($P_{\text{turb,1}}$) of 885.942kW is obtained by the generator. In the second stage, a power output ($P_{\text{turb,2}}$) of 923.271 kW is converted, in the third 1235.842 kW ($P_{\text{turb,3}}$) and in the last stage 2374.44 kW of power output ($P_{\text{turb,4}}$). In the end, the air stream is released into the atmosphere at around 1 bar. The discharging process is shown in fig. 31 with all the relevant values from each step.

Table 6.: *Values of the main stream of LAES without TES.*

point	mass flow kg/s	pressure bar	temperature °C	specific enthalpy kJ/kg	specific entropy kJ/(kg K)
1	19.36	1.013	20	293.389	6.843
2	19.36	17	433.98	721.72	6.938
3	19.36	16.9	30	299.98	6.058
4	205.67	16.9	28.19	301.56	6.052
5	205.67	60	183.34	456.00	6.106
6	205.67	59.9	30	294.70	5.664
7	205.67	59.8	−103	126.28	4.918
7a	164.536	59.8	−103	126.28	4.918
7b	164.536	17.1	−153.989	93.265	4.956
8	41.13	59.8	−103	126.28	4.918
9	41.13	59.7	−141.8	−3.99	4.031
10	41.13	17.1	−158.31	−3.99	4.113
11	186.31	17.1	−157.61	73.81	0.789
11a	168.31	17.1	−157.61	86.414	4.895
11b	186.31	17	−140	115.177	5.129
11c	186.31	16.9	28	73.81	6.051
12	19.36	17.1	−157.61	−47.45	3.769
13	19.36	150	−145.47	−23.37	3.807
14	19.36	149.9	10	251.09	5.271
15	19.36	70	−41.88	205.33	5.301
16	19.36	69.9	10	266.69	5.541
17	19.36	32	−42.25	219	5.572
18	19.36	31.9	10	275.6	5.794
19	19.36	11	−56.88	211.77	5.837
20	19.36	10.9	10	280.818	6.118
21	19.36	1.013	−114.31	158.17	6.226

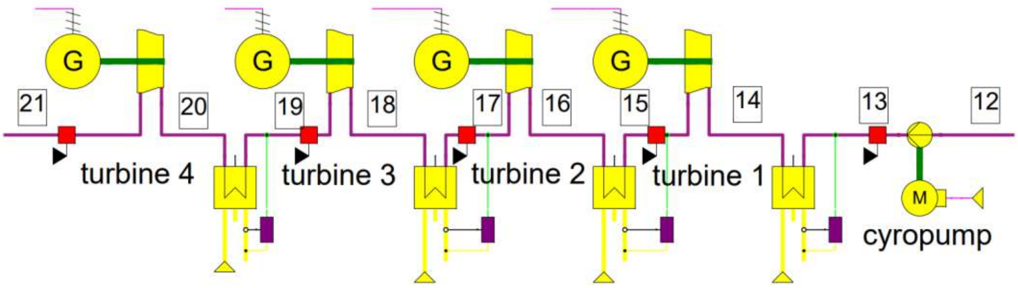


Figure 31.: *Discharging process of LAES system without TES.*

6.2.2. LAES with sandTES

This simulation comprises a LAES system with the thermal energy storage technology of sandTES, providing an alternative model of the conventional LAES system from Highview. The present model has the same charging and discharging process steps as the one presented by Highview. The only difference is that instead of oil and water, solid particles of quartz sand are used as the heat transfer and storage medium. By means of the sandTES HEX, heat energy recovered during the compression stages is used for the intermediate heating of the multistage turbine and cold energy obtained during the evaporation process is used for the cooling of the main air stream. The parameters for the main streams of this model are listed in table 7, 8 and 9.

Charging cycle

Fig. 32 shows the schematic of the charging process of the LAES system with sandTES HEX technology. The initial mass flow of air, as well as the liquefied air stream, are also set at 19.36 kg/s in this model. During the charging process, the ambient air is pressurized by the two-stage compressor and cooled in the intercoolers with the sandTES technology. In the first compression stage, the pressure is increased to 17 bar and then cooled in the sandTES heat exchanger to a temperature of 30 °C. A power input ($P_{\text{comp,1}}$) of 8292.432 kW is required for the first compressor. Before the stream is directed to the second compression stage, it is further mixed with the gaseous fraction coming from the phase splitter with a mass flow of 47.148 kg/s, which together makes a total of num66.508 kg/s compressed air. The pressure is then further increased to 60bar with a power input of 10 448.213 kW ($P_{\text{comp,2}}$) for the motor of the second compressor. The compression heat is transferred to quartz sand. The main stream is then directed through the cold boxes, representing the heat exchangers, where it gets cooled to −153.454 °C by the cold energy coming from the cold storage and by the gaseous fraction of air from the phase separator.

After the first cold box, a partial stream of 46.556 kg/s is directed via the bypass line to a turbine, where it gets further cooled. From the turbine, a power of 1342.377 kW ($P_{\text{turb,bypass}}$) can be obtained through the generator. Because of the temperature and pressure drop of the turbine, a part of the gaseous air is liquefied with a vapor quality x of 0.976. The throttle is placed after the heat exchanger and it serves to reduce the pressure and temperature of the main stream even further. The partly liquefied air stream is further mixed with the incoming stream of the bypass line, together resulting in a vapor quality x of 0.709. The charging process of the integrated sandTES technology is illustrated in Fig. 32.

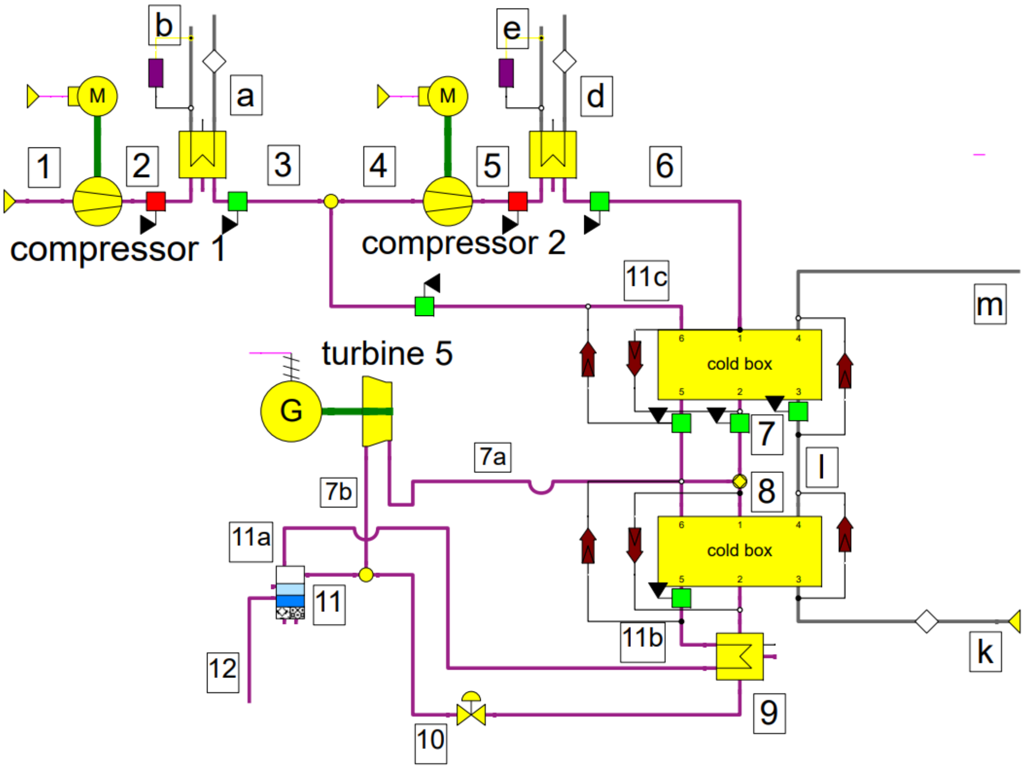


Figure 32.: *Charging process of LAES system with sandTES.*

Discharging cycle

In the discharging cycle, the liquefied air is directed to the cryopump to increase the pressure to 150 bar. The power required for the motor of the cryopump is 466.441 kW (P_{pump}). The high-pressure air is then vaporized, and the temperature is increased to −0.766 °C. Before the gaseous air enters the first turbine stage, it is pre-heated to 178 °C. In the first turbine stage, the pressure is reduced to 70 bar and 1502.663 kW ($P_{\text{turb},1}$) can be converted in the generator to electrical energy. In the next stage, a power output ($P_{\text{turb},2}$) of 1514.183 kW can be obtained with a pressure drop to 32 bar. The heat energy for the intermediate heating between these two turbines is recovered from the second compression stage. Then, the pressure is further decreased to 11 bar in the next turbine with 1977.628 kW ($P_{\text{turb},3}$) of power obtained. Before entering the last turbine, the stream is once again heated up by the recovered heat energy from the first compression stage. Through the final turbine 5782.698 kW power output ($P_{\text{turb},4}$) is obtained. The air is released to the atmosphere at around 1 bar and 104.776 °C. The described discharging cycle of the LAES system combined with sandTES is illustrated in fig. 33.

Table 7.: *Values of the main stream of LAES with sandTES.*

point	mass flow kg/s	pressure bar	temperature °C	specific enthalpy kJ/kg	specific entropy kJ/(kg K)
1	19.36	1.013	20	293.389	6.843
2	19.36	17	433.98	721.72	6.938
3	19.36	16.9	30	299.98	6.058
4	66.508	16.9	26.44	298.98	6.047
5	66.508	60	183.71	456.08	6.100
6	66.508	59.9	30	293.91	5.666
7	66.508	59.8	−110	112.30	4.840
7a	164.536	59.8	−110	112.30	4.840
7b	164.536	17.2	−157.092	83.469	4.877
8	19.952	59.8	−110	112.30	4.840
9	41.13	59.6	−153.434	−36.49	3.784
10	41.13	17.2	−158.20	−36.49	3.840
11	66.508	17.2	−157.5	49.481	4.567
11a	47.148	17.2	−157.5	86.348	4.893
11b	47.148	17.1	−135.321	121.37	5.173
11c	66.508	16.9	25	298.575	6.040
12	19.36	17.2	−157.5	−47.17	3.771
13	19.36	150	−145.32	−23.08	3.871
14	19.36	149.9	−0.77	237.31	5.231
15	19.36	149.8	168	433.90	5.786
16	19.36	70	91.41	356.28	5.819
17	19.36	69.9	168	438.07	6.023
18	19.36	32	90.24	359.56	6.055
19	19.36	31.9	169	440.68	6.258
20	19.36	11	66.5	338.53	6.302
21	19.36	10.9	393	677.59	7.002
22	19.36	1.013	104.78	378.9	7.099

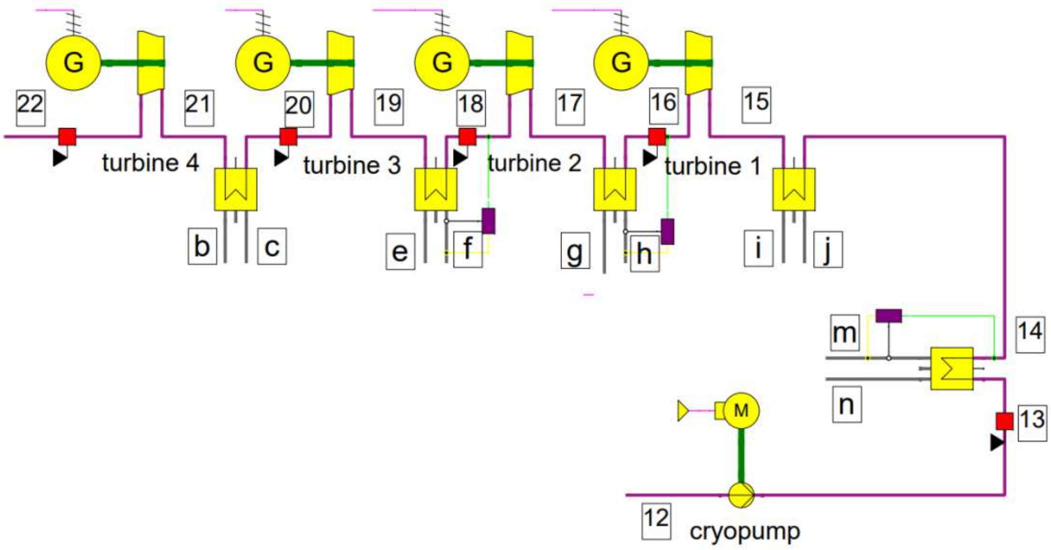


Figure 33.: *Discharging process of LAES system with sandTES.*

Table 8.: *Values for hot energy recovery loop.*

point	mass flow kg s	pressure bar	temperature °C	specific enthalpy kJ/kg	specific entropy kJ/(kg K)
a	22.149	1	20	14.312	0.051
b	22.149	0.9	403	382.937	0.833
c	22.149	0.8	109.859	56.58	0.264
d	80.383	1	26.44	298.98	0.051
e	80.383	0.9	178	148.491	0.413
f	22.291	0.8	100.243	78.293	0.242
g	22.881	0.9	178	148.491	0.413
h	22.881	0.8	178	148.491	0.246
i	35.221	0.9	178	112.30	0.413
j	35.221	0.8	54.229	112.30	0.141

Table 9.: *Values for cold energy recovery loop.*

point	mass flow kg/s	pressure bar	temperature °C	specific enthalpy kJ/kg	specific entropy kJ/(kg K)
k	65.09	1	−135.351	−74.479	−0.364
l	65.09	0.9	−120	68.315	−0.322
m	65.09	0.8	4.234	2.969	0.016
n	65.09	0.7	−135.351	−74.478	−0.353

6.3. Results of the thermodynamic evaluation

An exergy analysis is conducted on the LAES system with the sandTES HEX technology by looking at the exergy losses and determining the exergy efficiency. In table 10, the results of the analysis are listed. In this section, further results important for the thermodynamic evaluation are also listed in table 11, 13, 12 and 14.

Table 10.: *Results of the exergy analysis.*

component	exergy loss kJ/kg	exergy efficiency %
compressor 1	501.994	93.9
compressor 2	967.03	90.7
interocoling 1	86.261	97.3
intercooling 2	81.876	96.5
cold box 1	365.776	91.7
cold box 2	124.553	90.9
heat exchanger 3	231.704	89.6
turbine bypass	467.219	74.2
cryopump	201.25	56.9
evaporator	861.562	71
preheater	332.238	64.3
turbine stage 1	171.996	89.7
turbine stage 2	170.29	89.9
turbine stage 3	232.048	89.5
turbine stage 4	513.261	91.8
reheater 1	32.717	92.9
reheater 2	35.05	92.2
reheater 3	287.946	90

Table 11.: *Influence of pressure drop in RTE.*

Δp bar	η_{RT} %
0.1	60.134
0.5	58.631
2	52.934
5	30.636

Table 12.: *Values obtained for power of the LAES system without TES.*

	component	$\dot{m}_{air}$ kg/s	Power kW
Charging	compressor 1	19.36	8282.43
	compressor 2	205.67	32 586.55
	turbine_{bypass}	164.54	5432.46
Discharging	pump	19.36	466.26
	turbine 1	19.36	885.94
	turbine 2	19.36	923.27
	turbine 3	19.36	1235.84
	turbine 4	19.36	2374.44

Table 13.: *Values obtained for power of the LAES system with sandTES.*

	component	$\dot{m}_{air}$ kg/s	Power kW
Charging	compressor 1	19.36	8282.43
	compressor 2	66.674	10 448.17
	turbine_{bypass}	46.672	1342.38
Discharging	pump	19.36	466.44
	turbine 1	19.36	1502.66
	turbine 2	19.36	1514.18
	turbine 3	19.36	1977.63
	turbine 4	19.36	5782.70

Table 14.: *Comparison of the LAES system without TES and with sandTES.*

attribute	values without TES	values with sandTES	unit
W_{out}	4.95	10.22	MW
W_{in}	35.45	17.49	MW
$\dot{m}_L$	19.36	19.36	kg/s
$\dot{m}_{bypass}$	164.54	46.56	kg/s
$\dot{m}_C$	205.67	66.51	kg/s
w_{liq}	1830.92	903.56	kJ/kg
Y	9.41	29.11	%
η_{RT}	**13.97**	**60.13**	**%**

6.4. Discussion of the results for the thermodynamic evaluation

According to the results in table 10, the largest exergy losses occur in the compression stage and turbine stage. The exergy losses of the two compressors sum up to 149.024 kJ/kg. The losses of the turbines make up to 1554.814 kJ/kg, whereas in the last turbine of the discharging phase and in the turbine from the bypass line, the losses are the highest. High losses can also be observed in the evaporator with an exergy loss of 861.562 kJ/kg. The total exergy loss due to heat transfer in all heat exchangers makes up to 2439.781 kJ/kg. Exergy loss occurs when energy is converted into a form that cannot be used to perform useful work. Therefore, it is to important to minimize exergy losses in order to improve the overall efficiency of the LAES system. A method to minimize exergy loss in this system is improve the thermal efficiency of turbines and compressors. By designing systems that are optimized for their specific application, exergy losses can be decreased and efficiency can be maximized.

The component with the lowest exergy efficiency is the cryopump, with a value of only 56.9 %, followed by the preheater with 64.3 %. The two intercoolers have the highest exergetic efficiencies of 97.3 % and 96.5 %, with relatively little exergy losses of 86.261 kJ/kg and 81.876 kJ/kg, respectively. The performance of each component is important for the overall energy storage system. An increase in its isentropic efficiency leads to reduced exergy losses, increased exergy efficiencies and better round-trip efficiencies. Especially in the compression stages, a slight increase in the isentropic efficiency can significantly affect the LAES system's overall performance. Table 11 shows the influence of pressure drops in heat exchangers. Different pressure losses are applied for all the heat exchangers in the LAES system. This analysis indicates that the smaller the pressure loss, the better the performance of the system. In the present LAES system with sandTES HEX, a pressure drop of 0.1 bar is applied, resulting in an overall round-trip efficiency of 60.134 %.

Another significant impact on the overall performance of the system is the pinch-point temperature differences in heat exchangers. According to research from Denner [3] and Guizzi, Manno, Tolomei, *et al.* [37], the pinch-point temperature in the present system is kept as low as possible to reach higher round-trip efficiencies.

From the results of the calculations listed in table 11, it is easy to see the difference a thermal storage unit makes in a LAES system. Both the LAES model by Denner [3] and the present model with the thermal storage of sandTES have a round-trip efficiency of more than 60 %, while the system without any TES can only reach an RTE of not even 14 %. Considering both systems' charging and discharging cycles, conclusions can be drawn about the low efficiency of the model without TES.

Firstly, in the LAES system without TES, a much bigger amount of air is compressed with a mass flow of 205.67 kg/s. Neither cold nor hot thermal energy is stored during the process. Thus, more ambient air has to be introduced to the system in order to cool down or heat the air stream. The high rate of compressed air is also reflected in the results of liquid yield and specific work of liquefaction. The LAES system with sandTES has a liquid yield Y of 29.11 % and a specific work of 903.56 kJ/kg. In the LAES system with the integrated sandTES technology, liquid yield is almost three times greater, while the liquid work is half a time less than the system without TES. From this, it can be seen that much more power input is needed to liquefy the same amount of air, which is 19.36 kg/s in both cases.

In the first compression stage, an electric power input of 8292.432 kW ($P_{\text{comp},1}$) is needed in both systems. Due to the high amount of air stream of 205.67 kg/s being compressed in the following compression stage, a much higher power input of 32 586.552 kW ($P_{\text{comp},2}$) is required for the system without TES. However, a higher mass flow rate is also directed to the bypass line and more electric power ($P_{\text{turb,bypass}}$) can be obtained through the turbine. The motor power (P_{pump}) for the cryopump from both systems is around 466 kW. The electric power of the LAES system without TES being converted in the multistage turbine ($P_{\text{turb},1}$, $P_{\text{turb},2}$, $P_{\text{turb},3}$, $P_{\text{turb},4}$) is far lower than the model with sandTES. The power for each component during the charging and discharging process is listed in table 12 and table 13, respectively. The values of RTE and the other calculated results for both the LAES system with and without TES are given in table 14.

The heat source in the sandTES model, which is recovered from the liquefaction cycle, is well above ambient temperature. Therefore, a much higher enthalpy drop can be achieved, allowing the higher efficiency of the discharging cycle. Before entering the multistage turbine, the air evaporated enters the pre-heating device, which raises the inlet temperature of the turbine to 168 °C. Unlike the model without TES, in the present model with sandTES, the released cold energy during evaporation can be used in the liquefaction process for cooling. In the same way, the recovered heat energy from the second compression stage can be used for the pre-heating and reheating between the first multistage turbines to 168 °C. The reheating in the last turbine stage is driven by the recovered heat from the first compression stage, where the temperature increases to 393 °C.

To summarize, the LAES system integrated with sandTES shows a much higher round-trip efficiency of 60.134 % compared to the system without any TES. However, the efficiency is quite similar to the conventional system developed by Highview and to the one modeled by Denner [3].

7. Conclusion and Outlook

Liquid Air Energy Storage systems make use of the thermal energy reservoir to regenerate electrical and thermal energy. It has already been proven in many studies and even on commercial power plants that LAES systems have the potential to be a competitive local and grid-scale energy storage technology. In recent years, lots of research has been done in the field of LAES to operate the system in a commercial form.

In this work, an optimization or an alternative to the conventional LAES system is presented. Within the thesis work, the thermal energy storage technology sandTES is integrated into the LAES system. SandTES is a thermal energy storage developed by TU Vienna. The concept of this active countercurrent fluidized bed heat exchanger is based on using sand as a direct storage and heat transfer medium for the TES. The possible applications of the sandTES concept for increasing the flexibility of the electricity market are manifold and have been presented in the present work through the program EBSILON. The application possibility for LAES, currently a promising technology for large-scale industrial implementations, could be enabled by the sandTES technology. Thereby, two different concepts were modeled in the simulation program EBSILON.

In the first system, the LAES is simulated without TES. In the second model, the sandTES technology is integrated into the LAES system. The investigations of the two systems show that the efficiency can be increased enormously by adding a thermal energy storage system. For the simulation, the LAES model from Highview is used as a basis and it is shown that similar round-trip efficiencies of over 60% are obtained for LAES systems with TES. Based on the simulations and calculations, it is shown that the LAES system combined with the sandTES technology is a suitable alternative to the conventional method with similar overall efficiencies.

As the aim is to register the sandTES HEX integrated into the LAES system as a new invention, a patent analysis was carried out as part of this thesis. After extensive research, the result of the analysis is that there are currently patents existing describing solid materials in a TES system for the cryogenic energy storage system. However, in the patents, the solids are used for heat storage which provides direct or indirect heat transfer and it is not explicitly claimed that the heat storage media comprising solids are also used for transporting thermal energy directly from one to another medium, as it would be the case in the sandTES HEX method.

Furthermore, the patent in [32] has the kind code US-A, which means that it is a patent that has only been published in the US and has not been granted yet. To sum up, according to this research, it seems reasonable to suppose that in LAES applications, solids only act as the heat storage medium and a gaseous fluid is used as means for thermal energy transport. Therefore, there is a great chance that the LAES model in combination with the sandTES HEX method can be patented as a new invention.

Given the flexible supply of heating and cooling and the absence of geographical constraints, LAES is a promising thermos-mechanical energy storage method that is currently on the verge of industrial deployment. Due to simplicity reasons, the present system is simulated stationary on EBSILON, which means that the charging and discharging phases take place simultaneously. Although the model of LAES with sandTES is successfully demonstrated on EBSILON, in the next step, experimental investigations should be conducted on pilot plants to assess the performance of the system accurately. Furthermore, in future research, technical as well as economic studies should be conducted with a focus on cost analysis and participation in the electricity market of the LAES plant with sandTES HEX.

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A. General Appendix