Investigation of a working fluid for cryogenic energy storage systems

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Abstract. Cryogenic energy storage (CES) systems are promising alternatives to existing electrical energy storage technologies such as a pumped hydroelectric storage (PHS) or compressed air energy storage (CAES). In CES systems, excess electrical energy is used to liquefy a cryogenic fluid. The liquid can be stored in large cryogenic tanks for a long time. When a demand for the electricity is high, the liquid cryogen is pumped to high pressure and then warmed in a heat exchanger using ambient temperature or an available waste heat source. The vaporized cryogen is then used to drive a turbine and generate the electricity. Most research on cryogenic energy storage focuses on liquid air energy storage, as atmospheric air is widely available and therefore it does not limit a location of the energy storage plant. Nevertheless, CES with other gases as the working fluids can exhibit a higher efficiency. In this research a performance analysis of simple CES systems with several working fluids was performed.

1. Introduction
One of the most important goals of energy strategy for the European Union is to increase the share of renewables in electricity production. Most of the renewable energy sources, particularly solar and wind energy, are intermittent; they rely highly on the weather. As a result, renewable energy production is not coherent with the demand for electricity. Intermittency makes replacement of the conventional power plants with renewable energy sources difficult. Stabilization of the electrical grid system with large share of renewables is possible with use of the energy storage systems. When the renewable energy is available, generated electricity is transformed into another form of energy that can be stored. If energy demand is high and not enough electricity is generated in power plants, energy can be unloaded from the storage.

There are several technologies of electrical energy storage [1]. Most mature technologies are pumped hydroelectric storage (PHS), compressed air energy storage (CAES) and batteries. The main disadvantages of battery based energy storage are the environmental issues and quite low storage capacity. PHS and CAES can provide large storage capacity, but they can be placed only at specific sites (with specific topology and geology). Cryogenic energy storage (CES) does not have any of these drawbacks [2].

Figure 1 illustrates the working principle of CES: first stage of the process is the gas liquefaction - the off-peak electrical energy is used to liquefy cryogen, second stage is the storage of liquefied gas in the tank, while the last stage is energy recovery - liquid cryogen is pumped to higher pressure, heated using ambient and waste heat (if available) and expanded in a turbine. All of the mentioned stages are independent.
At the system level, CES technology is not considered mature yet, however, all the components used in such systems have been used for many years in large gas liquefaction and separation plants.

2. Exergy density of cryogenic fluids

To calculate the specific exergy of any cryogenic fluid, the following formula was used:

\[ e = T_a(s_a - s_l) - (h_a - h_l) \]  

(1)

where: \( T_a \) is an ambient temperature, \( s_a, h_a \) are specific entropy and enthalpy of cryogen at ambient conditions, \( s_l, h_l \) are liquid cryogen specific entropy and enthalpy respectively. Table 1 summarizes the exergy density data of some cryogenic fluids. Data for these and any further calculations was obtained using open-source thermophysical property library CoolProp.

![Diagram of cryogenic energy storage](image)

Figure 1. Cryogenic energy storage.

| Fluid     | \( e, \text{kJ/kg} \) | \( e, \text{kJ/m}^3 \) |
|-----------|----------------------|------------------------|
| Air       | 740                  | 647                    |
| Nitrogen  | 769                  | 620                    |
| Oxygen    | 635                  | 725                    |
| Argon     | 477                  | 666                    |
| Methane\(^a\) | 1092              | 461                    |

\(^a\) no chemical exergy included for methane

3. Analysed cryogenic energy storage plant

To compare mentioned cryogenic fluids, simple cryogenic energy storage system (figure 2) was considered. It consist of Joule-Thomson liquefaction facility, liquid cryogen tank (assumed to be perfectly thermally insulated) and power plant based on direct expansion cycle (with 2 turbine stages).

In the analysis the temperature at the inlet of the gas to the liquefier compressor as well as to the gas turbines are ambient temperature (293 K) while the gas pressure at the inlet to the compressor and at the outlet from the last expander are 0.1 MPa (ambient pressure). Table 2 summarizes the simulation parameters.

![Diagram of cryogenic energy storage](image)

Table 2. Simulation parameters

| Parameter                                      | Value   |
|------------------------------------------------|---------|
| Temperature of gas at the inlet of liquefier \( T_i \) | 293 K   |
| Gas pressure at the inlet of liquefier \( p_i \)    | 0.1 MPa |
| Liquefied gas pressure \( p_i \)                  | 0.1 MPa |
| Temperature at the turbine inlet \( T_{t=0} \)    | 293 K   |
| Pressure at the outlet of the last turbine stage \( p_o \) | 0.1 MPa |
| Isentropic efficiencies of turbines and pump      | 100%    |
3.1. Liquefaction plant

It is worth noticing that exergy density values shown in table 1 are equal to minimal work of gas liquefaction. However, the real work of gas liquefaction can be several times higher than the ideal case, because of irreversibilities that occur in real life liquefiers (in heat exchange processes, during throttling, as a result of friction, etc.) and heat from the surroundings. To compare the work of liquefaction, Joule-Thomson cycle (figure 3) was used as one of the simplest liquefaction cycles. It consists of isothermal compression (process 1-2), cooldown of compressed gas in the recuperative heat exchanger (2-3) and isenthalpic throttling (3-4). Part of the gas will liquefy (point 4') and will be stored in the liquefied gas tank, while the remaining stream (4'') will flow through the recuperative heat exchanger (4''-1).

![Figure 3. Joule-Thomson liquefaction cycle.](image)

To compare the liquefaction efficiency of the different working fluids, the work required to liquefy 1 kg of cryogen can be used. It is defined as:
\[ w_l = \frac{W_c}{y} \]  
\[ y = \frac{m_1}{m} = \frac{h_1 - h_2}{h_1 - h_{4'}} \]  
\[ W_c = \dot{m}[T_a(s_1 - s_2) - (h_1 - h_2)] \]  
where \( w_c \) is the work input to liquefier and \( y \) is the liquefaction yield of liquefier.

The liquefaction yield of Joule-Thomson liquefier can be determined using heat balances of liquefier:

\[ y = \frac{\dot{m}_l}{\dot{m}} = \frac{h_1 - h_2}{h_1 - h_{4'}} \]  
where \( \dot{m}_l \) is the mass flow rate of liquid phase and \( \dot{m} \) is the mass flow rate of gas at the inlet of liquefier.

Work input to the liquefaction stage of the CES stage is equal to work of isothermal compression that can be found from the equation (4):

\[ W_c = \dot{m}[T_a(s_1 - s_2) - (h_1 - h_2)] \]  
Thus, work required to liquefy 1 kg of cryogen is then equal to:

\[ w_l = \left( \frac{h_1 - h_2}{h_1 - h_{4'}} \right) [T_a(s_1 - s_2) - (h_1 - h_2)]. \]  

3.2. Work extraction process

The simplest way to recover the energy stored in the liquefied gas is to perform the direct expansion cycle (figure 4). At first, the liquid cryogen is pumped to high pressure (process 4'-5), then it is heated using ambient or, if available, waste heat (5-6). Finally the gas is expanded in two stages on the turbines (processes 6-7 and 8-9) driving an AC generator. Between high and low pressure turbines, the gas is reheated to the ambient temperature (7-8). The intermediate pressure was obtained using formula:

\[ P_{int} = \sqrt{P_tP_a} \]  
Specific work of turbines can be calculated as follows:

\[ w_t = (h_6 - h_7) - (h_8 - h_9) \]  
Specific pump work can be determined in similar way:

\[ w_p = h_5 - h_{4'} \]  
The net work output is difference between work of the turbine and the pump work:

\[ w_{net} = w_t - w_p \]
4. Results

To compare different working fluids for cryogenic energy storage, the following values were compared: liquefaction efficiency, work recovery efficiency and energy storage efficiency. The liquefaction efficiency ($\eta_l$) is the ratio of exergy contained in liquid cryogen and the energy needed to liquefy it.

$$\eta_l = \frac{e}{w_l} \tag{9}$$

Liquefaction efficiencies of selected cryogens are shown on figure 5. The highest liquefaction efficiency can be achieved for methane (above 30%) while for other analysed working fluids the maximum value of liquefaction efficiency was in the range of 13% to 22%. The liquefaction efficiency maximum of Joule-Thomson cycle is obtained for large compressor discharge pressure ($p_2$) values – around 35 MPa for methane, 30 MPa for air and nitrogen, 45 MPa for oxygen and argon.

Recovery efficiency ($\eta_r$) is the ratio of net work produced in cryogen expansion and the available exergy of liquid cryogen:

$$\eta_r = \frac{w_{net}}{e} \tag{10}$$

![Figure 5. Liquefaction efficiencies of cryogens in considered cryogenic energy storage system.](image)

Figure 6 presents the recovery efficiency value of different types of the working fluids for different pressure at the turbine pressures. It can be found that the recovery efficiency values for each working fluid exhibit the maximum for a certain pressure at the inlet to the turbine. For the methane and argon this maximum is around 10 MPa while for the other gases the maximum is two or more times higher. It is also worth noticing that there is no large increase in recovery efficiency for turbine inlet pressures above 10 MPa.

Finally, the storage efficiency ($\eta_s$) is the ratio of work of cryogen expansion and work of liquefaction:

$$\eta_s = \frac{w_{net}}{w_l} \tag{11}$$
The storage efficiency was obtained for work of liquefaction ($w_l$) equal to minimal Joule-Thomson liquefaction work (maximal liquefaction efficiency – figure 5). The highest storage efficiency (up to 12%) can be achieved for methane while for other analysed gases this value is 2-4 times lower (around 7% for argon and oxygen, 5% for air and 4% for nitrogen). Efficiency values are very low in the analysed system. Both liquefaction and gas expansion cycles used for the working fluids comparison are the most basic ones, and therefore, their liquefaction and recovery efficiencies are low. Further research should focus on more complex and more efficient liquefaction and cryogen expansion cycles.

**Figure 6.** Recovery efficiencies of cryogens in considered cryogenic energy storage system.

**Figure 7.** Storage efficiencies of cryogens in considered cryogenic energy storage system.
5. Conclusions
Air is presently the most commonly used working fluid for the CES systems as it is available everywhere (therefore it does not limit the possible location of storage plant), and its thermodynamic properties are decent. Nevertheless, thermodynamic comparison of other cryogenic fluids shows that methane had the highest recovery efficiency and liquefaction efficiency and, therefore, the highest storage efficiency. Availability of natural gas for this purpose is high as natural gas pipeline networks in many countries are highly developed and LNG tanks are used to store natural gas instead of underground storage facilities [3]. This means that processed natural gas can be a promising working fluid in cryogenic energy storage systems. Other cryogens are generally not suitable for cryogenic energy storage because of the low efficiency and availability.

Large recovery efficiency of methane and nitrogen indicate that energy recovery systems using the cold energy of liquid nitrogen (which is waste product from oxygen separation) or LNG (in LNG regasification stations [4,5]) are promising technology.

Presented cryogenic energy storage system is very basic, and its efficiency is very low. Joule-Thomson liquefaction cycle used in the analysed storage system has low efficiency and requires high pressures. In more complex systems, Joule-Thomson cycle can be replaced with the one that utilises expander instead of throttling valve. Claude cycle and its modifications can provide much higher liquefaction yield and therefore higher liquefaction efficiency. Also, the cryogen expansion cycle used in the analysis can be replaced with another more complex one with higher efficiency. Nevertheless, the main disadvantage of a direct expansion cycle is that the thermal exergy of the cryogen is destroyed in the heater (processes 5-6 and 7-8). There are few solutions for that problem. The cold from the expansion cycle can be stored and used in a liquefaction cycle to increase its efficiency. Additional cycles, such as Organic Rankine Cycle or Brayton cycle, can be incorporated using cryogen as low temperature heat source. Direct expansion cycle efficiency can be also increased by adding more turbine stages or by increasing $T_6$ and $T_8$ temperatures using available waste heat sources (heat of compression from liquefaction cycle [6,7] or waste heat available in thermal power plants or industrial processes). Waste cold (for example from the LNG evaporation process) may be used to improve the liquefaction yield of the plant. The most important problem to be solved in further research is to determine the best way of utilizing the thermal exergy of the cryogen.

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