Cold Energy Storage for Boil-off Gas On-Board Reliquefaction

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The increase in energy demand and the need for lower CO₂ emissions have increased the importance of natural gas as the cleanest fossil fuel in the energy market. Natural gas is mainly transported using pipelines or as liquefied natural gas (LNG). LNG is stored and transported in cryogenic storage tankers, where a part of the LNG evaporates, generating boil-off gas (BOG). The BOG is used normally as fuel for propulsion engines, but at low navigation speed, it is more than the engines’ fuel needs, and the excess quantity is either burnt or reliquefied. Existing technologies for on-board reliquefaction consume a large amount of energy and are costly, which arises the need for new concepts of reliquefaction technologies. The new proposed system operates on two modes; the first is the charging mode in which cold energy is stored when the LNG is evaporated to supply the LNG carrier propulsion system at high speed. The second is the discharging mode, in which the stored cold energy is used to condense the excess BOG at low navigation speed. The novel reliquefaction system utilizes latent or sensible heat storage materials that haven’t been examined before for cryogenic applications. A preliminary energetic assessment for the system is carried out using Aspen HYSYS, Excel and VBA, to study the impact of the variation of the operating conditions on the choice of suitable storage material and its performance. Results showed that low LNG evaporation and high BOG reliquefaction pressures offer higher energy storage capacity for all types of thermal energy materials, with better performance for the latent ones. Further investigation on this technology helps in providing a suitable replacement for the costly available reliquefaction systems and avoids the burning of BOG with its consequent high CO₂ emissions.

1. Introduction

Nowadays, natural gas almost meets a quarter of the global energy demand, out of which 47 % of the global gas trade is supplied by LNG and 53 % using pipelines (IGU et al., 2020). During the LNG transportation, the storage tankers are not perfectly insulated, and the heat ingress from the surrounding constitutes the main trigger to evaporate the liquid, generating what is called boil-off gas (BOG) (Dobrota et al., 2013). The difference between the loading and unloading LNG volumes is the amount of BOG generated during the trip. These losses are significantly affected by the containment system design and performance, altering the boil-off rate (BOR) value. The BOR is defined as the amount of BOG evaporating due to heat leakage, and it is expressed as the percentage of the total LNG volume per day (Dobrota et al., 2013). The evolution of the containment system technologies has helped in decreasing the BOR values, in which 0.07 % can be attained nowadays, and 0.05 % BOR is expected in the future (Corkhill, 2018).

The continuous generation of BOG increases the pressure inside the tanks, and it should always be eliminated to maintain the tank under safe pressure conditions (Hasan et al., 2009). The generated BOG is ideally used as a fuel for the propulsion system in conjunction with LNG when navigating at high speed. The LNG is extracted from the storage tanks, gasified, compressed, and then supplied with the BOG to the engines (Lee et al., 2008). However, when the LNG carrier is at low speed or rest, the BOG is in excess of the propulsion needs. The most common handling of this excess BOG is by burning it using gas combustion units that produce a massive amount of CO₂ emissions. Another option is to reliquefy the excess BOG using an on-board reliquefaction unit (Fernández et al., 2017). Different novel reliquefaction technologies exist based on the reverse Brayton cycle, the mixed refrigerant cycle, or the Joule-Thomson effect. All these technologies require a high-power supply and are costly, rendering them infeasible to implement, especially for low BOR values. A novel reliquefaction
system is presented in this research work to avoid the BOG burning and potentially provide a more competitive reliquefaction solution with minimal extra operating power and cost.

The proposed system relies on the concept of cryogenic thermal energy storage (TES) and operates on the charging and discharging modes. During charging, the LNG carrier navigates at high speed, and LNG is evaporated to supply the high energy demand of the propulsion system that the available BOG cannot provide solely. The cold energy generated from the LNG evaporation is stored in suitable materials to be used later. During discharging, the LNG carrier is at low navigation speed, and the BOG available is in excess of its fuel needs. The stored energy is then released to reliquefy this excess BOG. TES systems are used in different applications where the energy available does not match the demand and where extra supply is needed. Most studies target medium to high-temperature applications such as solar panels and buildings (Sharma et al., 2009). However, the research on sub-zero applications, especially those at temperatures below -100 °C as the LNG applications, is limited and requires further development (Yang et al., 2021). In this article, different sensible and latent heat TES materials are proposed for this LNG application and similar cryogenic utilizations. A parametric study is carried out using Aspen HYSYS, Excel, and VBA to assess the impact of the operating conditions and the selection of the energy storage material on the TES system performance on the LNG carrier.

2. Process description

The simplified LNG carrier mechanical system is modeled using Aspen HYSYS, as presented in Figure 1. The TES unit is conceptually presented as two split heat exchangers: ‘HX1:Ch’ and ‘HX2:Dch’, where each one operates solely according to the mode of operation. The storage material (SM) is represented using two streams: ‘Hot SM’ and ‘Cold SM’. These streams are used to assess the performance of the LNG evaporation and the BOG liquefaction flows at different conditions. On the other hand, the BOG is normally evaporating at a constant rate inside the LNG tankers and is represented using the stream ‘NBOG’. This BOG is used as fuel for the propulsion system that is divided into the constant load and the main engines. The constant load represents the hotel load (supplying the basic running electric utilities), while the main engines are used to drive the carrier. During charging, the navigation speed is high, and the NBOG available is insufficient as fuel; hence, LNG is evaporated using the TES unit. During evaporation, the cold energy is stored inside the SM. This phenomenon is represented by the stream ‘FLNG-in’ evaporating inside the ‘HX1:Ch’. An additional evaporator is added downstream to ensure the total evaporation of the flow before it enters the compressors. Simultaneously, ‘NBOG’ that is continuously evaporating joins the evaporated LNG and is then compressed to 13 bar and cooled down before entering the propulsion system. During discharging, the LNG carrier speed is low, and the ‘NBOG’ is more than the fuel needs. In this mode, ‘HX1:Ch’ does not operate while the ‘NBOG’ is compressed and cooled to be used as fuel. The ‘Excess BOG’ left may be further compressed and cooled down before entering the ‘HX2:Dch’. A separator is added afterward, where the totally liquefied flow ‘Liq BOG’ is injected into the tankers and the vapor stream ‘Vap BOG’ is recycled back to the system.

Figure 1: Ship simplified mechanical system presentation on Aspen HYSYS

The main assumptions considered in this model are:
- The BOR is considered 0.05 % and is equivalent to 1,600 kg/h of ‘NBOG’.
The constant load required is 3 MW and is equivalent to 500 kg/h. The charging is considered at the maximum navigation speed requiring full load on the engines (24 MW), which accounts for 3,500 kg/h. The discharging mode is when the carrier is totally at rest and results in 1,100 kg/h of 'Excess BOG'.

The respective properties and composition of the ‘LNG’ and ‘NBOG’ at 1 bar are presented in Table 1.

### Table 1: LNG and NBOG properties and composition

<table>
<thead>
<tr>
<th>Properties</th>
<th>LNG</th>
<th>NBOG</th>
<th>Molar Composition</th>
<th>LNG</th>
<th>NBOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (bar)</td>
<td>1</td>
<td>1</td>
<td>CH₄</td>
<td>0.9200</td>
<td>0.8654</td>
</tr>
<tr>
<td>T (°C)</td>
<td>-162.5</td>
<td>-120</td>
<td>C₂H₆</td>
<td>0.0550</td>
<td>0.0001</td>
</tr>
<tr>
<td>ρ (kg/m³)</td>
<td>454</td>
<td>1.41</td>
<td>C₃H₈</td>
<td>0.0150</td>
<td>0</td>
</tr>
<tr>
<td>LHV (kJ/kg)</td>
<td>49,185</td>
<td>39,355</td>
<td>n-C₃H₁₀</td>
<td>0.0025</td>
<td>0</td>
</tr>
<tr>
<td>Cp (kJ/kg.K)</td>
<td>1.92</td>
<td>1.84</td>
<td>i-C₄H₁₀</td>
<td>0.0025</td>
<td>0</td>
</tr>
<tr>
<td>ΔHᵥ (kJ/kg)</td>
<td>655</td>
<td>499</td>
<td>N₂</td>
<td>0.0050</td>
<td>0.1345</td>
</tr>
</tbody>
</table>

3. Material selection

During charging and discharging, the TES unit undergoes thermal cycling to store and release the cold energy. TES can be attained using sensible heat storage material, latent heat storage material, or by combining both types. Latent heat storage (LHS) can be achieved using phase change materials (PCMs) that change their physical characteristics when absorbing or releasing heat. During charging, the PCM first cools down and stores the cold energy in the form of sensible heat until it reaches its fusion temperature (T₁), where it then undergoes a phase change until it solidifies totally. Afterward, the temperature of the PCM continues to decrease and reaches that of the fluid entering (LNG). During discharging, the cold calories are released in a reverse way. The energy stored/released inside the PCM (E₁) is represented using Eq(1) (Sharma et al., 2009).

\[
E_{\text{LHS}} = \int_{T_1}^{T_f} m \cdot C_p \cdot dT + m \cdot \Delta H_f + \int_{T_1}^{T_f} m \cdot C_p \cdot dT
\]  

(1)

Where, E is in (kJ); m is the SM mass in (kg); C_p is the SM specific heat capacity in (kJ/kg.K); \( \Delta H_f \) is the heat of fusion in (kJ/kg); and T₁, T₂, and T_f are the initial, final and fusion temperatures respectively in (K).

The chosen PCM should encompass certain properties to fulfill the requirements of a suitable TES unit. First, the fusion temperature should be within the charging and discharging operation temperature range. The material should also possess good thermoysical properties, provide a compact system, have cycling and long-term chemical stability, inexpensive and environmentally friendly (Zeng et al., 2017). After evaluating different PCMs, it was observed that only organic compounds and specifically light hydrocarbons possess a very low fusion temperature suitable for cryogenic applications. Amongst these hydrocarbons, n-Butane, n-Pentane, and i-Hexane were selected for this application due to their suitable fusion temperatures, in addition to their high heat of fusion and stability (Bhatia, 2014).

On the other hand, sensible heat storage (SHS) materials store and release energy without undergoing a phase change. The stored/released energy (E₂) is calculated using Eq(2). The selected storage material should possess the same properties as that of the PCM except that concerning the phase change. However, the main drawback of such materials is the significant alterations of these properties with temperature (Menghare and Jibhakate, 2013). Several materials such as different types of minerals like sand, grout, and clay; metals like stainless steel and aluminum; and water ice were proposed for this application. Some types of these minerals have high density, good specific heat capacity, and/or thermal conductivity, such as ‘Grout’ (C_p = 6.412 kJ/kg.K).

The main drawback of these minerals is that their properties are highly affected by their water content, which consequently impacts their stability when operating at cryogenic conditions (Hamdhan and Clarke, 2010). Regarding the metals, even though they can offer a compact system due to their high density, the system will be massive. Another drawback is their relatively low specific heat capacities. These metals can be used later in the form of fins or metal foams to enhance the conductivity inside the SM and optimize the system. Ice, on the other hand, offers good thermo-physical properties and can act as a good candidate for this application.

\[
E_{\text{SHS}} = \int_{T_1}^{T_2} m \cdot C_p \cdot dT
\]  

(2)

The thermo-physical properties of the selected materials are presented in Table 2, and further energy study on their performance is presented in the next sections.
Parametric study, a higher SM temperature can be attained for acceptable recycling. The behavior of the SM during the charging and discharging is unknown. However, the SM temperature profile at the initial and final stages of each operation mode can be projected by monitoring the forced LNG evaporation (FLNG-in/out) and the excess BOG (EBOG-in/out) condensation temperature profiles. During the charging phase, the SM temperature drops until it reaches that of the LNG, where the charging terminates. Subsequently, this temperature will be the initial SM temperature of the discharging mode. During discharging, the SM temperature increases until it reaches that of the Excess BOG undergoing condensation, and then the discharging terminates. Afterward, the charging and discharging cycling continue. Consequently, the SM temperature at the end of charging/start of discharging can be represented by the LNG evaporation profile. Moreover, the SM temperature at the end of discharging/start of charging is expressed using the Excess BOG condensation profile. These curves are used instead of homogenized temperature profiles to present incomplete charging or discharging at the end of each phase, yielding more conservative energy results. During both operation modes, the pressure of the flows entering the TES unit is a critical design constraint that should be set to achieve the highest energy storage. During charging, the pressure of the forced LNG evaporating (FLNG-in) is incremented from 1 to 21 bar by a step of 2 bar and considering the temperature of the SM at -120 °C. During discharging, the pressure of the 'Excess BOG' is varied using the compressor 'BOG- Booster'. This pressure is increased by a step of 5 bar from 13 to 43 bar. Unlike the charging mode, it is observed that not only the pressure has an impact on the performance, but also the SM temperature 'Cold SM-in'. As the SM temperature increases, the total amount of excess BOG liquefied (EBOG-out) decreases. Consequently, the amount of vapor recycled to the system increases and the temperature and properties of the Excess BOG entering (EBOG-in) are affected. The 'Cold SM-in' stream temperature is increased from -160 °C by a step of 3 °C at each pressure step. This increase is subjected to two constraints: the first is to avoid the temperature cross inside the heat exchanger. The second is the amount of vapor recycled to the system, which is limited to 50 % of the inlet flow since it increases the load on the compressors and decreases the flow quality. At each pressure and temperature step, the different parameters such as composition, pressure, temperature, flow rates, power of the streams, and equipment are monitored by the link established between Excel and HYSYS using VBA. Tracking these parameters helps in assessing their impact on the storage system. Moreover, the temperature versus the power profiles at each pressure step are plotted as appears in Figure 2 to calculate the system energy storage capacity.

5. Performance results and discussion

The impact of the operating pressure is first assessed using the temperature versus the power profiles for the evaporation and liquefaction at each pressure step, as appears in Figure 2. Results showed that during charging, as the pumping pressure decreases, the final temperature of the SM attained, which is presented by the evaporating temperature profiles, also decreases. On the other hand, results in the discharging mode show that as the discharging pressure increases, a higher SM temperature can be attained for acceptable recycling percentages. The maximum SM temperature reached at 43 bar is -121 °C for 50 % recycling, while only -145 °C can be attained at 13 bar. Higher energy storage capacity can be achieved with a larger temperature difference in the SM. Thus, the lower the SM temperature reached at the end of charging and the higher this temperature is at the end of discharging, the larger the temperature difference would be. Based on the above data, the lowest evaporation pressure and the highest liquefaction pressure provide the highest temperature difference. The low pressure can be attained easily without increasing the pumping costs. However, increasing the discharging pressure increases the compression costs by a minimum of 250 kW, which consequently raises the operating costs and arises the need for a further economic assessment. Selecting the liquefaction pressure is a matter of precise dynamic modeling and economic study to see if its impact on energy storage is worth paying the extra compression charges.

### Table 2: Thermo-physical properties of the selected storage material

<table>
<thead>
<tr>
<th>PCM</th>
<th>MW (kg/kmol)</th>
<th>T&lt;sub&gt;f&lt;/sub&gt; (°C)</th>
<th>ΔH&lt;sub&gt;f&lt;/sub&gt; (kJ/kg)</th>
<th>ρ (kg/m³)</th>
<th>Cp (kJ/kg.k)</th>
<th>k (W/m.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane</td>
<td>58.122</td>
<td>-138.25</td>
<td>80.18</td>
<td>735</td>
<td>1.973</td>
<td>0.17656</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>72.149</td>
<td>-129.68</td>
<td>116.44</td>
<td>762</td>
<td>1.970</td>
<td>0.17502</td>
</tr>
<tr>
<td>i-Hexane</td>
<td>86.175</td>
<td>-153.55</td>
<td>72.76</td>
<td>807</td>
<td>1.775</td>
<td>0.14681</td>
</tr>
<tr>
<td>Ice</td>
<td>18.015</td>
<td>-</td>
<td>-</td>
<td>934</td>
<td>1.141</td>
<td>0.603</td>
</tr>
</tbody>
</table>

*Data in this table are collected from (NIST, 2018)*

A pseudo-static energy modeling is used to monitor the different states of the storage material (SM) during the LNG evaporation (charging) and the BOG liquefaction (discharging) at various operating conditions. The actual SM is static inside the TES unit; hence, high mass flow rates are assigned to 'Hot SM' and 'Cold SM' streams on HYSYS. The behavior of the SM during the charging and discharging is unknown. However, the SM temperature profiles at the initial and final stages of each operating mode can be projected by monitoring the forced LNG evaporation (FLNG-in/out) and the excess BOG (EBOG-in/out) condensation temperature profiles. During the charging phase, the SM temperature drops until it reaches that of the LNG, where the charging terminates. Subsequently, this temperature will be the initial SM temperature of the discharging mode. During discharging, the SM temperature increases until it reaches that of the Excess BOG undergoing condensation, and then the discharging terminates. Afterward, the charging and discharging cycling continue. Consequently, the SM temperature at the end of charging/start of discharging can be represented by the LNG evaporation profile. Moreover, the SM temperature at the end of discharging/start of charging is expressed using the Excess BOG condensation profile. These curves are used instead of homogenized temperature profiles to present incomplete charging or discharging at the end of each phase, yielding more conservative energy results. During both operating modes, the pressure of the flows entering the TES unit is a critical design constraint that should be set to achieve the highest energy storage. During charging, the pressure of the forced LNG evaporating (FLNG-in) is incremented from 1 to 21 bar by a step of 2 bar and considering the temperature of the SM at -120 °C. During discharging, the pressure of the 'Excess BOG' is varied using the compressor 'BOG- Booster'. This pressure is increased by a step of 5 bar from 13 to 43 bar. Unlike the charging mode, it is observed that not only the pressure has an impact on the performance, but also the SM temperature 'Cold SM-in'. As the SM temperature increases, the total amount of excess BOG liquefied (EBOG-out) decreases. Consequently, the amount of vapor recycled to the system increases and the temperature and properties of the Excess BOG entering (EBOG-in) are affected. The 'Cold SM-in' stream temperature is increased from -160 °C by a step of 3 °C at each pressure step. This increase is subjected to two constraints: the first is to avoid the temperature cross inside the heat exchanger. The second is the amount of vapor recycled to the system, which is limited to 50 % of the inlet flow since it increases the load on the compressors and decreases the flow quality. At each pressure and temperature step, the different parameters such as composition, pressure, temperature, flow rates, power of the streams, and equipment are monitored by the link established between Excel and HYSYS using VBA. Tracking these parameters helps in assessing their impact on the storage system. Moreover, the temperature versus the power profiles at each pressure step are plotted as appears in Figure 2 to calculate the system energy storage capacity.
The energy assessment is proceeded considering 1 bar charging pressure and over all the discharging pressure range, and the comparison is established based on the different SM specific energy results. The calculation is carried out for 1 kg of SM by integrating the obtained temperature profiles using Eq(1) and Eq(2). Results presented in Figure 3 show that at 13 bar discharging pressure, both n-Butane and i-Hexane offer the highest specific energy capacities. However, when higher pressures are considered, n-Butane becomes a better candidate. For pressures higher than 18 bar, n-Pentane shows a significant enhancement in its performance and offers the best results with specific energy reaching 180 kJ/kg at 43 bar. The main reason for the variation of the PCMs performance with pressure is their fusion temperature and its consequent effect on the percentage of material undergoing fusion. For example, at 13 bar, n-Pentane stores energy only in the form of sensible heat since its fusion temperature lies outside the operating temperature range (-162 °C to -130 °C). When the pressure is further increased, n-Pentane undergoes a phase change and stores a higher amount of energy. The same applies to n-Butane, which partially undergoes fusion at low discharging pressure. On the other hand, all the PCMs outperformed Ice due to the additional latent heat provided during fusion, which contributes to more than 60 % of their total energy storage capacity.

Figure 2: LNG evaporation and Excess BOG liquefaction temperature profiles

Figure 3: SM specific energy storage capacity at different discharging pressure steps

The mass and volume of the TES unit constitute limitations on the LNG carrier and should be considered in characterizing the system. These parameters are calculated for an operating liquefaction duration of 24 h and assuming that the tanker is at rest, which is equivalent to a goal of 4 MWh of cold energy storage. The SM mass and the total storage volume are presented using Figure 4a and Figure 4b, respectively. The total storage volume is calculated considering the SM expansion at 45 °C and a 20 % increase in the construction volume. Results show that the SM mass function of the discharging pressure varies inversely to that of the energy storage capacity. The mass of the different PCMs used does not exceed 200 tons for pressure above 18 bar, whereas the Ice mass remained very high at all pressure ranges reaching a minimum value of 380 tons. Similarly, the Ice total storage volume is elevated compared to the PCMs. Moreover, n-Butane and i-Hexane possess the lowest storage volumes below 18 bar, while n-Pentane offers the lowest volume at high pressures.
Figure 4: TES parameters to attain the energy storage goal: a. SM mass b. Total storage volume

6. Conclusion

Throughout this study, a new on-board BOG reliquefaction technology is presented based on thermal energy storage. The thermal energy storage unit operates on two modes: charging and discharging. Cold energy is stored in the form of latent and/or sensible energy when LNG is evaporated to be used later in reliquefying the excess BOG. A parametric energy assessment of the system performance was carried out for variable operating conditions and different types of storage materials. Results showed that maintaining a charging pressure of 1 bar and increasing the discharging pressure increases the energy storage capacity. The latter parameter should be subjected to further economic assessment due to the additional compression power needs and implicit investment costs. The storage material performance remarkably varied with these conditions; however, all PCMs showed better energy storage capacity offering a more compact system than Ice. n-Butane and i-Hexane showed good performance at all discharging pressures with a specific energy capacity ranging between 95 and 150 kJ/kg. n-Pentane presented optimum results at high pressures with a specific energy up to 180 kJ/kg at 43 bar. Regarding the environmental constraints, this system can eliminate the use of the gas combustion unit and decrease the ship’s CO₂ emissions.

References