CRYOGENIC TECHNOLOGIES FOR STORAGE
OF OIL AND OIL PRODUCTS

N. G. Kirillov

Technologies and principles of operation of plants for recovery of light hydrocarbon fractions (LHF) by direct liquefaction of LHF in low-temperature Stirling machines and use of an intermediate loop containing liquid nitrogen are discussed.

In using oil storage tanks, a serious ecological problem faced is how to recover the light hydrocarbon fractions (LHF) that comprise the major share of the loss of valuable materials and to prevent discharge of deleterious emissions into the ambient atmosphere.

In terms of sanitary standards for industrial enterprises, oil tank farms rank in the top category of environmental hazard and are at par with oil refining enterprises, whose sanitary protection area extends as far as 1000 m, and if oil containing <0.5% sulfur is refined, to not less than 500 m.

The process of oil and oil products evaporation from storage tanks under static conditions are profoundly affected by the ambient temperature, solar radiation, and several other factors, such as pressure and volume of the gas space, area of contact of the oil products with the gas space, atmospheric pressure, etc. [1].

The volume of oil and oil products loss during storage depends on the conditions of operation of the oil tank farms. Investigations have revealed that the structure of the evaporation loss in tank farms of oil refining enterprises is as follows: from ventilation of the gas space 60–65%, from “major breathing” 32–34%, and from “minor breathing” 3–6%. High loss from ventilation of the gas space is attributable to inadequate leak-tightness of the tanks, especially of the covers, and the loss from “major breathing” is due to high tank turnover (number of filling–withdrawal cycles). In the case of prolonged storage of oil products, the loss occurs essentially due to “minor breathing” of the tanks.

“Major breathing” of the tanks occurs due to escape of the vapor–air mixture to the surroundings in the process of filling of the tanks with oil and oil products, whereupon the gas space diminishes and that triggers the breathing valve. The reverse phenomenon, i.e., influx of air into the tank, occurs during withdrawal of the product. The volume of “major breathing” roughly matches the amount of the products drawn into the tank. The loss due to “major breathing” increases with increase of tank turnover and depends on the climatic zone. The loss data for overground tanks having fixed covers are given in Table 1.

To calculate the loss due to “major breathing” of fuel tanks, we can use the equation

\[ m_{\text{maj,b}} = 4.3511 \times 10^6 \rho p V k_t k_s, \]

where \( \rho \) is the density of the motor fuel, kg/m\(^3\); \( p \) is the pressure of the fuel vapor, Pa; \( V \) is the volume of the tank, m\(^3\); \( k_t \) is the tank turnover factor; and \( k_s \) is the correction factor characterizing the properties of the stored product.

“Minor breathing” of the tanks is caused by fluctuations in the ambient temperature. As the air temperature rises during daytime, the tank surface heats up, and the pressure and temperature of the vapor–gas mixture and so evaporation of the oil products, especially of LHF, increase. Pressure rise in the vapor–gas space causes triggering of the breathing valve and escape of the vapor–gas mixture into the ambient atmosphere. In this process, the degree to which the tank is filled with...
the oil products (for instance, with motor fuel) is of great importance: with increase of filling the gas space decreases and, consequently, evaporation loss of the light fractions diminishes. During the night, as the products cool down, the pressure of the vapor–gas mixture falls, a partial vacuum develops, and the reverse process occurs, i.e., through the intake valve air enters the gas space of the tank.

The loss due to “minor breathing” of tanks having a fixed cover is

\[ m_{\text{min,b}} = K_1 V^{2/3} \frac{K_2}{100} \exp \left( 0.039 T \right) \frac{M}{22.4 t^1} \]

where \( K_1 \) and \( K_2 \) are factors that depend on the properties of the motor fuel; \( M \) is the mean molecular mass of the motor fuel vapor; and \( t \) is the temperature in the gas space, K.

Nowadays, for utilization (loss reduction) of LHF during oil and oil products storage, various techniques and devices are employed: gas-leveling systems, torch burning, membrane separation of mixture of LHF, cooling with nitrogen, adsorption (activated charcoal), absorption (petroleum oils), floating covers, pontoons, etc. The major flaw of these technologies is that they do not guarantee recovery (trapping) of the LHF.

For instance, the Regulations for Oil Tank Operation recommend application of pontoons and reflecting disks for reducing loss of oil products. In conformance with these regulations, they reduce emissions by 80 and 20%, respectively. However, research has shown that these recommended devices are effective only in limited areas: pontoons, for tank capacities of 5000 m³ and above, and reflecting disks, for a tank turnover factor of more than 60 \[2\].

In view of this, development and choice of devices for reducing emission of vapors of oil products during their storage at oil tank farms are a pressing issue, which can be tackled only by wide application of modern oil product vapor reduction techniques and by storing oil products by methods that prevent release of pollutants into the atmosphere.

A comparative assessment was made at the Institute of the Problems of Petrochemical Processing of the Academy of the Sciences of the Republic of Bashkorstan (IPNKhP AN RB) of the level of atmospheric pollution because of application of the aforementioned methods at the goods and raw materials parks of oil refineries \[3\]. Considering that the parks have different capacities (number of tanks) for receiving and storing oil products, the calculation was carried out in terms of specific quantities (for one ton of the oil products present in the emission). The comparative assessment was based on standardization principle (reducing the emission mass to the equivalent mass of sulfur dioxide), which is used in calculations of the atmospheric pollution index (API):

\[ \text{API} = \frac{M}{\text{MPC}_i} \text{MPC}_{\text{SO}_2}, \]

where \( M \) is the mass of the emission of the \( i \)th substance and \( \text{MPC}_i \) and \( \text{MPC}_{\text{SO}_2} \) are the maximum permissible concentration of the \( i \)th substance and of sulfur dioxide.

\begin{table}
\centering
<table>
<thead>
<tr>
<th>Tank capacity, m³</th>
<th>Oil products loss from overground tanks (ton/yr) at annual tank turnover factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12</td>
</tr>
<tr>
<td>400</td>
<td>2.9/4.8</td>
</tr>
<tr>
<td>1000</td>
<td>6.7/11.2</td>
</tr>
<tr>
<td>2000</td>
<td>12.6/22.2</td>
</tr>
<tr>
<td>3000</td>
<td>20.5/34.8</td>
</tr>
<tr>
<td>5000</td>
<td>28.4/60.4</td>
</tr>
</tbody>
</table>
\end{table}

Note: The data for the northern climatic zone are given in the numerator and for the southern, in the denominator.