Analysis of selected aspects of a tank gassing-up process on board liquefied petroleum gas carrier. Part I

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Abstract The paper is a thermodynamics analysis of the removal of any inert gas from the tank using the vapors of any liquefied petroleum gas cargo (called cargo tank gassing-up operation). For this purpose, a thermodynamic model was created which considers two boundary cases of this process. The first is a 'piston pushing' of inert gas using liquefied petroleum gas vapour. The second case is complete mixing of both gases and removal the mixture from the tank to the atmosphere until desired concentration or amount of liquefied petroleum gas cargo in the tank is reached. Calculations make it possible to determine the amount of a gas used to complete the operation and its loss incurred as a result of total mixing of both gases.

Nomenclature

c_E	–	gas E concentration in tank at any moment of filling
c_{outE}	–	gas E concentration in the tank
c_{pE}	–	gas E specific heat at a constant pressure, J/kgK
c_{pinE}	–	gas E introduced to the tank specific heat at a constant pressure
c_v	–	specific heat at constant volume
c_{vA}	–	gas A specific heat at constant volume, J/kgK,
c_{vE}	–	specific heat at constant volume
C	–	any constant of m_E function

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dm_E	–	change of a gas E mass, kg
dm_{inE}	–	gas E introduced to the tank change, kg
dm_m	–	change of a gas mass in tank, kg
dp_z	–	change of tank pressure, Pa
$d\tau$	–	time rate increase, s
$d\tau_A$	–	change of time for gas A, s
dU	–	change of internal space energy, J/kg
dU_E	–	change of internal energy of gas E, J/kg
f_{inE}	–	area cross section of a pipe introducing gas E to the tank, m^2
f_{outm}	–	area cross section of a pipe removing a gas mixture from the tank, m^2
h	–	enthalpy, J/kg
h_{inE}	–	enthalpy of a gas E introduced to the tank, J/kg
h_{outm}	–	enthalpy of a gas mixture removing from the tank, J/kg
$\dot{L}$	–	work done flux, W
m	–	mass, kg
m_A	–	gas A mass in the tank at any moment of filling, kg
m_E	–	gas E mass in the tank at any moment of filling, kg
m_{Ex}	–	gas E mass introduced to the tank during stage I
m_{inE}	–	gas E mass introduced to the tank, kg
m_{lossE}	–	gas E loss, kg
m_{totE}	–	total gas mass used to gassing-up process, kg
m_z	–	both gas mass in the tank at any moment of filling, kg
$\dot{m}$	–	mass flow, kg/s
$\dot{m}_{inE}$	–	mass flow of gas E introduced to the tank, kg/s
$\dot{m}_{outm}$	–	mass flow of gas removing from the tank, kg/s
$\dot{Q}$	–	heat flux supplied to the system, W
p	–	pressure, Pa
p_A	–	gas A pressure, Pa
p_{atm}	–	atmospheric pressure, Pa
p_E	–	gas E pressure, Pa
p_{inE}	–	gas E pressure introduced to the tank, Pa
p_z	–	tank pressure, Pa
R_A	–	gas A individual constant, kJ/kg
R_E	–	gas E individual constant, kJ/kg
R_i	–	individual gas constant, kJ/kg
T	–	temperature, K
T_A	–	gas A temperature in the tank, K
T_{inE}	–	gas E temperature introduced to the tank, K
T_z	–	tank temperature at any moment of filling, K
U	–	energy, J/kg
U_A	–	gas A energy in tank, J
U_E	–	gas E energy in tank, J
U_z	–	tank energy, J
v_A	–	gas A specific volume, m^3/kg
v_{inE}	–	gas E introducing to the tank specific volume, m^3/kg
V	–	volume, m^3
V_z	–	tank volume, m^3

Greek symbols

κ_A – gas A adiabat exponent
κ_E – gas E adiabatic exponent
μ – ratio of the stream narrowing
ψ – value of a flow cross section function
τ – time, s
τ_1 – time of the operation including pressure increase by the use of gas E, s

1 Introduction

Liquefied petroleum gas (LPG) gas carriers are used to transport liquefied gases. Depending on the temperature value and pressure at which individual cargo should be transported, gas carriers are divided into three groups: fully refrigerated ships that carry cargo at ambient temperature, semi-pressurised vessels and vessels carrying cargo at atmospheric pressure, which allow transport of cargo with temperatures down to minus 104°C (169 K), slightly below ethylene boiling point at atmospheric pressure [5].

The most important loading operations are the aerating of tanks and their inerting, which is preparation for the gassing-up process. Before carrying out cargo operations, for specific loads, each tank must undergo a visual inspection. The condition of the material is checked for possible presence of corrosion or cracks in the bottom of the tank, cleanliness and correctness of protection of all equipment elements in the tank. Also check that there is no water on the bottom of the tank. When the visual inspection is completed, tanks must be sealed and the inerting operation by the use of nitrogen or carbon dioxide can be started [1].

Inverting is an operation to create an inert atmosphere in the tank and all pipelines (without oxygen) to avoid creating an explosive mixture between a cargo and the oxygen. This procedure is performed before each cargo is loaded. The required oxygen level is achieved by flushing the tanks with inert gas, such as nitrogen or carbon dioxide, which can be delivered from the shore or generated on the ship, e.g., using the pressure swing adsorption (PSA) installation. The compressor draws in and compresses air, which after preliminary drying and cleaning passes through membrane modules dividing the air into two parts, nitrogen and oxygen mixed with other gases. Nitrogen thus obtained with a purity up to 99.9 vol% is introduced into tanks during inerting of cargo tanks [9].

None of the gases being an inert gas that can be used on ships, nitrogen or carbon dioxide, can be liquefied by the ship's reliquefaction plant. Therefore, it is necessary to remove an inert gas from the cargo tank. This possibility is provided by the operation of gassing-up – introducing cargo vapour to the tank removing inert gas at the same time, carried out at ambient temperature. Inappropriate inert gas removal causes an emergency stop of the cargo compressors due to too high condensing pressure of a gas mixture. In order to solve the problem, thermodynamics model of gassing-up operation after inerting the tank was built [3, 8].

2 Theoretical computational model – tank gassing-up by the use of cargo vapour

2.1 Outline of the model

The purpose of calculation model is to determine the optimal technical parameters at which gassing-up should be carried out, the amount of cargo used in relation to various temperatures and pressures in the tank, cargo loss of gassing-up, and thus, the elimination of additional cargo loss during tank cooling caused by improper gassing-up process, as well as to determine the time the operation will be carried out. The model consists of two stages. The first stage is to introduce the cargo vapours (gas E) into a tank filled with inert gas (gas A). Gas A is under specified technical parameters, i.e. pressure and temperature. Gas E is introduced into the tank with a defined mass flow until the desired pressure in the tank is reached. The second stage is the removal of gas A from the tank (completely or up to a certain concentration/a mass of gas E). Two cases of the second stage were considered, i.e. 'piston ejection' of gas A using gas E and complete mixing of both gases and removal the mixture from the tank until desired concentration or mass of gas E in the tank is achieved (Fig. 1).

2.2 Filling the tank beneath the inert gas with cargo vapour to the set pressure in the tank

Due to the fact that the analyzed system takes or releases the substance outside, the tank is considered as an open system. In accordance with the first law of thermodynamics, which states that the rate of internal energy change of the system, ΔU, is equal to the sum of the rate of heat supplied, $\dot{Q}$, and the power in the system, $\dot{L}$. The equation of the considered system
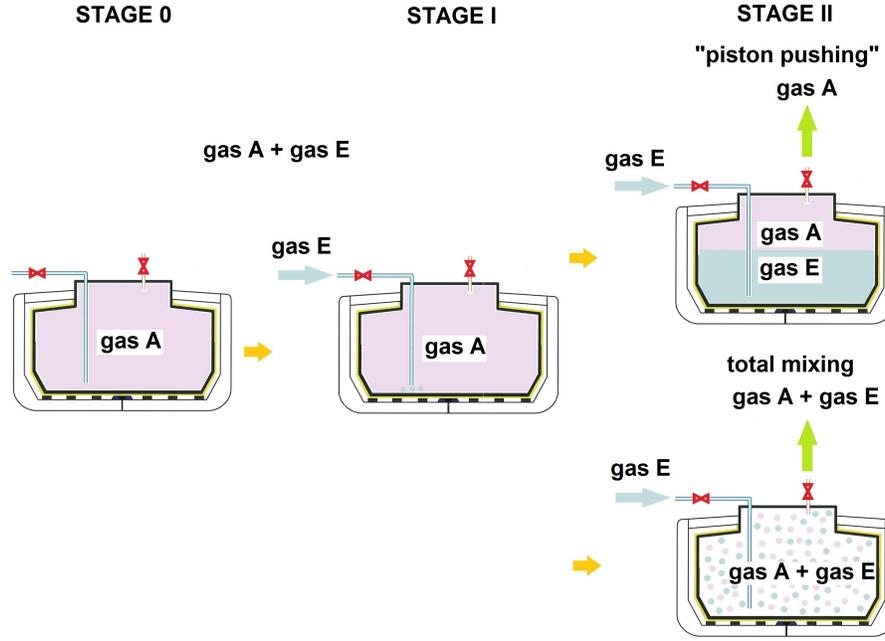
Figure 1: Stages and assumptions of the gassing-up computational model, filling the tank with gas E and removing gas A by 'piston pushing' and total mixing of both gases.

taking into account the energy change in the function of time for open system takes the following form [6,7]:

$$\frac{dU}{d\tau} = \sum (\dot{m}h)_{in} - \sum (\dot{m}h)_{out} + \dot{Q} - \dot{L} \,. \tag{1}$$

The isothermal model is taken into consideration. It assumes that in the first stage, i.e., filling with gas E the tank under atmosphere of gas A to the set pressure in the tank p_z. The system does not release the substance outside, and no work is carried out. According to the above, for built model, formula (1) takes the form

$$\frac{dU}{d\tau} = \dot{m}_{inE} h_{inE} \,. \tag{2}$$

According to the law of mass conservation [9], the increase of the ethylene mass in the tank, m_E, in the function of time, τ, has the form [2]

$$\frac{dm_E}{d\tau} = \dot{m}_{inE} \,. \tag{3}$$

Substituting formula (3) into formula (2) is given:

$$\frac{dU_E}{d\tau} = \frac{dm_E}{d\tau} h_{inE} \,, \tag{4}$$

$$dU_E = dm_E h_{inE} \,. \tag{5}$$

Because the product of a mass and internal energy for a molar quantity is equal to the product of specific heat at a constant volume, mass and temperature [7, 11]

$$mU = c_v mT, \tag{6}$$

and internal energy for molar quantity is the product of mass, m, and internal energy, u, in general [10]

$$U = mu \,, \tag{7}$$

then

$$U = c_v mT, \tag{8}$$

and after differentiating above equation, differential of total internal energy yields [4]

$$dU = c_{vE} d \left(m_{inE} T_{inE} \right). \tag{9}$$

For simplicity of calculations, gas A and gas E are considered as ideal gases. To calculate the differential of internal energy, dU, we use the ideal gas law (Clapeyron equation) [2]

$$pV = mR_i T \,. \tag{10}$$

Eq. (10) is substituted to Eq. (9), to give

$$m_{inE} T_{inE} = \frac{p_{inE} V_z}{R_E} \,, \tag{11}$$

and finally dU_E is received

$$dU_E = c_{vE} d \left(\frac{p_{inE} V_z}{R_E} \right) = \frac{c_{vE}}{R_E} d \left(p_{inE} V \right). \tag{12}$$

Consequently

$$dU_E = \frac{c_{vE}}{R_E} \left(dp_{inE} V_z + p_{inE} dV_z \right). \tag{13}$$

Because volume of the tanks, V_z, is constant and hence $p_E dV_z = 0$, than

$$dU_E = \frac{c_{vE}}{R_E} V_z dp_z \,. \tag{14}$$

If the enthalpy of ethylene introduced into the tank is equal to

$$h_{inE} = c_{pinE}T_{inE} \,, \tag{15}$$

then substituting Eq. (15) into Eq. (5) returns

$$U_E = c_{pE}T_{inE}dm_E \,. \tag{16}$$

Substituting above formula to Eq. (14) the following is received

$$c_{pE}T_{inE}dm_E = \frac{c_{vE}}{R_E}V_z dp_z \,. \tag{17}$$

Using Dalton's law, which says that the sum of partial pressures of gases is equal to the total pressure of the gas mixture in the tank [13], i.e.,

$$p_z = p_E + p_A \,, \tag{18}$$

after transformation, the formula for the gas E partial pressure is given as

$$p_E = p_z - p_A \,. \tag{19}$$

Substituting the partial pressure of gas E, p_E, into Eq. (17), the following equation is obtained

$$c_{pE}T_{inE}dm_{inE} = \frac{c_{vE}}{R_E}V_z d\left(p_z - p_A\right) \,. \tag{20}$$

According to the ideal gas law (10), the partial pressure of gas A is

$$p_A = \frac{m_A R_A T_A}{V_z} \,. \tag{21}$$

Equation (20) takes the form

$$c_{pE}T_{inE}dm_{inE} = \frac{c_{vE}}{R_E}V_z d\left(p_z - \frac{m_A R_A T_A}{V_z}\right) \,, \tag{22}$$

and after transformation

$$\frac{c_{pE}}{c_{vE}}T_{inE}dm_{inE} = \frac{V_z}{R_E}d\left(p_z - \frac{m_A R_A T_A}{V_z}\right) \,. \tag{23}$$

Since the κ coefficient is equal to the quotient of specific heat at constant pressure c_p to specific heat at constant volume, c_v, [12], the κ_E coefficient for ethylene is

$$\frac{c_{pE}}{c_{vE}} = \kappa_E \,. \tag{24}$$

Equation (23) thus takes the form

$$\kappa_E T_{inE} dm_{inE} = \frac{V_z}{R_E} d\left(p_z - \frac{m_A R_A T_A}{V_z}\right),$$ (25)

and afer transformation

$$\kappa_E T_{inE} dm_{inE} = \frac{V_z}{R_E} dp_z - \frac{m_A R_A}{R_E} dT_A.$$ (26)

Flow rate, $\dot{m}$, can be calculated treating throttling in the pipeline as from the nozzle flow equation. Because the model assumes flow through a constant diameter pipeline, the flow through the de Laval nozzle was assumed for simplification of calculations, according to the formula [7,12]

$$\dot{m}_E = \frac{dm_E}{d\tau} = \mu f_{inE} \sqrt{\frac{p_{inE}}{v_{inE}}} \psi.$$ (27)

Because value ψ is given by the formula (26)

$$\psi = \sqrt{\frac{2\kappa_E}{\kappa_E - 1}\left[\left(\frac{p_z}{p_{inE}}\right)^{\frac{2}{\kappa}} - \left(\frac{p_z}{p_{inE}}\right)^{\frac{\kappa_E+1}{\kappa_E}}\right]},$$ (28)

the weight differential of ethylene in time is given by the formula

$$\frac{dm_E}{d\tau} = \mu f_{inE} \sqrt{\frac{p_{inE}}{v_{inE}}} \sqrt{\frac{2\kappa_E}{\kappa_E - 1}\left[\left(\frac{p_z}{p_{inE}}\right)^{\frac{2}{\kappa_E}} - \left(\frac{p_z}{p_{inE}}\right)^{\frac{\kappa_E+1}{\kappa_E}}\right]}.$$ (29)

The formula for the gas E mass increase in the tank is obtained from Eq. (26) in the form

$$dm_E = \frac{V_z}{R_E \kappa_E T_{inE}} dp_z - \frac{m_A R_A}{R_E \kappa_E T_{inE}} dT_A.$$ (30)

Substituting Eq. (30) to Eq. (29) returns the following

$$\frac{V_z}{R_E \kappa_E T_{inE}} \frac{dp_z}{d\tau} - \frac{m_A R_A}{R_E \kappa_E T_{inE}} \frac{dT_A}{d\tau}$$
$$= \mu f_{inE} \sqrt{\frac{p_{inE}}{v_{inE}}} \sqrt{\frac{2\kappa_E}{\kappa_E - 1}\left[\left(\frac{p_z}{p_{inE}}\right)^{\frac{2}{\kappa_E}} - \left(\frac{p_z}{p_{inE}}\right)^{\frac{\kappa_E+1}{\kappa_E}}\right]}.$$ (31)

To simplify calculations, the isothermal model was adopted, therefore

$$\frac{dT_A}{d\tau} = 0\,, \tag{32}$$

Equation (31) takes the form

$$\frac{V_z}{R_E \kappa_E T_{inE}} \frac{dp_z}{d\tau}$$
$$= \mu f_{inE} \sqrt{\frac{p_{inE}}{v_{inE}}} \sqrt{\frac{2\kappa_E}{\kappa_E - 1} \left[\left(\frac{p_z}{p_{inE}} \right)^{\frac{2}{\kappa_E}} - \left(\frac{p_z}{p_{inE}} \right)^{\frac{\kappa_E+1}{\kappa_E}} \right]}\,, \tag{33}$$

$$dp_z = \frac{R_E \kappa_E T_{inE}}{V_z} \mu f_{inE}$$
$$\times \sqrt{\frac{p_{inE}}{v_{inE}}} \sqrt{\frac{2\kappa_E}{\kappa_E - 1} \left[\left(\frac{p_z}{p_{inE}} \right)^{\frac{2}{\kappa_E}} - \left(\frac{p_z}{p_{inE}} \right)^{\frac{\kappa_E+1}{\kappa_E}} \right]} d\tau\,. \tag{34}$$

Substituting the numerically integrated pressure values from Eq. (34) to Eq. (29), the mass of gas E, m_{inE}, introduced into the tank is given relative to time, according to the changing pressure in the tank, p_z.

The percentage gas E concentration in the tank is calculated according to the following formula, obtained by inserting the mass of gas E into Eq. (29):

$$c_E = \frac{m_E}{m_E + m_A} 100\%\,. \tag{35}$$

Gas A mass is calculated using the Clapeyron formula

$$m_A = \frac{p_z V_z}{R_A T_z}\,. \tag{36}$$

2.3 Removing gas A from the tank filled with gas A and gas E

According to the model assumptions, the second stage of calculations constitutes of removal of gas A from the tank until required concentration of E gas in the tank is obtained. In this stage the tank is filling and at the same time the mixture is removed from the tank. From the mass balance,

the mass difference of the mixture, m_z, in the tank at time τ, can be determined, equal to the quotient of the mass flow rate of gas E introduced into the tank $\dot{m}_{inE}$ and the mass flow rate of the mixture removed from the tank $\dot{m}_{outm}$

$$\frac{dm_m}{d\tau} = \dot{m}_{inE} - \dot{m}_{outm} \,. \tag{37}$$

According to the principle of energy conservation [6], the energy of an isolated system does not change, despite changes taking place in its interior. The energy balance for the system is written in the form

$$\frac{dU_m}{d\tau} = \dot{m}_{inE}h_{inE} - \dot{m}_{outm}h_{outm} \,. \tag{38}$$

From the transformation of Eq. (37) there can be determined the mass flow rate

$$m_{inE} = \frac{dm_m}{d\tau} + \dot{m}_{outm} \,, \tag{39}$$

which is next substituted to the energy balance Eq. (38), to give

$$\frac{dU_m}{d\tau} = \left(\frac{dm_m}{d\tau} + \dot{m}_{outm} \right) h_{inE} - \dot{m}_{outm}h_{outm} \,. \tag{40}$$

The internal energy of the mixture is referred to as [12]

$$U = c_v T m \,. \tag{41}$$

Total internal energy of the mixture in the tank is

$$U_m = U_E + U_A \,. \tag{42}$$

By developing the above formula the following is given

$$U_m = m_E c_{vE} T_E + m_A c_{vA} T_A \,. \tag{43}$$

To simplify the calculations, a model assuming a constant temperature in the tank has been adopted, i.e., $T_E = T_A = T_z$ with the constant pressure in the tank $p_z = $ const. Differentiating the Eq. (43) by time

$$\frac{dU_m}{d\tau} = \frac{d\left(m_E c_{vE} T_E\right)}{d\tau} + \frac{d\left(m_A c_{vA} T_A\right)}{d\tau} \,. \tag{44}$$

If the differential of a mass mixture in tank is equal to the sum of differentials of ethylene mass, dm_E, and nitrogen mass, dm_A, in tank, i.e.

$$dm_m = dm_E + dm_A \,, \tag{45}$$

after transforming formulas (40) and (44) the following equation is given

$$c_{vA}T_z\frac{dm_A}{d\tau} + c_{vE}T_z\frac{dm_E}{d\tau} =$$
$$= \frac{dm_E}{d\tau}h_{inE} + \frac{dm_A}{d\tau}h_{inE} + \dot{m}_{outm}h_{inE} - \dot{m}_{outm}h_{outm}\,, \qquad (46)$$

which after simplifications reads

$$(c_{vA}T_z - h_{inE})\frac{dm_A}{d\tau} + (c_{vE}T_z - h_{inE})\frac{dm_E}{d\tau} = \dot{m}_{outm}(h_{inE} - h_{outm})\,. \quad (47)$$

The calculation model considers two extreme cases of gas A removal from cargo tank – 'piston pushing' of gas A, without cargo loss (gas E) and complete mixing of both gases and removing the mixture until the set gas E concentration in the tank, c_E, is achieved.

2.4   'Piston pushing' gas A by the use of gas E

The first case of removal of gas A from the tank is the 'pushing' of this gas by the use of gas E which operates like a piston pushing out gas A from the tank. For 'piston pushing' of gas A from the tank it is assumed that $\dot{m}_{outm} = \dot{m}_{outA}$. Due to the fact that for 'piston pushing' of gas A there is no cargo – gas E loss, then

$$\frac{dm_{outE}}{d\tau} = 0\,, \qquad (48)$$

gas A flow introduced to the tank might be described by the formula

$$\dot{m}_{inE} = \frac{dm_E}{d\tau}\,, \qquad (49)$$

and nitrogen mass flow removing from the tank

$$\dot{m}_{outA} = \frac{dm_A}{d\tau}\,. \qquad (50)$$

According to above assumptions, Eq. (47) takes the form

$$(c_{vA}T_z - h_{inE})\frac{dm_A}{d\tau} = \dot{m}_{outm}(h_{inE} - h_{outm})\,. \qquad (51)$$

By determining the nitrogen mass difference dm_A from the above formula, we obtain the equation for changing the mass of gas A in the tank

$$dm_A = \dot{m}_{outm}\frac{h_{inE} - h_{outm}}{c_{vA}T - h_{inE}}d\tau\,. \qquad (52)$$

According to the model assumptions, gas A is removed from the tank to atmosphere. In addition, the amount of gas we introduce into the tank is equal to what is removed from the tank, $\dot{m}_{in} = \dot{m}_{out}$ (and $h_{in} = h_{out}$). Using the formula for the flow rate through the de Laval nozzle [10], it is possible to determine the increase of the amount of gas A in the tank, dm_A, in time τ.

For considered case of 'piston pushing out' of gas A from the tank, the formula for gas outflow from the tank to the atmosphere $\dot{m}_{outm}$ is given in the form

$$\dot{m}_{outm} = \mu f_{outm} \sqrt{\frac{p_z}{v_m}} \sqrt{\frac{2\kappa_m}{\kappa_m - 1} \left[\left(\frac{p_{atm}}{p_z} \right)^{\frac{2}{\kappa_m}} - \left(\frac{p_{atm}}{p_z} \right)^{\frac{\kappa_m + 1}{\kappa_m}} \right]} . \qquad (53)$$

Substituting the above formula to Eq. (50), we obtain the equation for mass of gas A in the tank

$$dm_A = \dot{m}_{outm} \frac{h_{inE} - h_{outm}}{c_{vA}T - h_{inE}} \mu f_{outm} \sqrt{\frac{p_z}{v_m}}$$
$$\times \sqrt{\frac{2\kappa_m}{\kappa_m - 1} \left[\left(\frac{p_{atm}}{p_z} \right)^{\frac{2}{\kappa_m}} - \left(\frac{p_{atm}}{p_z} \right)^{\frac{\kappa_m + 1}{\kappa_m}} \right]} d\tau . \qquad (54)$$

By determining f_{outm} from the obtained equation, the cross sectional area equation of a nozzle through which the gas flows is given

$$f_{outm} = \frac{\dot{m}_{outm}}{\mu \sqrt{\frac{p_z}{v_m}} \sqrt{\frac{2\kappa_m}{\kappa_m - 1} \left[\left(\frac{p_{atm}}{p_z} \right)^{\frac{2}{\kappa_m}} - \left(\frac{p_{atm}}{p_z} \right)^{\frac{\kappa_m + 1}{\kappa_m}} \right]}} . \qquad (55)$$

Because gas A is pushed out by gas on the principle of a piston, above equation takes the form

$$f_{outA} = \frac{\dot{m}_{outA}}{\mu \sqrt{\frac{p_z}{v_A}} \sqrt{\frac{2\kappa_A}{\kappa_A - 1} \left[\left(\frac{p_{atm}}{p_z} \right)^{\frac{2}{\kappa_A}} - \left(\frac{p_{atm}}{p_z} \right)^{\frac{\kappa_A + 1}{\kappa_A}} \right]}} . \qquad (56)$$

Substituting obtained result into the equation for the increase of mass of gas A in the tank dm_A, assuming that $\dot{m}_{outm} = \dot{m}_{outA}$, the increase in the amount of gas A in the tank and the time of this operation will be determined.

2.5 Removing gas A from the tank with complete mixing of gas A and gas E

The second extreme case of gas removal from tank A is a complete mixing of both gases and removal from the tank of the mixture until complete removal of gas A or until the specified content of gas A in the mixture is reached.

General equation of gas E increase in the tank dm_E in time τ can be determined as

$$\frac{dm_E(\tau)}{d\tau} = \dot{m}_{inE} - c_{outE}\dot{m}_{outm} \,, \tag{57}$$

while the concentration of gas E removed from the tank

$$c_{outE} = \frac{m_E(\tau)}{m_m} \,. \tag{58}$$

Due to the large number of unknowns, which are continuously changing (depending on the concentration of both gases in the tank), the technical parameters in Eq. (54), i.e., mass flow of the mixture flowing out of the tank $\dot{m}_{outm}$, enthalpy of this mixture h_{outm}, its specific volume v_m and the coefficient $\kappa_m$changing as a function of time τ to determine the amount of gas E used for the gassing-up process and the time of carrying out this operation for the case of complete mixing of both gases, the calculation model has been significantly simplified. It is assumed, that the mass mixture in the tank during the process m_z is constant and is equal to mass of gas in the tank after finishing introduction of gas E to gas A to the determined pressure in tank (stage 0) m_A

$$m_z = \frac{p_A V_z}{R_A T_A} \,. \tag{59}$$

After substituting the formulas (56) and (57) into Eq. (55), there is obtaine the linear differential Eq. (62), where for the shortening of the notation we marked A and B being equal, respectively, i.e.

$$A = \dot{m}_{inE} \,, \tag{60}$$

$$B = \frac{\dot{m}_{inE}}{m_z} \,. \tag{61}$$

Therefore

$$\frac{d\dot{m}(\tau)}{d\tau} + B\dot{m}_E(\tau) = A \,. \tag{62}$$

After transforming the above equation according to the scheme of solving differential linear equations [12], we obtain the formula for the mass of ethylene as a function of time

$$m_E(\tau) = e^{-Bt} \int Ae^{Bt}\,\mathrm{d}\tau = e^{-Bt}\left(\frac{Ae^{Bt}}{B} + C\right) = \frac{A}{B} + Ce^{-Bt}\,, \qquad (63)$$

where C is any constant, for each real number C function m_E fulfil Eq. (62).

The calculation model has been extended by two cases.

2.5.1   Case I

It assumes, that only gas A is in the tank (the pressure in the tank was not increased by introducing additional gas E, i.e. at the same time the valves introducing gas E into the tank and removing the mixture of gas A and gas E from the tank were opened). Therefore, for $m_E(0) = 0$, the constant in Eq. (63) is having a form

$$C = -\frac{A}{B}\,. \qquad (64)$$

After substitution (64) to formula (62), mass of gas E in time τ is equal to

$$m_E(\tau) = \frac{A}{B}\left(1 - e^{-Bt}\right) \qquad (65)$$

(and the above equation will be mathematically correct for a specific value m_E).

To simplify the calculations, the equation that has been developed assumes performing calculations for a specific (desired) mass of gas E m_E in the tank after the gassing-up process is completed. After transforming Eq. (65), it can be calculated the gassing-up time without tank pressure increase at the beginning

$$\tau = -\frac{1}{B}\ln\left(1 - m_E\frac{B}{A}\right). \qquad (66)$$

Knowing the time of gassing-up operation and the mass flow of gas E introduced into the tank, it can be determined the total amount of gas E used in this process m_{totE} and cargo loss m_{lossE} respectively:

$$m_{totE} = \dot{m}_{inE}\tau\,, \qquad (67)$$

$$m_{lossE} = m_{totE} - m_E\,. \qquad (68)$$

2.5.2   Case II

It assumes that a specific amount of E, m_{Ex}, was introduced into the tank first, which increased the pressure in the tank, then the atmosphere removal valve was opened (the valves were opened, the mixture was removed from the tank until a certain amount of gas E was received in the tank). Therefore, for $m_E(0) = m_{Ex}$, C from Eq. (62) is

$$C = m_{Ex} - \frac{A}{B}\,, \tag{69}$$

thus

$$m_E(\tau) = \frac{A}{B} + \left(m_{Ex} - \frac{A}{B} \right) e^{-Bt}, \tag{70}$$

whereas

$$\tau = \frac{1}{B} \ln \left(\frac{A - m_{Ex}B}{A - m_E B} \right). \tag{71}$$

Taking into account the time during which the pressure in the tank was increased, the formula will take the form

$$\tau_1 = \frac{1}{B} \ln \left(\frac{A - m_{Ex}B}{A - m_E B} \right) + \frac{m_{Ex}}{\dot{m}_{inE}}\,. \tag{72}$$

The total amount of gas E used in this process, m_{totE}, and cargo loss, m_{lossE}, can be calculated by formulas respectively:

$$m_{totE} = \dot{m}_{inE}\tau + m_{Ex}\,, \tag{73}$$

$$m_{lossE} = m_{totE} - m_E\,. \tag{74}$$

3   Summary

Developed thermodynamic model makes it possible to determine the amount of cargo used to gassing-up, its loss during the operation, concentration at any moment of the process, according to temperature and pressure in the cargo tank and a gas mass flow rate at the inlet and outlet of the tank for both extreme cases of calculations, i.e. 'piston pushing' and total mixing of inert gas and cargo vapor. Due to too many variables, it is necessary to make appropriate assumptions in case of total mixing of both gases.

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