

## OPERATIONAL PROBLEMS OF ETHYLENE TRANSPORT BY LPG GAS CARRIERS

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### Abstract

Ethylene is one of the basic raw materials of the petrochemical industry used for the production of plastics, mainly plastic packaging. The USA is the largest producer of this compound. The enormous increase in demand for Ethylene has been observed in recent years in China as well as in the Middle and Far East. This caused an unprecedented increase in the demand for transport of this cargo by sea. Ethylene carriers for its transport are special construction LPG vessels, having a cascade cycle with Propylene medium (less often the refrigerant R 404 A). They have been designed in such a way as to withstand a working pressure of up to 5.4 bar, and the minimum temperature of the transported load is minus 104°C for fully cooled Ethylene. This cargo is explosive in the mixture with air (within concentrations of 2.75-2.6%) and during heating under elevation pressure. Therefore, it is required to transport Ethylene in with an inert gas, most often Nitrogen. During the operation of LPG carriers carrying Ethylene, processes of aeration, inerting, gassing-up, cooling tanks and a cargo are repeatedly carried out. The most problematic to carry is gassing-up operation, because it is associated with significant amounts of Ethylene loss, this causes large financial losses. In the article, the authors attempted to diagnose the most serious problems during carrying out the most important for cargo loss the cargo handling operations.

**Keywords:** gassing-up, gas mixing, LPG carriers, Ethylene, Nitrogen

### 1. Introduction

In the natural state Ethylene occurs in small amounts in natural gas. It is obtained on a technical scale during thermal decomposition of gaseous and liquid hydrocarbons, from gas products of petroleum refining processes and from coke oven gases. Ethylene is one of the basic raw materials of the petrochemical industry. In recent years, the demand for Ethylene has grown on a huge scale. Therefore, it was necessary to transport it by sea. Ethylene carriers (Fig. 1) are special construction LPG shops, having a cascade cycle with Propylene as a refrigerant. As the optimum temperature for ethylene transport is minus 104°C, this load must be carried on semi-refrigerated vessels in tanks designed to withstand pressures up to 5.4 bar.

Before the Ethylene cargo is loaded to cargo tanks, a few cargo-handling operations must be done before. The most important are: inerting, gassing-up and cooling the tanks and a cargo. Inerting means creating an inert atmosphere in tanks by the use of an inert gas like Nitrogen, what prevents flammable and explosive atmosphere with Oxygen. A gassing-up operation consists of pushing out an inert gas from tanks by the use of cargo vapour.

After an inert gas is totally removed, introducing cargo vapour is proceeded so that tanks are cooled enough not to make cracks of tanks bottom surface while cargo liquid is loaded.

### 2. Operation problems of Ethylene transport

To begin with, it is worth emphasizing that the content of Oxygen in Nitrogen in cargo tanks must be reduced to minimum, depending on the next cargo, not exceeds even 0.1%. Tab. 1 presents permissible Oxygen concentration in the tank for exemplary loads together with operations that must be done between loading different cargo.



Fig. 1. Ethylene carrier

Tab. 1. Activities before loading other cargo and allowable Oxygen concentration in the tank for exemplary loads

Next cargo \ Previous cargo	ETHYLENE	PROPYLENE	BUTADIENE	BUTAN-1
<b>ETHYLENE</b>		Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0.3% < 1000ppm P.CG Dewpoint -25°C	Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0,2% < 5% P.CG	Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0,1% < 5% P.CG Dewpoint -40°C
<b>PROPYLENE</b>	Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0.3% < 1000ppm P.CG Dewpoint -40°C		Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0,2% < 5% P.CG	Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0,1% < 5% P.CG Dewpoint -40°C
<b>BUTADIENE</b>	Visual inspection Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0.3% Dewpoint -40°C	Visual inspection Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0.3% Dewpoint -25°C		Visual inspection Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0,1% Dewpoint -40°C
<b>BUTANE-1</b>	Visual inspection Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0.3% Dewpoint -40°C	Visual inspection Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0.3% Dewpoint -25°C	Inerting N <sub>2</sub> Contents O <sub>2</sub> < 0,2% < 5% P.CG	

Visual inspection required  
 No visual inspection required

N<sub>2</sub> – Nitrogen  
 O<sub>2</sub> – Oxygen  
 P.CG – previous cargo

Thus, properly working pressure swing adsorption (PSA) system, which generates Nitrogen used to tank inerting, is very important for further operations.

Another crucial thing affecting the cargo handling operations is a state of tanks insulation. Heat transfer coefficient defining heat transfer through thermal barriers, determines the amount of heat passing into the partition with a unit surface area when there is a temperature difference between the surfaces equal to the temperature unit. The smaller coefficient, the better thermal insulation of the partition is. Deteriorating insulation condition results an increase a heat transfer coefficient that in turn translates into a decrease of a cooling capacity during the operation of cargo cooling.

In case of Ethylene cargo the most problematic operation is a gassing-up process. None of the inert gas, which may be used on ships, Nitrogen or Carbon dioxide, may be condensed by a system of reliquefaction plant of cargo on board. This is because the condensation temperature of

Nitrogen is below the critical condensation temperature of the Ethylene. Therefore, it is necessary to remove the inert gas from cargo tanks. This possibility is provided by the operation of gassing-up with the use of cargo vapours (coolant).

This operation can be carried parallel, means all tanks separately or in cascade, the first tank is filled with ethylene vapours, when the specified pressure, higher than atmospheric, is reached in the tank or after reaching 100% of hydrocarbons, the valve opens on the pipeline directed to the next tank to which the inert gas (vapour mixture) is directed, this operation is repeated for the third and fourth pair of tanks, the top of the last pair of tanks opens to the atmosphere. Normally pushing out Nitrogen is based on a densities difference of both gases. If cargo vapour is heavier than Nitrogen, it is introduced to the tank through the pipe at the bottom so that the Nitrogen could be pushed out by the pipe at the top of the tank. Contrary, if cargo vapour is lighter than Nitrogen, it is introduced to the tank by the pipe at the top, so that the Nitrogen was pushed out through the bottom pipe. The Ethylene gassing-up operation usually is made with a cascade system. A bottom pipe is used to introduce its vapour (Fig. 2).

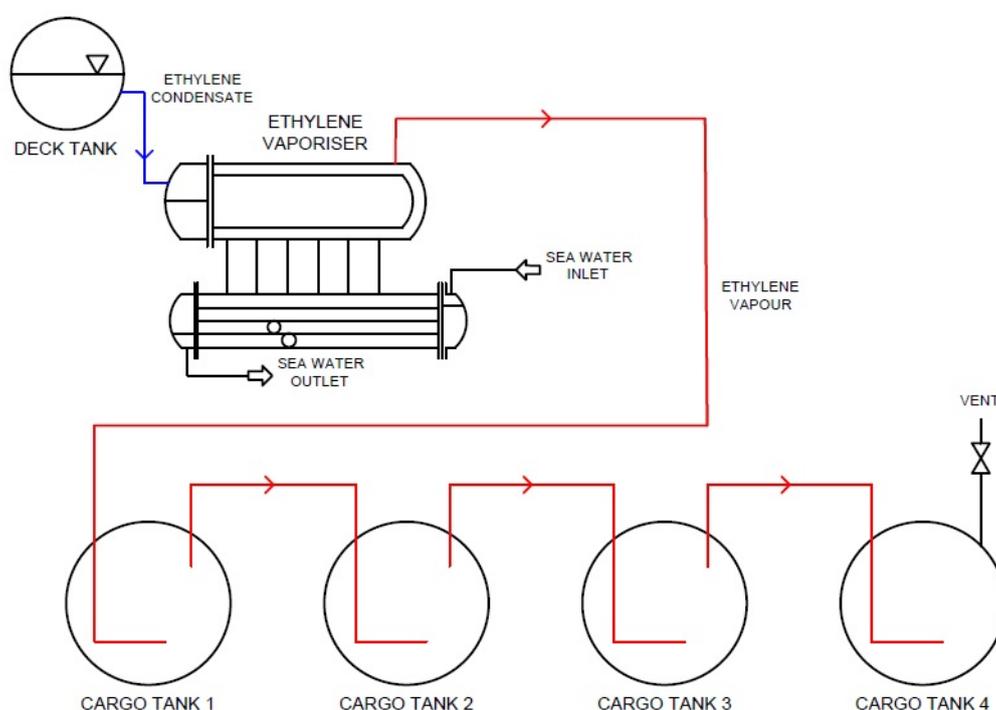


Fig. 2. Gassing-up, liquid cargo from deck tank, bottom to top

However, in next three tanks there is no temperature difference observed. Nitrogen atmosphere in tanks is closed to outside temperature, while Ethylene temperature from vaporiser, which “produces” vapour from liquid, is about minus 55 °C. Introducing mixture to other three tanks there is no sub-zero temperatures, what makes impossible to create stratification of gases and push out the Nitrogen by the use of Ethylene vapour on the principal of a piston.

Additional problem of creation the effect of a piston in tanks during gassing-up is a very small difference of densities at particular temperatures (Tab. 2).

As presents scheme in Fig. 2, during the gassing-up operation an Ethylene vaporizer should be used. The device enables the “production” of an Ethylene vapour or Ethane used to maintain pressure in tanks during cargo loading or during the process of gassing-up. The Ethylene vaporiser consists of two shell-and-tube heat exchangers (Fig. 3) connected in circulation with propylene, used as a refrigerant to prevent the water from freezing in the exchanger. Due to the inadequate supply of the vaporizer with liquid coolant under the appropriate pressure, the device is ignored during tank gassing-up operation.

Tab. 2. Ethylene and Nitrogen density with reference to particular temperatures

Temperature (°C)	ETHYLENE (kg/m <sup>3</sup> )	NITROGEN (kg/m <sup>3</sup> )	Temperature (°C)	ETHYLENE (kg/m <sup>3</sup> )	NITROGEN (kg/m <sup>3</sup> )
0	1.24	1.23	-100	2.00	1.95
5	1.22	1.21	-95	1.94	1.89
10	1.20	1.19	-90	1.88	1.84
15	1.17	1.16	-85	1.83	1.79
20	1.15	1.14	-80	1.78	1.74

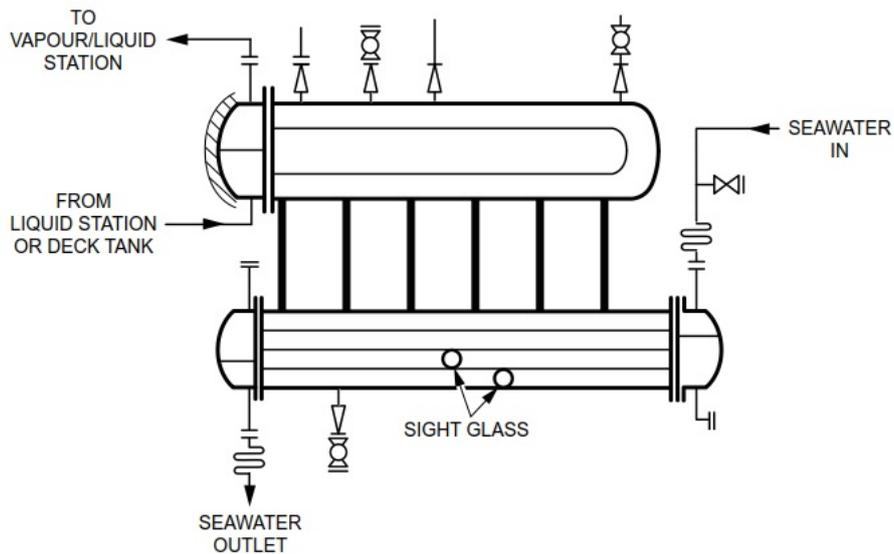


Fig. 3. Scheme of Ethylene vaporizer

The correct operation of the vaporizer is also influenced by the operation of the automatic valve located before Ethylene vaporizer (Fig. 4), which regulates the flow of Ethylene. On ships, there is often no attention paid for maintenance. The valve does not operate automatically, and the mass flow must be adjusted manually. This prevents the provision of a sufficiently high flow of Ethylene, which ensures the temperature of the Ethylene vapour of minus 90°C.



Fig. 4. An automatic valve before Ethylene vaporizer

Ethylene carriers are equipped with a cascade reliquefaction plant. The system consists of two circuits: open and closed. The open circuit uses charge as a refrigerant that allows cooling of cargo in cargo tanks, while the closed circuit uses propylene as a refrigerant (Fig. 5).

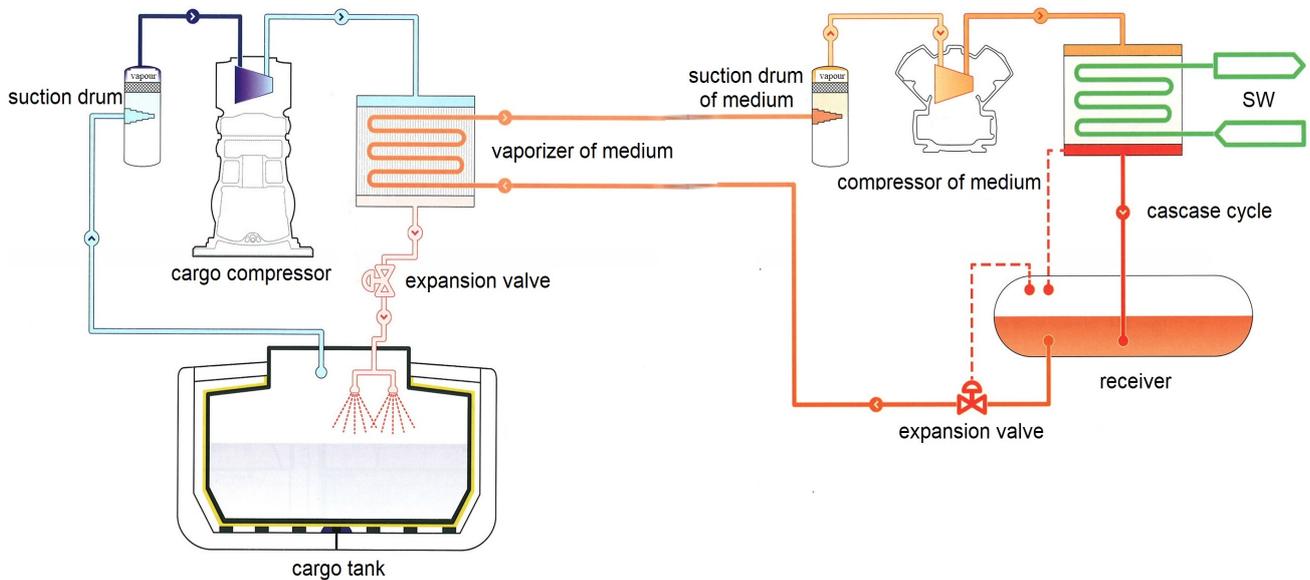


Fig. 5. Scheme of cascade cycle

The Nitrogen content of condensed Ethylene vapour has a direct effect on the cooling capacity of the cycle. The Nitrogen that creates with ethylene the mixture with a lower condensation temperature causes the stoppage the compressors due to the high condensing pressure. In order to avoid exceeding the operating pressure of the compressors, 18 bar during the cooling operation of the cargo, the valves on the condenser are opened, hot Ethylene vapours are directed to the cargo tanks and heat the load.

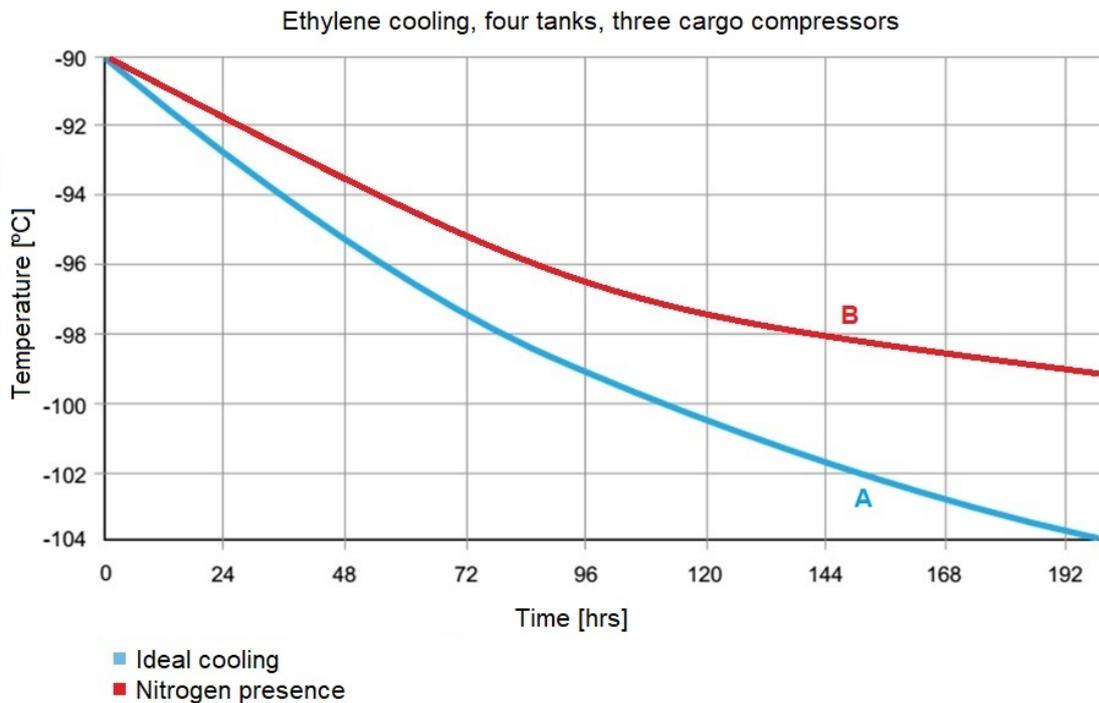


Fig. 5. A graph of parallel gassing-up operations with reference to ethylene temperature and a time of the operation through a bottom line

The open valve significantly reduces the mass flow of condensate (Fig. 6), and thus the capacity cooling. With the lowering Ethylene temperature, the pressure in the tanks, and thus the suction of the compressor, decreases, which causes a decrease in cooling capacity of the cycle. This is shown by the curve A in Fig. 6. As the temperature of Ethylene decreases, the gradient of the time unit needed for its cooling increases. This means that the more Ethylene need to be cooled, the more time the cooling process will take. Curve B shows the possible cooling speed with partial loss of a condensate mass flow with open valve on the condenser.



Fig. 7. Portable gas detector Riken Keiki GX-8000

The gassing-up operation is completed when in tank the concentration of Ethylene vapour should be 100%. To measure this concentration a portable gas detector Riken Keiki GX-8000 is used. The detector (Fig. 7) is a gasometer device with built-in electrochemical sensors or a galvanic cell containing electrolytes. It allows analysing the concentration of gases such as: Oxygen, flammable gases, toxic gases (Carbon monoxide and Hydrogen sulphide) in the air and high concentration of flammable gases in Nitrogen and inert gases.

The measurement margin of error of this device is 5%. A common problem on ships when measuring hydrocarbon concentrations during gassing-up operation of cargo tanks is not enough accuracy of the device. In order to properly carry out this process, measurements of inert gas concentration in such a mixture like Nitrogen and Ethylene must have a minimum accuracy of 1.5%. The GX-8000 gas detector does not provide this option. In addition, this model in the GX-8000 version is not suitable for analyses of high hydrocarbon concentrations.

### 3. Conclusions

Factors affecting the proper carrying the gassing-up operation, as well as minimizing cargo loss, are many. A thorough analysis of the method of carrying out this operation using Ethylene vapour should be made, as well as the lack of use during gassing-up the vaporizer, which is inconsistent with the instructions on the ships. Gassing-up in a cascade is not an optimal method, on contrary; it generates substantial loss of Ethylene, which translates into financial losses. In addition, it is necessary to look at the device used to measure the concentration of hydrocarbons in cargo tanks, which is very inaccurate to measure high hydrocarbon concentrations. Inappropriate measurements make difficulties during the most demanding cargo handling operation, which is a gassing-up process.

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