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**THERMODYNAMIC PROCESSES INVOLVING LIQUEFIED NATURAL GAS
AT THE LNG RECEIVING TERMINALS****PROCESY TERMODYNAMICZNE Z WYKORZYSTANIEM SKROPLONEGO GAZU ZIEMNEGO
W TERMINALACH ODBIORCZYCH LNG**

The increase in demand for natural gas in the world, cause that the production of liquefied natural gas (LNG) and in consequences its regasification becoming more common process related to its transportation. Liquefied gas is transported in the tanks at a temperature of about 111K at atmospheric pressure. The process required to convert LNG from a liquid to a gas phase for further pipeline transport, allows the use of exergy of LNG to various applications, including for electricity generation. Exergy analysis is a well known technique for analyzing irreversible losses in a separate process. It allows to specify the distribution, the source and size of the irreversible losses in energy systems, and thus provide guidelines for energy efficiency. Because both the LNG regasification and liquefaction of natural gas are energy intensive, exergy analysis process is essential for designing highly efficient cryogenic installations.

Keywords: LNG, liquefied natural gas, exergy, thermodynamic cycle, unloading terminal, regasification

Wzrost zapotrzebowania na gaz ziemny na świecie powoduje, że produkcja skroplonego gazu ziemnego (LNG), a w konsekwencji jego regazyfikacja, staje się coraz bardziej powszechnym procesem związanym z jego transportem. Skroplony gaz transportowany jest w zbiornikach w temperaturze około 111K pod ciśnieniem atmosferycznym. Przebieg procesu regazyfikacji niezbędny do zamiany LNG z fazy ciekłej w gazową dla dalszego transportu w sieci, umożliwia wykorzystanie egzergii LNG do różnych zastosowań, między innymi do produkcji energii elektrycznej. Analiza egzergii jest znaną techniką analizowania nieodwracalnych strat w wydzielonym procesie. Pozwala na określenie dystrybucji, źródła i wielkości nieodwracalnych strat w systemach energetycznych, a więc ustalić wytyczne dotyczące efektywnego zużycia energii. Ponieważ zarówno regazyfikacja LNG jak i skraplanie gazu ziemnego są energochłonne, proces analizy egzergii jest niezbędny do projektowania wysoce wydajnych instalacji kriogenicznych.

Słowa kluczowe: LNG, skroplony gaz ziemny, egzergia, obieg termodynamiczny, terminal rozładunkowy, regazyfikacja

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1. Introduction

The increase in demand for natural gas in the world, cause that the production of liquefied natural gas (LNG) and in consequences its regasification becoming more common process related to its transportation. The task of unloading LNG terminal is to receive the cargo of liquefied natural gas from methane reservoirs that followed, according to the schedule of operation – to process liquid LNG in the gas phase and at a certain pressure to introduce gas into the transmission system. Strategically, the LNG regasification plants start playing a decisive role.

Despite the development of liquefaction techniques and technologies oriented to the lowering of the energy consumption, liquefaction remains a very energy-consuming process at the place where it is performed (Remelje, 2006). The basic source of energy used is gas itself or products coming from gas processing at the liquefaction plants. Obviously, at least part of the energy used in the liquefaction and regasification processes should be retrieved. This energy is frequently lost after regasification directly on the sea, where the waters constitute a source of heat. Cold energy can be recuperated and they depend on the type of regasification used. The efficiency of the thermal cycle is proportionate to the difference of heat source and cold source temperatures. In advanced technologies the LNG can be used as a cold source in the direct production of electric energy (Liu & You, 1999). Hisazumi et al. (1998) investigated possibilities of using waste heat from associated gas-operated power plants for LNG evaporation, without marine water. The source of heat in the Rankine cycle is condensation enthalpy from a steam turbine and heat of waste gases in the waste boiler. Zhang and Lior (2006) analyzed possibilities of using indirect Rankine cycles with CO₂ in the supercritical phase. Szargut and Szczygieł (2009) evaluated the feasibility of thermodynamic sequences with the use of various working fluids, and also evaluated the economic aspect of the processes. The problem of optimum thermodynamic use of cold sources, exemplified by LNG, to the electric energy production was also presented by Olivetti et al. (2012). The proposed configuration of LNG installation was based on Rankine cycle water steam used by a waste combustion facility to improve its efficiency as far as the produced energy and also thermodynamic efficiency are concerned.

That installation is based on Rankine second closed cycle employing LNG temperature exergy and Rankine third open cycle based on pressure exergy. These three cycles enable more efficient thermodynamic use of cold sources: heat coming from water steam condensation is used for vaporization of ammonia, whereas ammonia condensation heat is applied for LNG evaporation. The proposed configuration gives operating independence both for the regasification and combustion installations. In the ideal subcritical Rankine cycle, the fluid is initially compressed and heated as liquid, evaporating at constant temperature and constant pressure, regardless the selected working fluid. Overheated at constant pressure and then isentropically decompressed. The next process is liquefaction at constant temperature and pressure to the original state, and the process is repeated.

The efficiency of thermodynamic process has been recently investigated by several others. Dispenza et al., (2009), investigated the usability of module regasification with ethane or ethylene for generating electric energy and energy transport within the established range of temperatures. Liu and Guo (2011) proposed a method of thermal energy recovery from LNG regasification with the use of two-component mixtures (tetrafluoromethane and propane) associated with steam absorption processes. Shi and Che (2011) investigated the efficiency of associated systems employing Rankine cycle with a mixture of ammonia water as the working fluid. Therefore, LNG as a cold energy source seems to be advantageous in any case when thermal energy waste is generated to the environment (Hang & Lior, 2006).

2. Energy and exergy recuperation in the process of LNG regasification

Liquefied natural gas (LNG) is sea-transported by the methane tankers in reservoirs under atmospheric pressure and at temperature of about 111 K. The LNG industrial infrastructure mainly consists of gas liquefaction installations, loading terminal, tankers (methane tankers) and unloading terminal, where it is regasified.

The works on the unloading terminal can be divided into three basic stages: unloading, storing and regasification, (Łaciak & Nagy, 2010).

At the unloading stage the methane tanker is moored to the reception terminal, connected to the storing collector by unloading lines and pipelines. Pumps at the methane tanker pump the LNG from the tanker to the on-land storing collectors.

The storing stage refers to only one type of storing collectors, the design of which enables safe storing of LNG within the cryogenic range of temperatures.

At the regasification stage the LNG is heated in heat exchangers (vaporizers), LNG changes its phase to gaseous. The quality parameters of the gas meet the standards for further transport (possible mixing of gases), (Łaciak, 2012).

During unloading, LNG is pumped out of the tanker with ship pumps and transported to the on-land storing reservoirs. To avoid the formation of voids in the tanker under the influence of rapidly decreasing volume of liquid, a counterbalancing volume of gas should be added. The gas vaporization inside the reservoirs is evoked by the heat passing through the walls and also a quantity of heat generated by the submersible pump engine. The unloading is performed with unloading lines made of hydraulically powered stainless nickel steel.

Liquefied natural gas is sent through the unloading collector and parallel recirculation pipeline. The LNG vapors BOG (*Boil Off Gas*), which form as the collector is being filled out, are sent back to the tanker. One of the unloading lines is a hybrid line which can be used as return line for the gas when the BOG return line does not work. At the initial stage of unloading, as a result of cooling of the unloading pipeline, an increased rapid evaporation is observed at the filling stubs. Lower pressure in the collectors allows for maintaining suitable pressure if greater quantities of BOG are produced.

Transformations, which methane undergoes in the regasification process on the off- and on-shore terminals have been presented in the enthalpy-pressure system (fig. 1). Saturated LNG is transported from the ship collectors to the regasification terminal, then is compressed from atmospheric pressure to supercritical pressure, heated at constant pressure to ambient temperature. Heat for regasification comes from marine water or indirect medium, combustion of some of evaporated LNG.

The amount of energy needed for LNG regasification constitutes about 1.5 to 1.7% of total energy used at the terminal.

Obtaining supercritical pressures at the end of compression is justified by the fact that maximal pressures in the transport networks usually exceeds 7 MPa, and the gas after LNG regasification should be forwarded under appropriately high pressure. As the compression takes place in the liquid phase, the required LNG pumping power is not high. It is also advantageous that the transport of the liquid phase means concentration of volume which is connected with the change of the phase equal to 1/600 under the atmospheric pressure.

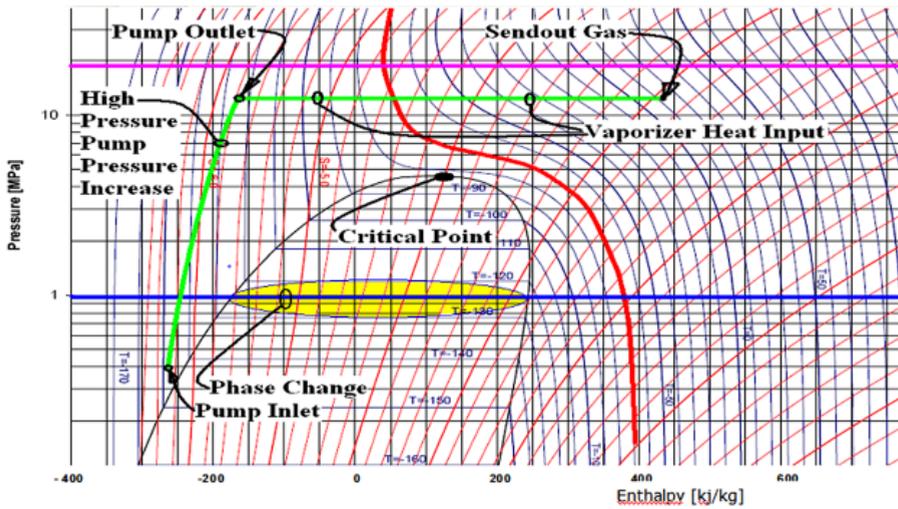


Fig. 1. LNG regasification process (after Vitale, 2012)

Natural gas liquefaction is energy consuming: about 850 kWh of energy is needed to produce 1 ton of LNG. Moreover, gas has to be regasified at the receiver, which is also very energy-consuming. If a cold source, i.e. LNG can be used, then the general energy balance shall increase. When cold is used for energy production, then 1 ton of LNG can be used for the production of about 240 kWh of electric energy.

The exergy analysis is very important for the evaluation of energy systems. It may help determine distribution, source and magnitude of irreversible losses in energy systems, i.e. establish guidelines for efficient use of energy. As both liquefaction of natural gas and LNG regasification are energy-consuming, the process of exergy analysis is necessary for designing highly efficient cryogenic installations.

The exergy is defined as maximal work, which a thermodynamically open system can perform in a given environment, reaching the state of equilibrium with it.

Exergy has the following properties (Szargut & Szczygieł, 2009):

- defines what happens with work input from the beginning of the studied process;
- defines the magnitude of work needed by a given substance to perform with respect to the environment;
- does not follow the preservation law;
- allows for determining the quality of the process;
- electric energy, kinetic energy and mechanical work make up pure exergy;
- exergy E_x of heat Q given away to the environment is calculated as maximal work which the Carnot engine can perform at a given level of temperatures:

$$E_x = Q \left(1 - \frac{T_n}{T} \right) \quad (1)$$

where T_n is ambient temperature, T – temperature of substance giving off heat;

- physical exergy (no chemical exergy) of substance at temperature T can be calculated from the equation;

$$E_x = H - H_n - T_n (S - S_n) \quad (2)$$

where H – enthalpy, S – entropy depending on temperature and pressure. Index in „ H_n ” denotes environmental parameters.

After taking into account the way in which enthalpy is calculated, the analysis of equation (2) reveals that the following substances have high physical energy:

- high temperature, fit for driving heat machines,
- high pressure,
- considerable underpressure as, e.g. opening of vacuum collector’s valve may result in performing work.

Substances having parameters similar to those of the environment do not have exergy.

Accordingly, exergy is maximal work obtained from a certain form of energy and in the vaporization process depends both on temperature (T_s) and pressure of LNG, as well as on ambient temperature and pressure, (exergy is *availability of energy*).

In a particular case, exergy may be calculated as a sum of two terms:

- Thermal exergy connected with a difference of temperatures:

$$E_{x,t} = E_x(p, T) - E_x(p, T_0) \quad (3)$$

$$E_{x,t} = \left(\frac{T_n}{T_s} - 1 \right) r + \int_{T_n}^{T_s} c_p \left(1 - \frac{T_n}{T} \right) dT \quad (4)$$

where r is enthalpy of vaporation, being the enthalpy difference between gaseous and liquid phases.

- Exergy coming from a difference of pressures (in constant temperature):

$$E_{x,p} = E_x(p, T_0) - E_x(p_0, T_0) \quad (5)$$

$$E_{x,p} = \int_{p_n, T_n}^{p, T_n} v dp \quad (6)$$

Total exergy is a sum of both terms:

$$E_x(p, T) = E_{x,t} + E_{x,p} \quad (7)$$

3. Thermodynamic processes at the LNG unloading terminal in Świnoujście

The primary planned volume of the LNG terminal build in Świnoujście will be 2.5 mld m³ to finally reach 7.5 mld m³ at the second stage.

Two reservoirs 160,000 m³ each are being built in Świnoujście at the first stage of the investment. A place for the third reservoir was also designed to provide possibility of further development of the terminal. The main task of the terminal will be regasification of LNG to gaseous state. The LNG vaporization system will consist of three gas-fired regasifiers SCV (Submerged Combustion Vaporizers). Two of them will service the terminal operation and the third one will be a technical reserve. The SCV systems consist of pipe-coil made of stainless steel tube and an installation system of a combustion burner submerged in water bath, surrounded by a concrete cover. LNG enters the SCV system at a temperature of -134°C, leaving it in a gaseous form at a temperature of 5°C. The system of regasifiers may be developed at further stages of the project as the terminal starts reaching it assumed efficiency.

The first delivered liquefied gas will come from Qatar and its composition is given in table 1. LNG composition is given in the first column, molar composition after regasification (BOG) under pressure of 0.1 MPa and at temperature of 111.89 K in the second column. The methane and nitrogen composition significantly change the vapor composition after regasification. At this stage the remaining natural gas components appear in trace quantities.

TABLE 1

Composition of *Qatar* gas, LNG and BOG

Composition	Liquid Phase	Vapor Phase
	Mole Frac. [%] LNG	Mole Frac. [%] BOG
Methane	89.87	94.011
Ethane	6.65	0.011753
Propane	2.30	0.00 (4.264 × 10 ⁻⁵)
n – Butan	0.57	0.00 (1.556 × 10 ⁻⁷)
i – Butane	0.41	0.00 (2.29 × 10 ⁻⁷)
n – Pentane	0.00	0.00
i – Pentane	0.01	0.00 (2.61 × 10 ⁻¹⁰)
Nitrogen	0.19	5.977

LNG density at temperature of 112 K (at pressure of 0.1013 MPa) is 459.8 kg/m³ and has calorific value equal to about 50 MJ/kg (21.5 GJ/m³). In normal conditions, one cubic meter of regasified LNG has density about 0.79 kg/m³, and its calorific value is about 34 MJ/m³. If the whole change of enthalpy connected with LNG regasification from 112 K to ambient temperature is used, then the corresponding energy is about 724 kJ per 1 kg of LNG.

Owing to the isobaric heating effect (from 112 K to ambient temperature), LNG undergoes the phase change and overheating. Fig. 3 represents exergy changes as a function of ambient temperature.

Differences in exergy as a function of pressure are presented in fig. 4.

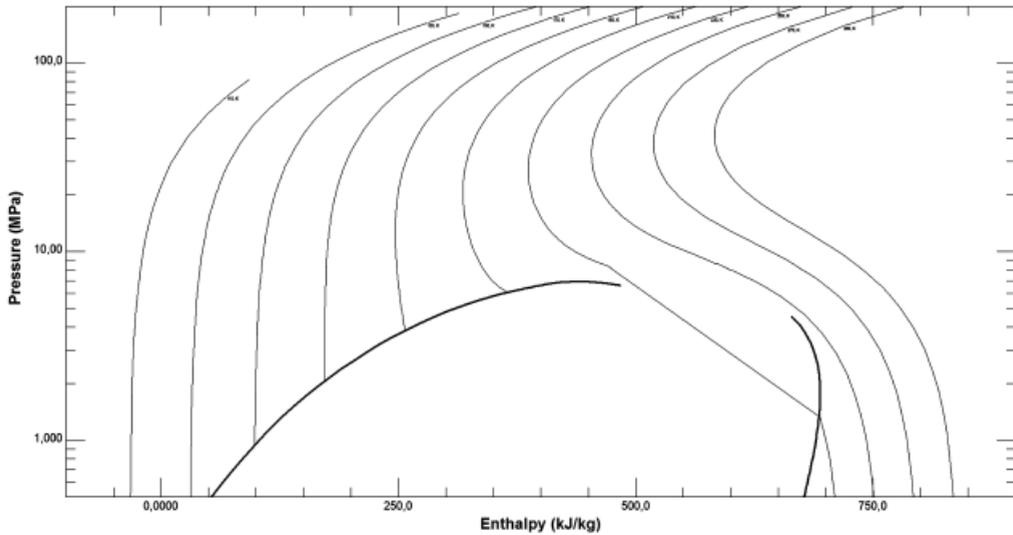


Fig. 2. Phase plot of p - h for gas having composition as in table 1 ($p_K = 5.7448$ MPa, $T_K = 214.67$ K)

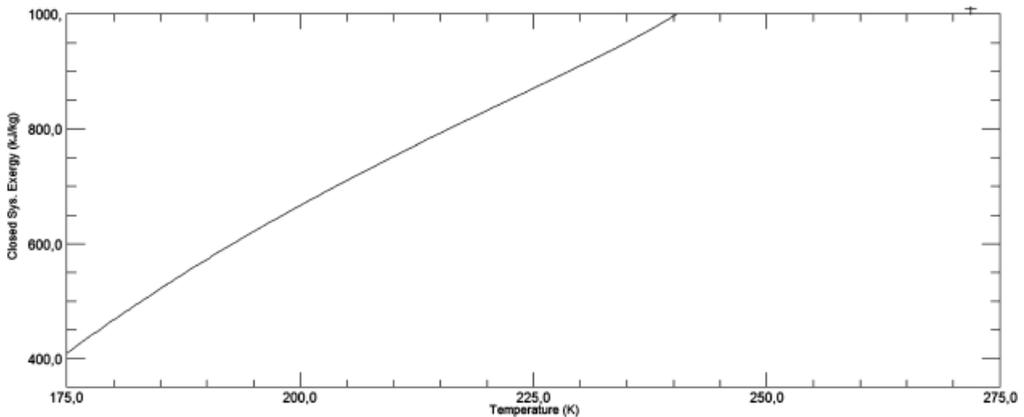


Fig. 3. Exergy changes vs. ambient temperature in LNG regasification process

With the increase of pressure, the corresponding increase of pressure exergy takes place. Thermal exergy decreases due to the increase of temperature, at which the phases change and the enthalpy of condensation decreases. The thermal effect dominates and the total exergy decreases. Increasing of the total exergy “with respect to” pressure is negligible for pressures over 2.1 MPa, reaching almost constant value of about 0.9 MJ/kg. Total specific exergy reaches about 0.9 MJ/kg for external temperature of about 275 K. Accordingly, the energy recovery system can be applied with the use of two different cycles. They allow for the use of pressure exergy (through the systems of indirect expansion at high pressures) and thermal exergy (Rankine cycle of fluids of low boiling point). The analysis of the course of the plots reveals that relative values of thermal

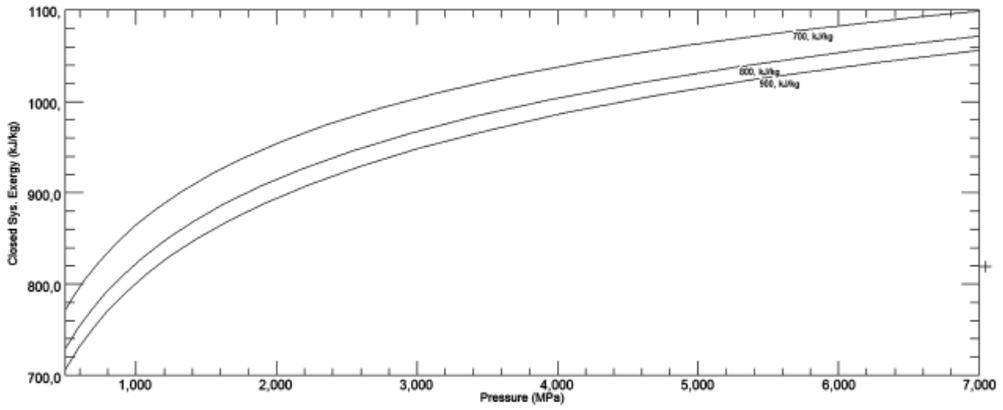


Fig. 4. Exergy changes vs. pressure for various enthalpy

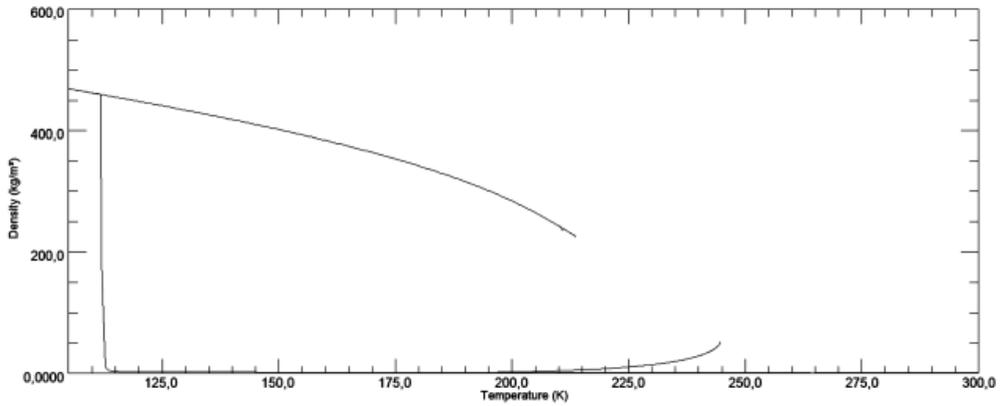


Fig. 5. LNG density changes vs. temperature

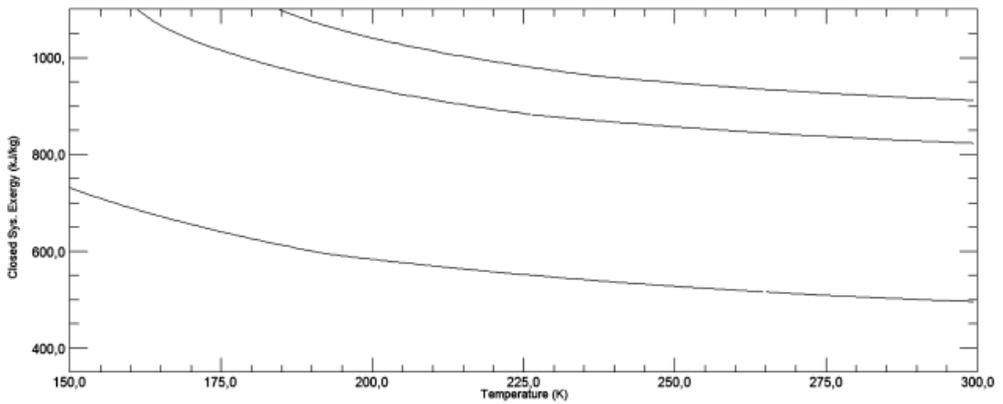


Fig. 6. Total specific exergy changes vs. temperatures for different pressures (0,1 MPa, 1,1 MPa, and 2,1 MPa)

exergy and pressure exergy are not constant. Importantly, it denotes that in practice various types of exergy can be recovered with various thermodynamic circulations.

Recuperation of cold energy of LNG and using low-quality energy sources are important for saving energy and environmental protection. Energy available during LNG regasification may be used, especially within the low temperature range for decreasing the energy demand in the process of air, nitrogen, oxygen and argon liquefaction.

4. Cooling and liquefaction of BOG

During unloading of a methane tanker at the reception terminal, great quantities of liquefied gas are pumped out of its reservoirs in a very short time, causing local underpressure. To counteract this effect and to maintain working pressure in the collectors at a constant level the pumped out LNG is replaced with methane. Part of demand for gas to fill out the collectors is covered by vapors (*Boil Off Rate*), but the remaining part has to be supplied from outside. The natural BOG (*Boil Off Gas*) is used here. At the initial stage of unloading, after the unloading lines are connected to the ship manifolds, BOG is used for cooling the lines and auxiliary systems in the pier. The missing quantity of gas is supplied from the reception terminal with „vapor return line”. Opposite to the unloading line, this pipeline is not maintained at low temperature, therefore the outflowing gas has to be properly chilled down before it reaches the collectors on the ship. The cooler on the unloading platform with LNG as a source of cold is used at this stage. The LNG vapors are cooled down before they are compressed to 4 do 6 bar and directed to the liquefier. This refers to the main pipeline through which BOG is transported.

Chilling down gaseous vapors (BOG) is done only to lower the temperature, not to liquefy them. In the cooling systems some quantities of LNG are introduced (injected) to the running stream of gas, or directed up the standing column or countercurrent, mixing them up with the stream of chilled BOG. On average, about 0.225 kg of LNG is used for cooling 1 kg of BOG.

The aim of BOG liquefaction is lowering energy consumption.

Most of the vapors are liquefied and in a liquid phase they are pumped to the regasification installation. The energy used for re-pumping a given mass of liquid natural gas (volume ca. 600 times smaller than in the gaseous phase) is about 30 times lower as compared to the compression of the same mass in gaseous phase to a definite pressure.

In the recondenser both phases mixes: ca. 3 kg of cooled LNG per ca. 0.5 kg gaseous vapors, under a pressure of 4 to 6 bar. Gas liquefies through isobaric cooling process from the temperature gas has before the liquefaction to the temperature of boiling. Then in the course of isobaric-isothermal transformations, condensation heat is recuperated. Liquefied gas exchanges heat with cooled LNG. Thermodynamic processes of LNG vaporization has been visualized in fig. 7. The course of plots illustrating the pathway of LNG starts from the inlet to the pump in the storing collector (point A), through the outlet of pump 1° (point B), inlet of LNG to re-condenser (point C – of the same enthalpy as point B), outlet of the evaporator (point D) and outlet of pump 2° (point E).

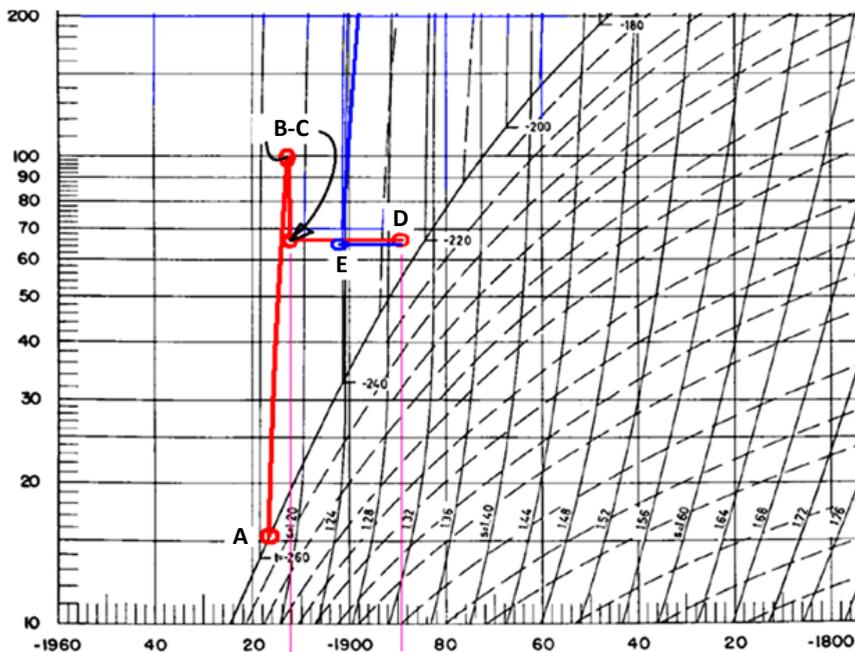


Fig. 7. Diagram of fluid (LNG) flow in recondenser, during gas liquefaction (BOG), (after Vitale, 2012)

5. Concluding remarks

Technological processes taking place at LNG unloading terminals are connected with a number of thermodynamic changes covering both evaporation, cooling and liquefaction of natural gas, i.e. heat exchange processes. The analysis of exergy is crucial for the evaluation of energy systems and designing highly-efficient cryogenic installations. Properly designed use of operation methods at the terminal may considerably increase the thermal and exergetic efficiency of LNG unloading and regasification processes, e.g. by additional production of electric energy. This will greatly contribute to the saving of energy and environmental protection.

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