

On Some Thermodynamic Processes Possibly Involved in the Technological Flow of Liquefied Natural Gas

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A global increase in the usage of LNG is expected in the subsequent years. More and more countries are starting to produce LNG, while others are starting to import it, using this energetic solution as a complementary source. The present paper consists of data and calculation relationships regarding certain thermodynamic properties of liquid methane. Also, it discusses a few case studies concerning some thermodynamic processes possibly involved in the technological flow of liquefied natural gas. A calculation model is provided regarding the thermal flow necessary for methane heating, vapourisation and overheating at an LNG unloading terminal. A calculation relationship is also provided for the evaluation of the specific latent heat of liquid methane vapourisation depending on temperature.

Key words: liquefied natural gas, thermodynamic processes

When natural gas cannot be transported from the producer to the user through pipelines, it will be liquefied.

Recent data on the LNG industry show a series of important aspects such as:

- the significant growth of the LNG global market in the last 10 years [1];

- the forecasts for the subsequent years suggest the increasing tendency of the transactions with this fuel, which has been a source of energy in China, India, Japan and other countries in Asia-Pacific for tens of years. As regards the European Union, LNG has already been imported in countries such as Poland and Lithuania [2, 3];

- a stimulus for LNG usage is the lower value of the carbon dioxide emission coefficient, ϵ_{CO_2} , in the case of obtaining heat through burning, as compared to other fossil fuels [4, 5]. According to the data provided by S.C. Enel Energie Muntenia S.A., the CO_2 emissions vary between 370 and 448 g/kWh in Romania depending on the primary sources used for obtaining electrical energy (coal, naphtha, nuclear, other sources), and for methane, $\epsilon_{CO_2} = 178$ and 198 g/kWh, respectively, and on the net and gross calorific values, respectively [6]. Therefore, there is less chemical pollution in the case of methane combustion;

- regarding the energy strategy of a country, LNG could be a complementary source of energy for providing the necessary burning fuel in order to produce heat [7];

- there are markets (South Korea and Taiwan) in favour of LNG that prefer using gas to using nuclear energy;

- as far as global prices are concerned, it is worth mentioning that, even though the price of LNG has considerably gone down in recent years, there is a high level of competition in the market taking into account the gas recently discovered in various parts of the world, on the one hand, and the one transported through pipelines, on the other hand. As for the production of electrical energy, the price of LNG does not depend on that of coal, and that must be analysed [1];

- in order to effect transactions with LNG significant financing is required both for the exporter and the importer. That will allow the development of the infrastructure necessary for the technological flow of LNG production, delivery, transportation and usage.

After mentioning these arguments, which are either pro or against, it can be said that the LNG market is growing, which justifies the study of a few thermodynamic aspects possibly involved in case this energy source is chosen.

LNG (liquefied natural gas) means, in fact, liquefied methane. Liquid methane is a cryogenic fluid necessary for the cooling cycles used for obtaining very low temperatures. However, it is mainly used as fuel. Fossil fuels are substances that burn, generating heat; they contain carbon, hydrogen and sulphur. When opting for fuel supply certain conditions have to be fulfilled, such as: the fuel should be easily obtained naturally; it should not be toxic; it should be cheap and in sufficient quantity so that the cost of the obtained heat should be competitive on the energy market.

In [7] it is proposed that LNG, liquid methane respectively, should be considered and named a complementary source of energy. As regards a country's energy strategy, it can be agreed that, depending on the nearby natural resources and the country's energy policy, the sources of energy are of two types: basic and complementary. In other words, LNG, as a *complementary source of energy*, belongs to the first type in order to cover consumption depending on conjectural factors such as high energy consumption within a limited time frame, purchasing opportunities, imposing the zonal reduction of pollutant emissions, technical failures, natural calamities, etc.

The technological flow of LNG exploitation consists of the following stages: Extraction of combustible natural gas (gaseous state) → Transportation of natural gas through pipelines → Liquefaction of natural gas (obtaining liquid methane) → Marine transportation of liquid methane → Storage of liquid methane → Vapourisation of liquid methane (obtaining methane in gaseous state) and the heating of methane in gaseous state → Storage / Transportation / Consumption of methane in gaseous state → User.

Extraction of combustible natural gas (gaseous state) Upon extraction, natural gas is a mixture with various compositions.

The transportation of natural gas through pipelines is the most advantageous method of establishing the link between the producer and the user.

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Liquefaction of natural gas (obtaining liquid methane).

Methane liquefaction is carried out either by isobaric cooling or by expansion [6]. Natural gas liquefaction can be carried out off-shore, too, on vessels named Floating Liquefied Natural Gas (FLNG) platforms. Prelude Shell is the largest floating facility ever constructed. It liquefies, stores and offloads the gas extracted from offshore wells to large carriers. The advantage of methane liquefaction at sea is that it is no longer necessary to build long pipelines that are far from the shore, which is extremely expensive. The vessel operates at approximately 200 km off the Australian coast, in the Browse Basin. Its production capacity is: 3.6 mtpa (million tonnes per annum) of LNG, 1.3 mtpa of condensate and 0.4 mtpa of liquefied petroleum gas (LPG) [8, 9]. It is worth mentioning that by isobaric cooling of a mixture of natural gas the vapourisation/condensation (liquefaction) temperatures of the compounds are reached. Thus, as temperature drops, these component gases reach a liquid state. If the process is isobaric, during the liquefaction of a mixture compound the temperature stays constant, too. It can be argued that this thermodynamic process of *fractional liquefaction* is an efficient method of separating the various gases that form a natural gas mixture.

Marine transportation of liquid methane, during which the thermodynamic state is: pressure of approximately 1.2 bar, temperature of $-162\text{ }^{\circ}\text{C}$. The first LNG carrier in the world, Methane Pioneer (5.034 DWT), left the Calcasieu River in Louisiana on January 25th, 1959. It was carrying the first ocean cargo of LNG and headed to Great Britain where the cargo was unloaded. The subsequent development of that industry has led to fleet expansion until today when LNG carriers are extremely large. Two types of LNG carriers are being used: vessels with spherical tanks (Moss type vessel) or vessels with prismatic tanks.

The latter use the form of the vessel's hull more efficiently, and the space between the methane tanks and the ballast ones is smaller. MOSS-type carriers, (fig. 1), are fitted with 4 or 5 spherical tanks. There is a thick insulation layer on the outside shell of the sphere. Over this layer there is a thin layer of *foil* under which there is an atmosphere of nitrogen that prevents burning. The nitrogen atmosphere is constantly checked -in case methane is detected, there must be a leak in the tank. Also, the surface of the tank is checked every 3 months -any cold spots would indicate the occurrence of cracks in the insulation. Along its circumference the tank is supported by a metal ring that is held by a circular metal shell which bears the tank's weight to the vessel's structure. This shell enables tank expansion and contraction during heating and cooling operations, which is why all the junction lines are made of flexible elements [10]. The vessels with prismatic tanks, (fig. 2), are fitted with membrane tanks. The membrane is made of stainless steel with compensators for thermal contraction/ expansion when the tank is cooled/ heated. The primary barrier, made of stainless steel, is 1.2 mm (0.047 in) thick and is in direct contact with the cargo liquid. Above this barrier there is a primary insulation layer which in turn is covered by a secondary barrier made of a material named Triplex which is, in fact, a metal foil sandwiched between two glasswool sheets.

This is again covered by a secondary insulation layer which is supported by the vessel's hull structure. From the innermost to the outermost layers of the tank, they are as follows: primary barrier; primary insulation; secondary barrier with Triplex membrane; secondary insulation (also called insulation space); vessel's hull structure [10].



Fig. 1. Moss-type LNG carrier [10]

Floating storage and regasification units - FSRU - have significantly developed in the last decade. They are offshore mobile floating installations that reconvert LNG back to natural gas. This type of installation is cost-effective and has flexible location, unlike onshore installations. The usage of these installations has opened new markets in South America, Pakistan and Middle East [1]. The thermodynamic processes of heating, vapourisation and overheating that take place at the LNG unloading terminal at constant pressure, (fig. 3), will regasify liquid methane so that it should be appropriate for user consumption [10].

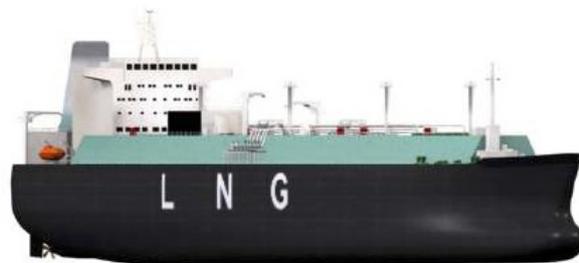


Fig. 2. Membrane-type LNG carrier [10]



Fig. 3. LNG loading-unloading terminal [10]

The heat necessary for methane heating, vapourisation and overheating at constant pressure from liquid to gaseous state

Figure 4 shows the basic diagram of a methane heating, vapourisation and overheating installation at a LNG unloading terminal, which comprises: 1 - Marine vessel transporting liquid methane from the loading to the unloading terminal; 2 - Liquid methane area in the unloading tank; 3 - Gaseous methane area in the tank; 4 - Torch; 5 - Compressor; 6 - Gaseous methane heater ($0\text{...}20^{\circ}\text{C}$); 7 - Gaseous methane heater ($-162\text{...}20^{\circ}\text{C}$); 8 - Methane vaporiser; 9 - Liquid methane heater; 10 - Pump; 11 - Separator.

The sequence of the thermodynamic changes that take place at an LNG unloading terminal is shown in diagram T-s, figure 5.

The heat necessary for the isobaric heating of 1 kg of liquid methane, from temperature T_A to temperature T_B , after the isobaric process A-B (fig.5), is:

$$q_i = q_{AB} = \int_{T_A}^{T_B} c_p dT \cong c_{i,m} (T_B - T_A) \quad (1)$$

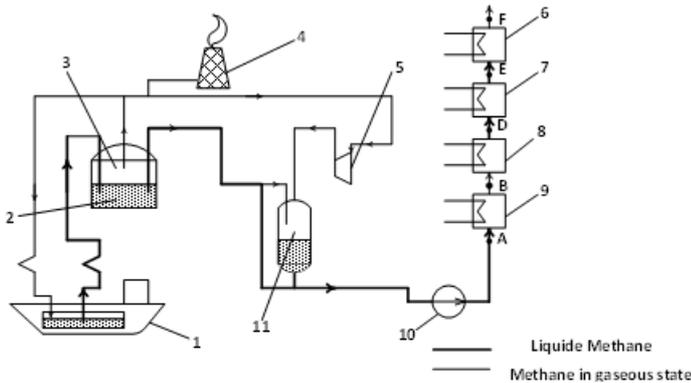


Fig. 4. Basic diagram of LNG unloading terminal scheme

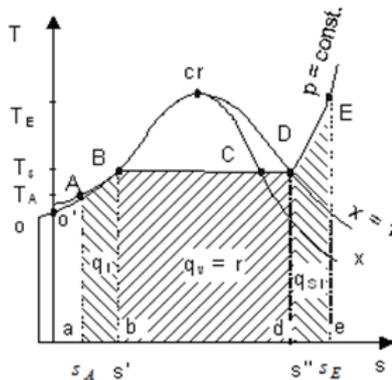


Fig. 5 The heat necessary for methane heating, vapourisation and overheating at constant pressure from liquid to gaseous state

where: $c_p = c_{l,m}$ is the average molar heat capacity of liquid methane between T_A and T_B .

The saturated liquid state is used as a starting point having the following parameters: temperature of -162°C and pressure of 1 bar. This state is shown in diagram T-s by point O (fig. 5).

When data is available regarding the enthalpy in liquid state, the heat necessary for isobaric heating has the following formula:

$$q_1 = q_{AB} = \int_A^B dh = h_B - h_A \quad (2)$$

h_A and h_B are the enthalpies of the liquid in states A and B, respectively, at temperature T_A and T_B , respectively, and pressure p , at which the heating takes place. If it is considered that state B is the saturated liquid state, then $h_B = h'_B$ (enthalpy of saturated liquid in state B). Hence, relationship 2 is as follows:

$$q_1 = h'_B - h_A \quad (3)$$

The heat necessary for heating, q_1 , corresponds to area *Abba* in diagram T-s (fig. 5).

The heat necessary for turning, at $p=\text{const.}$, $q_v = r$, 1 kg of saturated liquid (B) into dry saturated vapours (D) is called latent heat of vapourisation r . If during phase transition the pressure is constant, then the temperature is constant, too. In isobaric-isothermal conditions it is equivalent to enthalpy increase during vapourisation and is expressed by the following relationship:

$$q_v = r = h''_D - h'_B \quad (4)$$

h''_D is the enthalpy of dry saturated vapours in state D.

Hence, the latent heat of vapourisation r is defined by the following relationship:

$$r = h'' - h' \quad (5)$$

Taking into account that the $ds = \frac{\delta q}{T}$ relationship can be written as follows:

$$r = \int_B^D \delta q = \int_B^D T ds = T_s (s'' - s') \quad (6)$$

In diagram T-s in figure 5, the heat of vapourisation is given by area *BDdb*.

The heat necessary for the isobaric heating of vapours, q_{SI} from temperature $T_D = T_s$, that is, to temperature $T_{Si} = T_E$, is:

$$q_{SI} = q_{DE} = \int_{T_D}^{T_E} c_{p,v} dT = \int_{T_s}^{T_{Si}} c_{p,v} dT = \int_D^E T ds \quad (7)$$

in which $c_{p,v}$ is the molar heat capacity of overheated vapours at constant pressure. If the overheating process is isobaric, q_{SI} can be calculated as a function of enthalpy variation:

$$q_{SI} = \int_D^E \delta q = \int_D^E dh = h_E - h''_D \quad (8)$$

where h_E is the enthalpy of overheated vapours in state E, characterized by temperature T_E and pressure p at which the process takes place. In diagram T-s in figure 5, the heat exchanged with the exterior during the isobaric process of overheating D-E corresponds to area *DE_{ed}*. Relationships 3, 4 and 8 lead to the expression of the total heat q_t necessary for the heating, vapourisation and overheating, at $p=\text{const}$ and with no heat dissipation, of a monocomponent system from state A to state E:

$$q_t = q_1 + q_v + q_{SI} = h'_B - h_A + h''_D - h''_D + h_E - h''_D = h_E - h_A \quad (9)$$

Providing a calculation relationship for the variation of the latent heat of methane vapourisation as a function of temperature $r=f(T)$ using the linear regression method.

In order to select the right regression function the series of distribution will be represented by a correlation graph that will make it clear whether the line between two variables is straight or curved. In order to highlight the statistical lines and their trends, estimating equations are used corresponding to an analytical function. This function is called regression function and is graphically represented by the regression curve.

The regression function shows the way in which the resultative variable (y) changes if it is only the independent variable (x) that varies, while the other factors stay constant. If the graphical representation shows a linear trend, the regression equation that expresses this line is as follows:

$$y_i = b \cdot x_i + a \quad (10)$$

Parameter a is the y-intercept of the line and shows the level variable y would have reached if all the factors - except for the one recorded - had constantly influenced it.

Parameter b is also called regression coefficient and is geometrically represented by the slope of the regression line. This parameter is positive for a direct line and negative in the case of an inverted line and shows the average by which variable z changes if variable x changes by one unit. When $b=0$ the two variables are independent and $y_i = a$. Hence, the average value of the regression equation equals the value of the resultative variable ($y_i = y$) [11].

Results and discussions

The research has led to a series of results that will be discussed below.

a) Thermodynamic properties of liquefied methane

Depending on its thermodynamic states, some of the characteristics of methane are [6, 12]:

- At a temperature of 0°C and pressure $p=760$ torr: density $\rho = 0.7168$ kg/m³; massic heat capacity, $c_p = 2.117$ kJ/(kg K);

- At pressure $p=760$ torr: latent heat of fusion: $r_f = 58.615$ kJ/kg; melting temperature: $t_m = -182.5^\circ\text{C}$, $r_v = 90.65$ K, respectively; latent heat of vapourisation: $r_v = 548.471$ kJ/

Composition (mole %)	Composition	G 1	G 2	Boiling Point, °C
N ₂	Azote	0.26	0.37	-196
C ₁	Methane	59.78	69.35	-162
CO ₂	Carbon dioxide	3.28	4.03	-78.5
C ₂	Ethan	10.04	6.71	-88
H ₂ S	Hydrogen sulfide	18.50	14.82	-60
C ₃	Prophan	4.95	2.94	-42.04
iC ₄	IsoButane	0.59	0.35	-11.72
nC ₄	n-Butane	1.37	0.75	-0.5
iC ₅	IsoPentane	0.30	0.17	27.8
nC ₅	n-Pentane	0.32	0.17	36
nC ₆	n-Hexane	0.20	0.13	68.7
nC ₇	n-Heptane	0.16	0.10	98.4
H ₂ O	Water	0.25	0.11	100
Total	-	100	100	-

Thermodynamic process	Temperature °C	Thermal flow, q, kJ/kg
Liquid heating	-165 ... -162	10.500
Vapourisation (regasification)	-162	548.471
Gas heating (Overheating)	-162 ... 20	394.0
Total	-165 ... 20	953.03

Table 1
MOLAR COMPOSITION OF GAS MIXTURES

Table 2
HEAT NECESSARY FOR THE HEATING LIQUID METHANE, VAPOURISATION AND OVERHEATING (PER MASS UNIT)

kg; temperature of vapourisation: $t_v = -161.7^\circ\text{C}$, $T_v = 111.45$ K, respectively, and the liquid phase density at this temperature: $\rho_v = 415$ kg/m³.

At the critical point the parameters of methane are: critical temperature: $t_{cr} = -82.5^\circ\text{C}$, $T_{cr} = 190.65$ K, respectively; critical pressure: $p_{cr} = 46.29$ bar; critical density: $\rho_{cr} = 161.8$ kg/m³.

In order to evaluate certain thermodynamic properties of liquid methane a series of calculation relationships are suggested by the literature [6, 13], such as, for instance, the molar heat capacity, expressed in J/(kg K):

$$c = -79.7212 \cdot 10^2 + 290.223 \cdot T - 246.676 \cdot 10^{-2} \cdot T^2 + 705.31 \cdot 10^{-5} \cdot T^3 \quad (11)$$

valid when the temperature varies between 93 and 181 K.

b) Fractional liquefaction

Table 1 shows the molar composition of two gas mixtures, G 1 and G 2, [14]; the compounds are combustible and non-combustible gases. For these compounds the temperatures of vapourisation/condensation (liquefaction) are displayed in a tidy row, at the pressure of 760 mm Hg [12]. Fractional liquefaction allows the efficient separation of the compounds.

c) Heat necessary for liquid methane heating, vapourisation and overheating

The calculation model based on relationships (1)...(9) allows the evaluation of the heat necessary for the heating liquid, vapourisation and overheating of gas methane (per mass unit). The results obtained are shown in table 2.

d) Providing a calculation relationship for the variation of the latent heat of methane vapourisation as a function of temperature, $r = f(T)$, using the linear regression method. Data similar to saturated methane were used from the literature [15] in the graphical representation in figure 6.

The regression equation obtained is the following:

$$r = -4.2597 \cdot T + 996.41 \quad (12)$$

Following the research more similar relationships were found in the literature, all of them referring to $r = f(T)$ [6, 13, 15].

Out of these, Watson and Klein relationships [13] were chosen for comparison.

Linear Regression $r=f(T)$

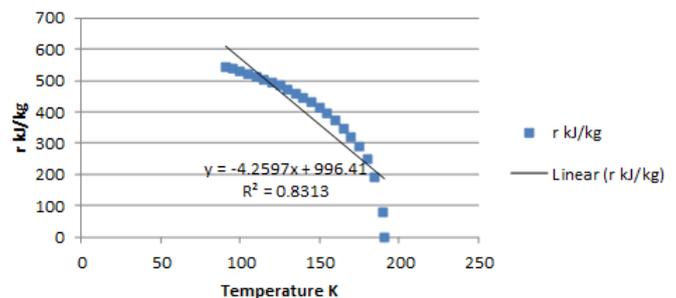


Fig. 6. Graphical representation of the latent heat of vapourisation as a function of T

Watson relationship

$$r = r_0 \cdot \left[\frac{T_{cr} - T}{T_{cr} - T_n} \right]^{0.38} \quad (13)$$

where:

r are the latent heat of vapourisation at temperature T and the normal boiling point, respectively, expressed in kJ/kmol or kJ/kg;

T_n is the normal boiling point, expressed in K, and T_{cr} is the critical temperature, expressed in K.

Klein relationship

$$r = \frac{8.318 \cdot T \cdot \ln(P_r)}{T_r - 1} \cdot \left(1 - \frac{P_r}{T_r^2} \right)^{0.5} \quad (14)$$

where r is the latent heat of vapourisation, expressed in kJ/kmol; T is the temperature, expressed in K; T_r is the reduced temperature (T/T_r); P_r is the reduced pressure corresponding to the equilibrium pressure at temperature T (p/p_{cr}); T_{cr} and p_{cr} - critical temperature and critical pressure, respectively.

Table 3 shows the results obtained after using various methods of evaluating the correlation $r = f(T)$.

The comparative analysis (table 3) led to the following observations:

The data obtained were compared with the ones from [15] and with the ones obtained using the relationship suggested by the authors.

Table 3
RESULTS OBTAINED AFTER USING VARIOUS METHODS OF EVALUATING THE CORRELATION $r = f(T)$

Temperature, T, K	r from table, kJ/kg	r calculated with the Watson relationship, kJ/kg	r calculated with Klein relationship, kJ/kg	r of regression, kJ/kg
111.15	512	519.5	793.09	521.45
160	372	356.8	2335.7	314.8
180	246.8	239.05	6597.2	229.6

*The calculation relationship cannot be used for temperatures above 180 K.

By using the Klein relationship for the three temperature values proposed it can be observed that the value of r goes up with increased temperature, which leads us to the conclusion that the relationship mentioned above fails to provide accurate results.

By contrast, the values obtained using the relationship proposed by the authors provides accurate results, which enables us to argue that it provides satisfactory results. Moreover, it is simple and easy to use.

Conclusions

Finally, a synthesis of the most important observations is deemed necessary:

- There are countries in the world that have large natural gas reserves, on the one hand, and highly developed countries that do not have enough energy resources, on the other hand. This aspect regarding the supply and demand leads to commercial transactions. Sometimes long distance does not allow the transportation of natural gas through pipelines. As a result, the sea transport of liquefied natural gas is used.

- LNG liquefaction, transportation, storage, reliquefaction and vapourisation involve a great variety of thermodynamic processes.

- The calculation model described in the present paper regarding the thermal flow necessary for methane heating, vapourisation and overheating at an LNG unloading terminal can prove useful for the elaboration of some complex calculation programs.

- A calculation relationship is proposed for the evaluation of the latent heat of vapourisation of liquid methane as a function of temperature. By comparing this relationship with similar examples found in the literature it can be observed that the relationship proposed by the authors provides satisfactory results. Consequently, this relationship, which is simple and easy to apply, is satisfactory when used in a similar calculation model.

- As regards a country's energy strategy, LNG can be an important complementary energy source. It can be stored both in liquid and gaseous state and is used in gaseous state, depending on the circumstances.

Nomenclature

c - Massic heat capacity, J/(kg K);
 h - Massic enthalpy, J/kg;
 q - Massic heat, J/kg;
 p - Pressure, Pa, bar;

r - Latent heat of phase change, J/kg;
 s - Massic entropy, J/(kg K);
 t - Temperature Celsius, °C;
 T - Thermodynamic temperature, K;
 x - factorial variable;
 y - resultative variable;
 Greeks:
 ρ - Density, kg/m³

Subscripts:

cr -critical;
 n - normal;
 p - at constant pressure;
 r -reduced;
 t - melting;
 T - at constant temperature;
 v - vaporization.

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